# THE GENERALIZED VALENCE BOND
# DESCRIPTION OF THE PI ELECTRON STATES
# OF CONJUGATED MOLECULES

Thesis by

George B. Levin

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To Tony, Fergie, JB, Al, Greg,
and even WEB for interjecting some sanity into it all
and thereby making what follows possible.

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# ABSTRACT

Using the generalized valence bond (GVB) wave function, the pi electron systems of ethylene, allyl cation, allyl radical, s-trans-1,3-butadiene and benzene were examined. The results were in good agreement with full configuration interaction calculations demonstrating the quantitative accuracy of the GVB method. The GVB description of the valence states systems includes a description of resonance and provides a rigorous quantum mechanical description of resonance in terms of spin couplings. It was found that the resonance stabilization energy is due to two effects, delocalization of orbitals onto additional centers while still maintaining their basically localized nature, and spin coupling optimization in a manner identical to the valence bond description of resonance.

It was found that the GVB wave function imposed restrictions upon the orbitals of excited states. To remove these restrictions the GVB wave function was generalized by including a spatial projection operator. The GVB(SP) wave function imposes no restrictions upon individual orbitals and represents the most general independent particle wave function as yet presented. The GVB(SP) method was used to examine allyl radical and butadiene. All states were described by localized orbitals and energies were in excellent agreement with configuration interaction results. A molecules-in-molecules model using ethylene pi electron states was found to provide a qualitative description of all the states of allyl radical and butadiene examined.

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# I. INTRODUCTION

Here we report the results of ab initio theoretical studies on the pi electron systems of some small organic molecules. This work was undertaken with the goal of providing some insight into the phenomenon of resonance and providing a consistent description of pi electron systems. Our calculations were performed using the generalized valence bond (GVB) method[1,2] and the spatially projected GVB method. The GVB wave function was used because in the GVB wave function all orbitals are singly occupied and thus include a consistent level of correlation for ground and excited states. In addition, the GVB wave function explicitly includes the Pauli principle and correct permutational symmetry so that all states are eigenfunctions of spin. However, the GVB wave function retains the independent particle approximation permitting interpretation of the results and developing models for systems, while yielding total energies and excitation energies in good agreement with ab initio full configuration interaction (CI) results.

The GVB wave function for most ground states includes localized orbitals. However, for the ground state of allyl radical and most excited states, both valence-like and Rydberg-like, the GVB wave function included delocalized symmetry orbitals. It was felt that this was due to restrictions in the GVB wave function. To eliminate these restrictions, the GVB wave function was generalized by including a spatial projection operator, thereby eliminating any restrictions upon the individual orbitals while insuring that the final state has the correct spatial symmetry. The resulting wave function is called the spatially projected GVB wave function and denoted GVB(SP). It was anticipated that the GVB(SP) description of all systems would be in terms of localized orbitals, and this was found to be the case.

Pi-electron systems containing two, three, four, and six electrons were examined. The systems are all linear except the six-electron system which is cyclic. The three, four, and six-electron systems display resonance in varying degrees. Thus, we have examined a cross section of the pi electron systems and are able to compare the various systems.

The two systems containing two pi electrons examined were ethylene and allyl cation. The results for these systems are presented in Appendix I. The GVB(SP) description of the ground and excited states of these systems includes localized orbitals. The total energies and excitation energies are in good agreement with full CI calculation. The ethylene pi system will serve as a "building block" and by combining ethylenic units, we will be able to generate the states of larger systems[3].

The three pi electron system examined was allyl radical. Allyl radical is the smallest pi electron displaying what is known as resonance in the classical valence bond theory. The GVB description of allyl radical includes resonance. Resonance is introduced into the GVB wave function through the electron spin coupling. At a specific spin coupling, the right and left orbitals are equivalent and the system displays resonance. The GVB results for allyl radical are presented in Appendix II.

The optimum GVB description of some states of allyl radical includes delocalized symmetry orbitals. It was considered that this resulted from restrictions imposed upon the individual orbitals by the GVB wave function. To test this hypothesis, the GVB wave function was generalized by introducing a spatial projection operator. The form of the resulting wave function, denoted by GVB(SP) is such that the final wave function has a definite symmetry, but that the individual orbitals need not have a definite symmetry and in general will possess components of all possible symmetry types. The GVB(SP) method was applied to allyl radical with the expectation that all states would be described by localized orbitals, and, indeed this was the case. The GVB(SP) description of the ground state of allyl radical also includes resonance, but the resonance arises from the spatial symmetry of the system. The GVB(SP) results for allyl radical are presented in Appendix III.

The four pi electron system examined was s-trans-1,3-butadiene (henceforth referred to simply as butadiene). The GVB results are contained in Appendix IV. The GVB wave function for three of the states was in terms of localized orbitals, and these states were well described by combining ethylenic units. The GVB wave function for the remaining excited states examined included delocalized symmetry orbitals. Application of the GVB(SP) method yielded localized orbital descriptions of all states examined. The GVB(SP) descriptions of the states of butadiene were consistent with the fused ethylene model[3].

The GVB(SP) results for butadiene are contained in Appendix V.

The pi electron system of benzene was the six pi electron system examined using the GVB method. These results are contained in Appendix VI. Only states with valence-like orbitals were examined. The GVB wave function provided a localized orbital description of the valence states. As with allyl radical, resonance is included in the GVB wave function for the pi electrons of benzene by a specific coupling of the electron spins. In benzene, the effect of the specific spin coupling is to make the spin coupling between any two adjacent orbitals the same. We find the GVB description of resonance in benzene consistent with the valence bond (VB) description of resonance in benzene and yielding total energies and excitation energies in good agreement with extensive CI results. Further, we find that the VB type resonance effect does not account for all of the stabilization energy relative to an ethylenic type double bond as in cyclohexene. While maintaining a basically localized nature, the individual orbitals delocalize and acquire amplitude on all six centers. This accounts for a great deal of stabilization in the benzene pi electron system.

In Appendix VII, the GVB(SP) wave function is presented in full detail. The variational equations, which were used to obtain the optimum wave function, are derived. The GVB(SP) equations for three electrons are presented in full detail and generalized to an arbitrary number of electrons.

Appendix VIII is a report of some work on generating matrix representations of $S_N$, the symmetric group on N objects, and is included herein to provide a record for posterity's sake. Using a method developed by Gabriel[4], a computer program was developed for obtaining the generators for a matrix representation of $S_N$ . Gabriel's method is outlined and the computer program and the generators for three representations of $S_7$ are listed. This is the only listing of the $S_7$ generators known to the author, most probably because there has not been an overwhelming demand for the $S_7$ generators.

In Section II, some of the results contained in Appendices I through VI are summarized and the conclusions reached from the total body of work are summarized. In Section III, we discuss the conclusions obtained from the total body of work. Analysis of the individual systems is contained in the applicable appendix.

## II. SUMMARY OF RESULTS AND CONCLUSIONS

### A. Results

Some of the results contained in Appendices I through VI are summarized.

1. Table I contains a summary of all the calculated GVB and GVB(SP) total energies and excitation energies for the states of ethylene, allyl cation, allyl radical, butadiene, and benzene studied. In each system, the same basis set was used for the GVB and GVB(SP) calculations.

2. In Tables II through V, the pi electron energies calculated from the GVB, GVB(SP) and CI methods are given. The same basis set was used for all calculations in each system. The CI calculations were full or complete within the basis set calculations (except for benzene, where the calculations were extensive) and thus represent the limit of the accuracy of the basis set. We see from these tables that the GVB and GVB(SP) results agree well with the CI results.

3. The ordering of states or the nature of the states differs in some cases from that expected from Hartree-Fock (HF) or molecular orbital (MO) considerations. The first excited ($^2B_1$) state of allyl radical would not be well described by HF theory since this state has the character of a double excitation state in CI terminology. In the GVB description the $^2B_1$ is a spin excitation state, in that the GVB wave function includes orbitals which are quite similar to the ground state orbitals, including the orthogonal spin coupling.

## Table I

## SUMMARY OF GVB AND GVB(SP) TOTAL ENERGIES AND EXCITATION ENERGIES

| | GVB | | GVB(SP) | |
|---|---|---|---|---|
| System | Total Energy(h) | Excitation Energy (eV) [a] | Total Energy(h) | Excitation Energy (eV) [a] |
| Ethylene | | | | |
| N($^1A_g$) | -78.034134 | 0.0 | -78.046172 | 0.0 |
| T($^3B_u$) | - | - | -77.891962 | 4.20 |
| V($^1B_{1u}$) | - | - | -77.742095 | 8.27 |
| Allyl Cation | | | | |
| $1^1A_1$ | -116.163675 | 0.0 | -116.172789 | 0.0 |
| $1^3B_2$ | - | - | -116.062719 | 3.00 |
| $1^1B_2$ | - | - | -115.959400 | 5.81 |
| $1^3A_1$ | - | - | -115.898766 | 7.46 |
| $2^1A_1$ | - | - | -115.833770 | 9.23 |
| Allyl Radical | | | | |
| $1^2A_2$ | -116.416438 | 0.0 | -116.418612 | 0.0 |
| $1^2B_1$ | -116.297120 | 3.25 | -116.301432 | 3.19 |
| $2^2B_1$ | -116.237380 | 4.87 | -116.245898 | 4.70 |
| $2^2A_2$ | - | - | -116.221249 | 5.37 |
| $3^2B_1$ | -116.209966 | 5.61 | -116.217433 | 5.47 |
| $4^2B_1$ | - | - | -116.140243 | 7.58 |
| $3^2A_2$ | - | - | -116.136173 | 7.69 |
| $4^2A_2$ | - | - | -116.135127 | 7.71 |

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[a] 1 eV = 27.2117 hartrees

Table I (continued)

| | | | | |
|---|---|---|---|---|
| Butadiene | | | | |
| $1^1A_g$ | -154.93555 | 0 | -154.93575 | 0 |
| $1^3B_u$ | -154.80627 | 3.52 | -154.80946 | 3.44 |
| $1^3A_g$ | -154.74673 | 5.14 | -154.75223 | 4.99 |
| $2^1A_g$ | -154.67881 | 6.99 | -154.68545 | 6.81 |
| $1^1B_u$ | -154.66360 | 7.40 | -154.677778 | 7.02 |
| $2^3B_u$ | -154.65961 | 7.51 | -154.67435 | 7.11 |
| $3^1A_g$ | | 8.04 | - | - |
| $2^1B_u$ | - | - | -154.63486 | 8.19 |
| $3^3B_u$ | - | - | -154.63113 | 8.29 |
| $4^3B_u$ | - | - | -154.62991 | 8.32 |
| Cation($^2B_u$) | 154.59576 | 9.25 | -154.59964 | 9.15 |
| Benzene | | | | |
| $1^1A_g$ | -230.70992 | 0.0 | | |
| $1^3B_{1u}$ | -230.57213 | 3.75 | | |
| $1^1B_{2u}$ | -230.51435 | 5.32 | | |
| $1^3E_{1u}$ | -230.50945<br>-230.50846 | 5.44<br>5.48 | | |
| $1^3E_{2g}$ | -230.44020<br>-230.43809 | 7.34<br>7.40 | | |
| $1^1E_{2g}$ | -230.48971<br>-230.38928 | 8.90<br>8.91 | | |
| $^3B_{1u}$ | -230.30293 | 11.07 | | |
| $^3A_{2g}$ | -230.27345 | 11.88 | | |
| $^3E_{1u}$ | -230.22773<br>-230.21505 | 13.12<br>13.47 | | |
| $^1A_{1g}$ | -230.16552 | 14.81 | | |

# Table II

## COMPARISON OF CI AND GVB PI ELECTRON ENERGIES FOR ETHYLENE AND ALLYL CATION

| | Pi-Electron Energy(h) | | | Excitation Energy (eV) | | |
|---|---|---|---|---|---|---|
| System | GVB | GVB(SP) | CI [b] | GVB | GVB(SP) | CI [b] |
| Ethylene | | | | | | |
| $N(^1A_g)$ | -1.208606 | -1.210035 | -1.210320 | - | 0 | 0 |
| $T(^3B_{1u})$ | - | -1.055720 | -1.055729 | - | 4.20 | 4.21[a] |
| $V(^1B_{1u})$ | - | -0.807247 | -0.807335 | - | 8.27 | |
| Allyl Cation | | | | | | |
| $^1A_1$ | -1.725134 | -1.734248 | -1.734879 | - | 0 | 0 |
| $^3B_2$ | - | -1.624178 | -1.624184 | - | 3.00 | 3.01 |
| $^1B_2$ | - | -1.520859 | -1.520962 | - | 5.81 | 5.82 |
| $^3A_1$ | - | -1.460225 | -1.460357 | - | 7.46 | 7.47 |
| $2^1A_1$ | - | -1.395229 | -1.397986 | - | 9.23 | 9.17 |

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[a] Excitation energy includes changes sigma core energy

[b] Reference 14

## Table III

## COMPARISON OF GVB AND CI ENERGIES FOR ALLYL RADICAL

| | Pi-Electron Energy(h) | | | Excitation Energy (eV) | | |
|---|---|---|---|---|---|---|
| State | GVB | GVB(SP) | CI | GVB | GVB(SP) | CI |
| $1^2A_2$ | -1.977897 | -1.980071 | -1.982548 | 0 | 0 | 0 |
| $1^2B_1$ | -1.858579 | -1.862898 | -1.864849 | 3.25 | 3.19 | 3.20 |
| $2^2B_1$ | -1.798839 | -1.807356 | -1.809769 | 4.87 | 4.70 | 4.70 |
| $2^2A_2$ | - | -1.782708 | -1.783648 | - | 5.37 | 5.41 |
| $3^2B_1$ | -1.771425 | -1.778891 | -1.781396 | 5.61 | 5.47 | 5.47 |
| $4^2B_1$ | - | -1.701702 | -1.706583 | - | 7.52 | 7.51 |
| $3^2A_2$ | - | -1.697631 | -1.699438 | - | 7.69 | 7.70 |
| $4^2A_2$ | - | -1.696585 | - | - | 7.71 | - |

## Table IV

## COMPARISON OF GVB AND CI ENERGIES FOR BUTADIENE

| | Pi Electron Energy (h) | | | Excitation Energy (eV) | | |
|---|---|---|---|---|---|---|
| State | GVB | GVB(SP) | CI[a] | GVB | GVB(SP) | CI[a] |
| $1^1A_g$ | -3.273011 | -3.293204 | -3.29761 | 0 | 0 | 0 |
| $1^3B_u$ | -3.163731 | -3.166915 | -3.17073 | 3.52 | 3.44 | 3.45 |
| $1^3A_g$ | -3.104190 | -3.109688 | -3.11235 | 5.14 | 4.99 | 5.04 |
| $2^1A_g$ | -3.036266 | -3.042905 | -3.04869 | 6.99 | 6.81 | 6.77 |
| $1^1B_u$ | -3.021058 | -3.035235 | -3.03839 | 7.40 | 7.02 | 7.05 |
| $2^3B_u$ | -3.017068 | -3.031811 | -3.03521 | 7.51 | 7.11 | 7.14 |
| $2^1A_g$ | 2.999518 | - | -3.01016 | 8.04 | - | 7.82 |
| $2^1B_u$ | - | -2.992312 | -3.00127 | - | 8.19 | 8.06 |
| $3^3B_u$ | - | -2.988630 | -3.00056 | - | 8.29 | - |
| $4^3B_u$ | - | -2.987370 | - | - | 8.32 | - |
| Cation | -2.943221 | -2.957303 | - | 9.25 | 9.15 | - |

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[a] Reference 5

## Table V

## COMPARISON OF GVB AND CI ENERGIES FOR BENZENE

| | Pi-Electron Energy (h) | | Excitation Energy (eV) | |
|---|---|---|---|---|
| State | GVB | CI[a] | GVB | CI[a] |
| $1^1A_{1g}$ | -6.426629 | -6.440101 | 0 | 0 |
| $1^3B_{1u}$ | -6.28841[b] | -6.299359 | 3.75 | 3.83 |
| $1^1B_{2u}$ | -6.231065[b] | -6.256218 | 5.32[b] | 5.00 |
| $1^3E_{1u}$ | -6.22570 | -6.256988 | 5.44 | 4.98 |
| $2^3E_{2g}$ | -6.155868 | -6.172630 | 7.40 | 7.28 |
| $2^1E_{2g}$ | -6.088204 | -6.133961 | 9.21 | 8.33 |
| $^3B_{1u}$ | -6.019643 | -6.032514 | 11.07 | 11.09 |
| $3^3A_{2g}$ | -5.990165 | -6.025651 | 11.88 | 11.28 |
| $^3E_{1u}$ | -5.938106 | - | 13.30 | - |
| $^1A_{1g}$ | -5.882233 | - | 14.81 | - |

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[a] Reference 15

[b] Using self-consistent orbitals for the state, the PI-electron energy is -6.246327h and the excitation energy is 4.90 eV.

In butadiene, the lowest singlet excited state found is the $2^1A_g$ state. MO considerations indicate that the first excited state should be the $^1B_u$ state. CI calculations[5] verify that the $2^1A_g$ state has the characteristics of a double excitation state. This state is described as a spin excitation state in the GVB wave function.

For benzene, VB and GVB considerations indicate that the valence states should have the spatial symmetries $1^1A_{1g}$, $1^1B_{2u}$, $1^1E_{2g}$ and $2^1A_{1g}$ for the singlet states, while MO considerations[6] indicate the symmetries should be $1^1A_{1g}$, $1^1B_{1u}$, $1^1E_{1u}$, $1^1E_{2g}$. From GVB and CI calculations using the GVB orbitals as a basis, additional low-lying states are found in the spectrum of benzene states. Some of these states are ionic-like, in that these states are tight or valence-like in spatial extent, but have two orbitals centered about one carbon. The MO spectrum of excited states includes some of these ionic-like states.

4. Many low-lying excited states have one diffuse orbital and may be considered as Rydberg-like states. Some examples are the $V(^1B_{2u})$ state of ethylene (in the planar geometry) and the $^1B_u$ state of butadiene. The Rydberg orbitals may have $3p\pi$, $4p\pi$, $3d\pi$, etc. character. Quantum defects were calculated and are consistent with experimentally determined values.

5. Resonance energies for allyl radical, butadiene, and benzene were calculated by comparing single configuration GVB G1 wave function energies with the optimum GVB energies. In Table VI we summarize these results. We note in general that GVB calculations seem to underestimate the resonance energy when compared to the conventional

## Table VI

## SUMMARY OF RESONANCE ENERGIES

| | Resonance Energy (Kcal) | | | |
|---|---|---|---|---|
| System | VB | GVB | GVB(SP) | EXPERIMENTAL |
| Allyl Radical | | | | |
| $1^2A_2$ | 15.9 | 11.4 | 14.3 | 10.0[a] |
| $1^2B_1$ | -61.9 | -57.9 | -59.2 | |
| Butadiene | | | | |
| $1^1A_g$ | 2.3 | 0.7 | 0.8 | 3.6[b] |
| $2^1A_g$ | -5.3[c] | - | 17.6 | |
| $^3B_u$ | 18.9 | 9.9 | 11.9 | |
| $^3A_g$ | 16.3 | 27.4 | 24.0 | |
| Benzene | | | | |
| $^1A_{1g}$ | 13.8 | 20.9 | - | 36 Kcal [b] |
| $^1B_{2u}$ | | | | |

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[a] Reference 7

[b] Reference 8

[c] These are destabilization energies measured relative to (12).

experimental values. Underestimating of the resonance energy in the GVB model is attributed to a difference in definition of the reference state between the experimental determination of the resonance energy and the GVB calculations. This will be examined fully in Section III.

6. In Appendices II through VI, VB results are reported. These were ab initio VB calculations in that a double zeta basis set was used for these calculations. Table VII contains a summary of the VB results, which is probably the most complete set of ab initio VB results available. Ab initio VB total energies do not agree well with full CI results. The VB qualitative description of the system is consistent with the CI and GVB descriptions of covalent states. VB excitation energies are in fair agreement with CI results.

7. In allyl radical, butadiene, and benzene, the same spatial orbitals can be used to describe the valence states within the GVB model fairly well. The primary difference between valence states arises from different spin couplings, that is, different ways to combine the individual orbitals to the spin of the final state. Self-consistent adjustments of the orbitals at the particular spin coupling results in some differences in the orbitals.

8. With a general enough wave function, localized orbital description of states is obtained. The GVB description of excited states of allyl radical and butadiene included delocalized symmetry orbitals. Removing restrictions from the wave function by including a spatial projection operator resulted in a localized orbital description of all states of allyl radical and butadiene.

## Table VII

## SUMMARY OF VALENCE BOND RESULTS

| System | Total Energy (h) | Excitation Energy(eV) |
|---|---|---|
| Allyl Radical | | |
| $1^2A_2$ | -116.35544 | 0 |
| $1^2B_1$ | -116.23784 | 3.20 |
| Butadiene | | |
| $1^1A_g$ | -154.853622 | 0 |
| $1^3B_u$ | -154.738538 | 3.13 |
| $1^3A_g$ | -154.682475 | 4.66 |
| $2^1A_g$ | -154.604735 | 6.77 |
| $3^3B_u$ | -154.571517 | 7.68 |
| Benzene | | |
| $1^1A_g$ | -230.54931 | 0.0 |
| $1^3B_{1u}$ | -230.46958 | 2.17 |
| $1^1B_{2u}$ | -230.40387 | 3.96 |
| $1^3E_{1u}$ | -230.38269<br>-230.37514 | 4.53<br>4.73 |
| $1^3E_{2g}$ | -230.34708<br>-230.33456 | 5.50<br>5.84 |
| $1^1E_{2g}$ | -230.28444<br>-230.28366 | 7.21<br>7.23 |
| $1^3E_{2g}$ | -230.205929 | 9.34 |
| $^3A_2$ | -230.162458 | 10.53 |
| $^3E_{1u}$ | -230.13101<br>-230.10604 | 11.38<br>12.06 |
| $^3S^1Ag$ | 230.12802 | 11.46 |

## B. Conclusions

1. The GVB method provides a quantitatively and qualitatively useful and accurate description of electronic states. Five pi-electron systems, within the frozen core approximation, have been examined and in all cases the results agree with full (or extensive) CI results and with available experimental results. Further, in those cases where some character of the state has been determined from the CI wave function, the GVB results are consistent with these results.

2. Generalizing the GVB wave function by including a spatial projection operator results in a localized orbital description of all states and total energies in excellent agreement with full CI results. The GVB(SP) wave function for all states of all systems examined provides a description of these states in terms of localized orbitals. Since the GVB(SP) wave function is the most general and most accurate independent particle wave function, localized orbitals would appear to represent a more accurate and fundamental description of electron orbitals. The GVB(SP) wave function imposes no restrictions upon the individual orbitals. A description of a state of a system which is in terms of delocalized symmetry orbitals arises from restriction inherent in the wave function.

3. The GVB description of the ground state of allyl radical and the ground state of benzene is qualitatively the same as the VB description of these states. The VB theory describes these states as resonant combinations of VB canonical structures. The GVB description specifies the same mixture of VB canonical structures, but structures

represent possible spin couplings of the system. The VB canonical structures represent in the GVB model the different ways to couple the electron spins to achieve the final overall spin of the system.

The resonance stabilization energy of benzene was examined and found to result from two effects. The standard for the experimental determination of the resonance energy is cyclohexene[6]. The pi bond in cyclohexene should be similar to the ethylene pi bond. However, in mythical cyclohexatriene (benzene without resonance), the orbitals will be delocalized and have amplitude on all six centers, greatly reducing the energy. The remaining part of the resonance energy arises from the special spin coupling, which makes all six centers connected by the same permutational symmetry. This part of the resonance energy corresponds to the classical VB description of the resonance stabilization of benzene. A similar dissection of the allyl radical and butadiene resonance energies was also obtained.

4. Using fused ethylenes as a model for the pi-states of unsaturated organic molecules as originally proposed by Dunning[3] for butadiene proved to be very successful. In particular, the GVB(SP) results on allyl radical and butadiene are strictly in accordance with this model. We expect this model to be applicable directly to linear polyenes. For cyclic polyenes, e.g., benzene, direct application of this model will yield more states than in fact there are. Spatial symmetry considerations indicate the proper combinations of ethylene groups that should be used and the application of this model will be more difficult.

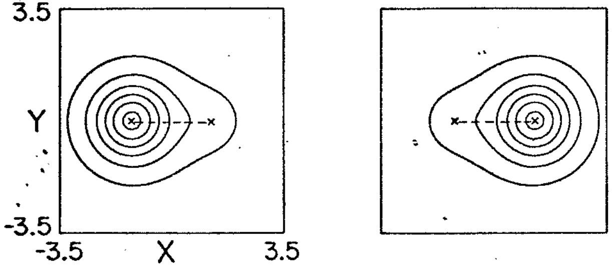
5. Comparing the GVB valence orbitals for the various systems examined shows that these orbitals are quite similar. As the systems become larger, individual orbitals become more delocalized by acquiring small amplitude on more centers while retaining their basic localized nature. The nature of the GVB pi orbitals which are valence-like at the site about which the orbital is centered for all of the systems examined is essentially the same. The GVB valence-like orbitals are atomic 2p-like, but delocalized in a bonding manner on nearest neighbors. The GVB pi orbitals for the ground states of ethylene, allyl radical, butadiene, and benzene are depicted in Figure 1. The GVB pi orbitals for some valence-like states of allyl radical, butadiene, and benzene are depicted in Figure 2. The similarity of these orbitals is obvious.

Figure 1

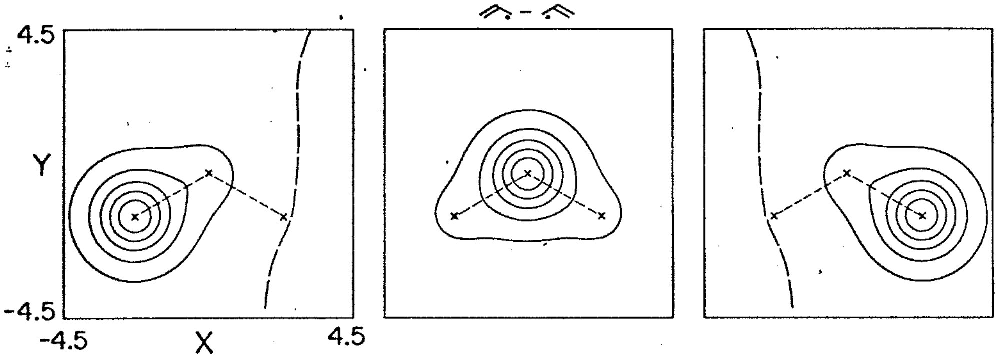
The GVB pi orbitals for the ground states of ethylene, allyl radical, butadiene, and benzene. All orbitals are shown in a plane 1.0 A.U. above and parallel to the molecular plane. In all plots the most diffuse contour has amplitude of 0.05 and each succeeding contour increases by 0.05. Nodal lines are represented by dashed lines. All plots are to the same scale. For allyl radical and ethylene all orbitals are shown. For butadiene one of two identical pairs of singlet coupled orbitals is shown. For benzene one of six identical orbitals is shown.

# GVB PI ORBITALS
# GROUND STATES

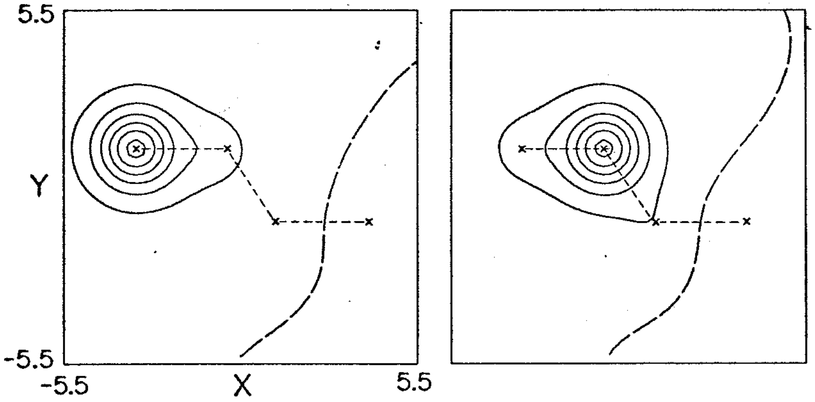
ETHYLENE ($^1A_g$)



ALLYL RADICAL ($^2A_2$)



TRANS BUTADIENE ($^1A_g$)



BENZENE ($^1A_{1g}$)

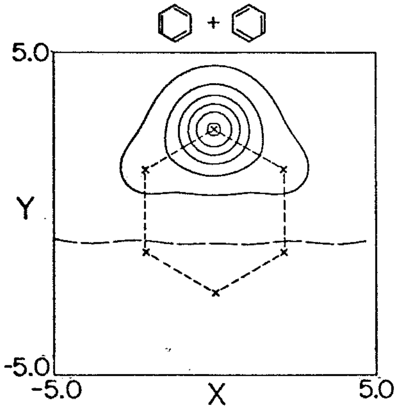
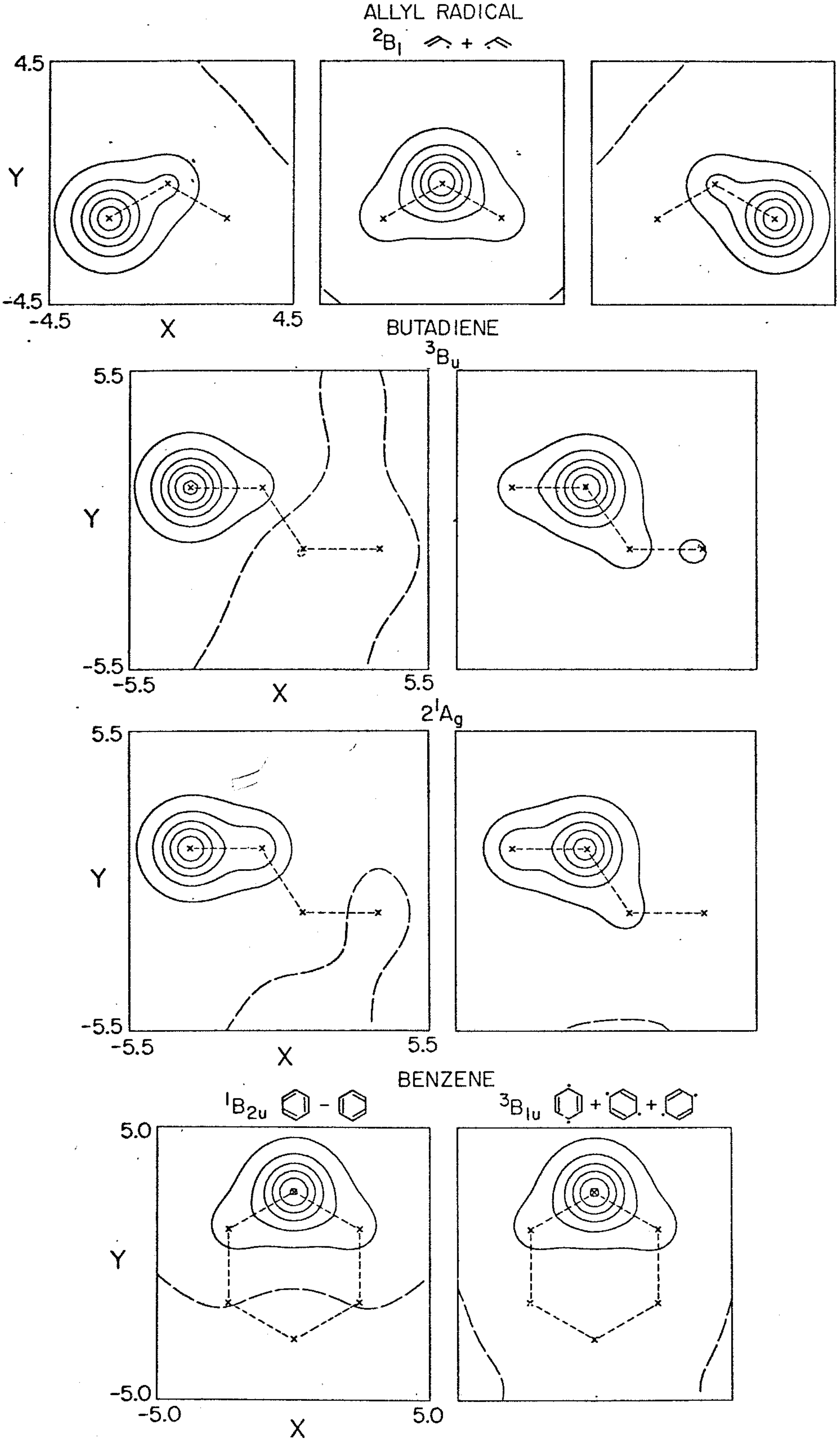


Figure 2

The GVB pi orbitals for the valence-like excited states of allyl radical, butadiene, and benzene. The plotting plane, contours, and scales are identical to Figure 1. All orbitals of the $1^2B_1$ state of allyl radical are shown. For the $2^1A_g$ state of butadiene, one of two identical pairs of triplet coupled orbitals is shown. For the $^3B_u$ state of butadiene one of the singlet coupled orbitals and one of the triplet coupled orbitals is shown. For benzene states, one of six identical orbitals is shown.

GVB PI ORBITALS
FOR VALENCE-LIKE EXCITED STATES



# III. CONCLUSIONS

The conclusions resulting from the body of work are presented in this section. The results in Appendices I through VI form the basis for these conclusions. The discussion will be general and not oriented to a particular system. Each particular system is discussed in detail in the applicable appendix.

## A. The Quantitative Accuracy of the GVB Method

The GVB method provides quantitatively accurate results limited only by the basis set. Most of the correlation energy is accounted for by the GVB wave function.

Five different pi electron systems have been examined using the GVB method. In addition to the ground state of each system, many excited states of each system were also examined and excitation energies obtained. Full (or complete within the basis set) configuration interaction (CI) results were used to compare the GVB results. Since these CI results represent the limit of the accuracy of the basis set and the same basis set was used for the GVB and CI calculations in all cases for each particular system, the CI results provide a test of the quantitative accuracy of the GVB calculations.

Pi-electron energies and excitation energies obtained from GVB, GVB(SP), and CI calculations are summarized in Tables II through V. Pi-electron energies are used for this comparison since all calculations were performed using a frozen Hartree-Fock sigma electron core. The core energy is an additive constant common to both the CI and GVB results and only makes the difference between the results appear smaller.

From these tables we see in all cases the order of states in the GVB and GVB(SP) results is identical to the order of states in the CI results. Although this does not seem to be a major achievement, HF or MO calculations in fact would not yield the same spectrum of states. In allyl radical, the $1^2B_1$ would not be well described by a HF calculation and be essentially missed entirely. This state is best described as a spin excitation state from the ground state in that the same spatial orbitals serve to describe both states but the orthogonal spin couplings are used. The $1^2B_1$ has the characteristics of a double excitation state as is demonstrated in Appendix II and would not appear in the HF or MO spectrum of states, since these methods describe only single excitation states.

The GVB spectrum of butadiene includes two states which have the characteristics of double excitation states[5]. The $2^1A_g$ and the $3^3B_u$ states both display characteristics normally associated with double excitation states. These states are valence-like states and will not be found in HF calculations.

For benzene the MO and GVB spectrums are very different if only covalent states are to be studied. Some of the states in the MO spectrum are probably ionic in nature and are lower lying than some valence-like states. In Appendix VI, full minimum basis set CI calculations using the GVB orbitals as the basis generate a spectrum of states which includes ionic-like state and poorly described Rydberg-like states. In this spectrum, even though the basis functions are valence-like and thus better suited to describing valence-like states rather than ionic-like states, ionic-like states are lower in energy than some valence-like states. This phenomenon occurs in both the singlet and triplet spectrums.

Examining Tables II through V in detail indicates that the GVB and CI results are in good agreement. For allyl radical, the typical difference between GVB and CI total energies is 0.01h, or less than 0.3 eV. Excitation energies agree with 0.17 eV. The GVB(SP) results, as would be anticipated, are in better agreement with the full CI results, with the maximum disagreement in total energies of 0.0048h and in excitation energies of 0.04 eV.

For ethylene and allyl cation, the GVB(SP) results differ from the full CI results by less than 0.003h for total energies and 0.06 eV for excitation energies. For butadiene, the difference between the GVB energies and the full CI energies is less than 0.03h, while the maximum difference between GVB(SP) and full CI energies is 0.009h and a more typical difference is 0.004h.

For those states of benzene for which optimum SCF GVB orbitals were found ($1^1A_{1g}$, $1^1B_{2u}$, and $1^3B_{1u}$ states) the difference between GVB and full CI energies is 0.02h or less. The GVB description of the valence states of benzene used the ground state spatial orbitals with the spin coupling appropriate for the excited state, so we expect the difference between the full CI energy and GVB energy to be typically greater, and it is about 0.04h.

In summary, we find full CI calculations and the GVB (and GVB(SP)) wave functions yield the same spectrum of state, total energies differing by a few hundredths of a hartree or less, and excitation energies differing by a few tenths or less of an electron volt. This should establish the quantitative reliability of the GVB method and that the GVB wave function includes the important correlation effects in a consistent manner for the ground states and excited states.

## B. Spatial Projection

The GVB wave function was generalized by including a spatial projection operator. Huestis[9] earlier had prepared a two-electron GVB(SP) computer program and performed calculations on $H_2$. Guberman[10] wrote a very specialized four-electron GVB(SP) computer program to study the excited states of $He_2$. In both cases, the GVB(SP) method provided localized orbital descriptions of the subject system and good agreement with experimental information. In both cases, the GVB(SP) calculations provided new insight into the nature of these systems.

Since the optimum GVB orbitals for some states of allyl radical and butadiene were delocalized and it was considered that restrictions in the GVB wave function caused the orbitals to be delocalized, a general three and four electron GVB(SP) wave function contains no restrictions upon the individual orbitals and is the most general independent particle wave function as yet presented.

The results of application of the GVB(SP) to allyl radical are in Appendix III and to butadiene in Appendix V. Examining Figures 3 through 6 we see that all of the orbitals are basically localized, each about a particular carbon atom. The optimum GVB orbitals for the ground state of allyl radical (see Figure 7) are delocalized symmetry

Figure 3

The GVB(SP) pi orbitals for 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 2.154 greater or a factor of 10 for each three contours.

ALLYL RADICAL
GVB(SP) PI ORBITALS FOR $A_2$ STATES

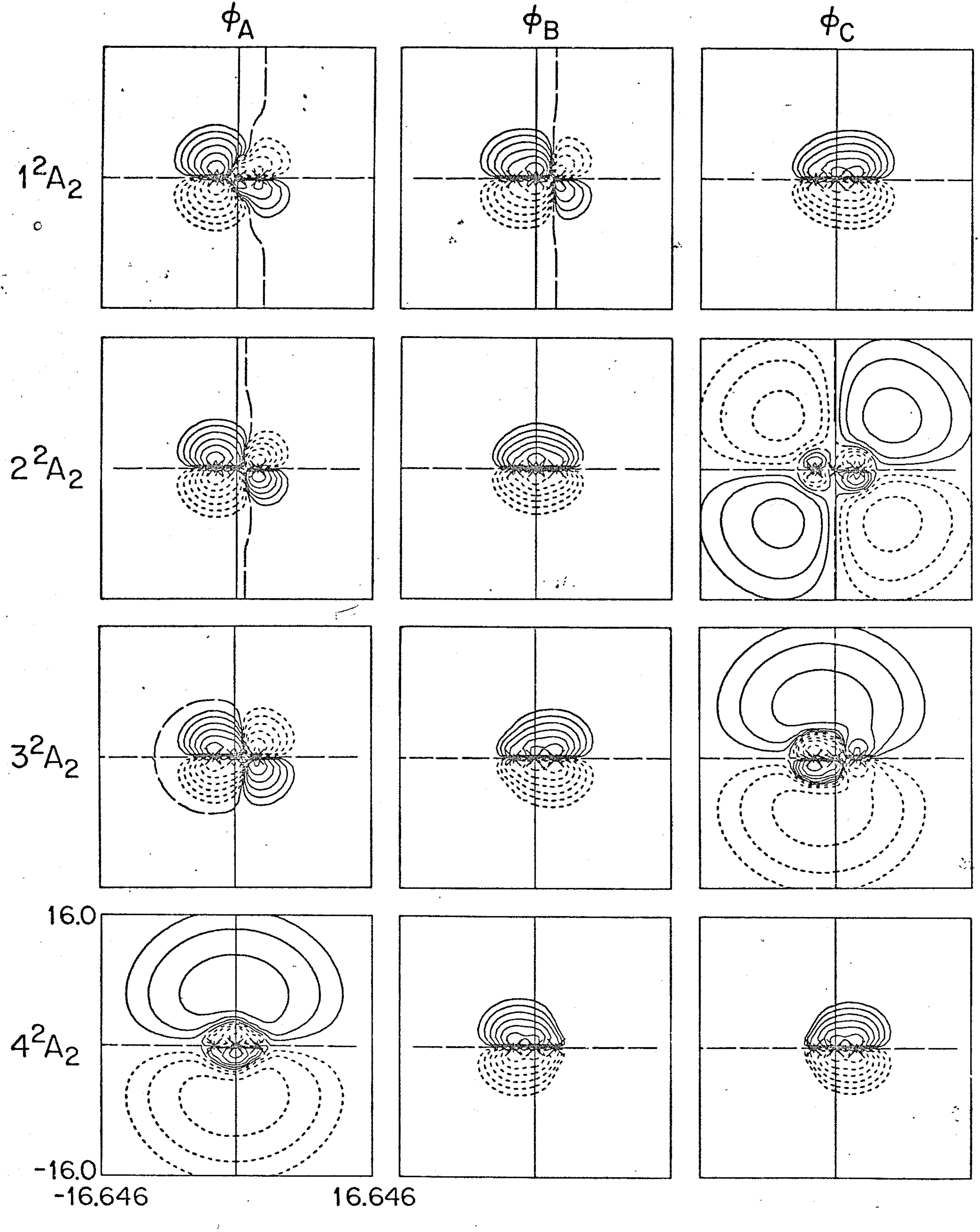


Figure 4

The GVB(SP) pi orbitals for the 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 Figure 3.

# ALLYL RADICAL
# GVB(SP) PI ORBITALS FOR $B_1$ STATES

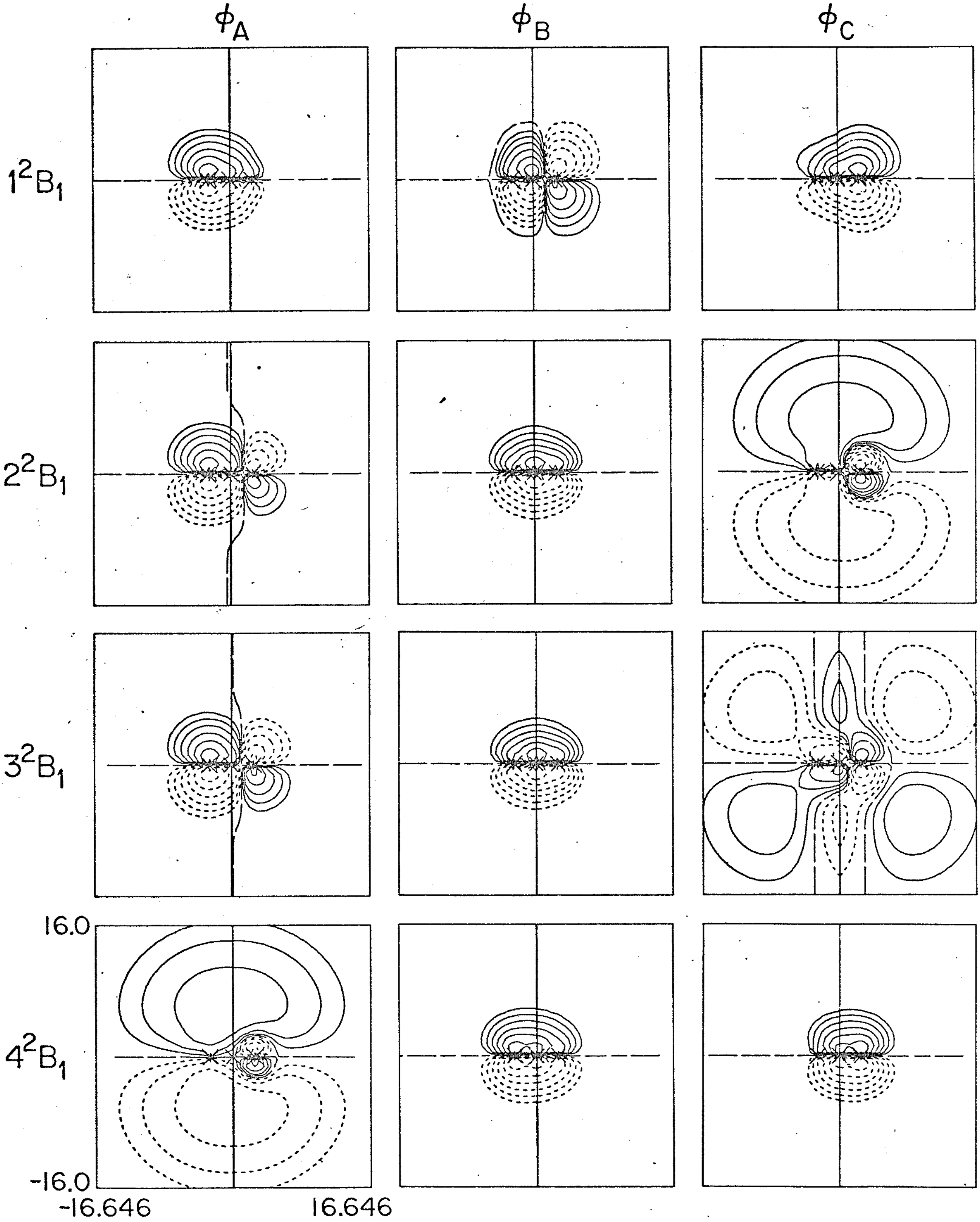


Figure 5

The GVB(SP) pi orbitals for the valence states of butadiene. The ordering of orbitals in each state is such that the first two are uniquely coupled in the predominate spin coupling. The amplitude of the most diffuse contour is 0.003. The amplitude of each succeeding contour is a factor of 2.154 greater or a factor of 10 for each three contours.

VALENCE STATES OF BUTADIENE
GVB(SP) PI ORBITALS

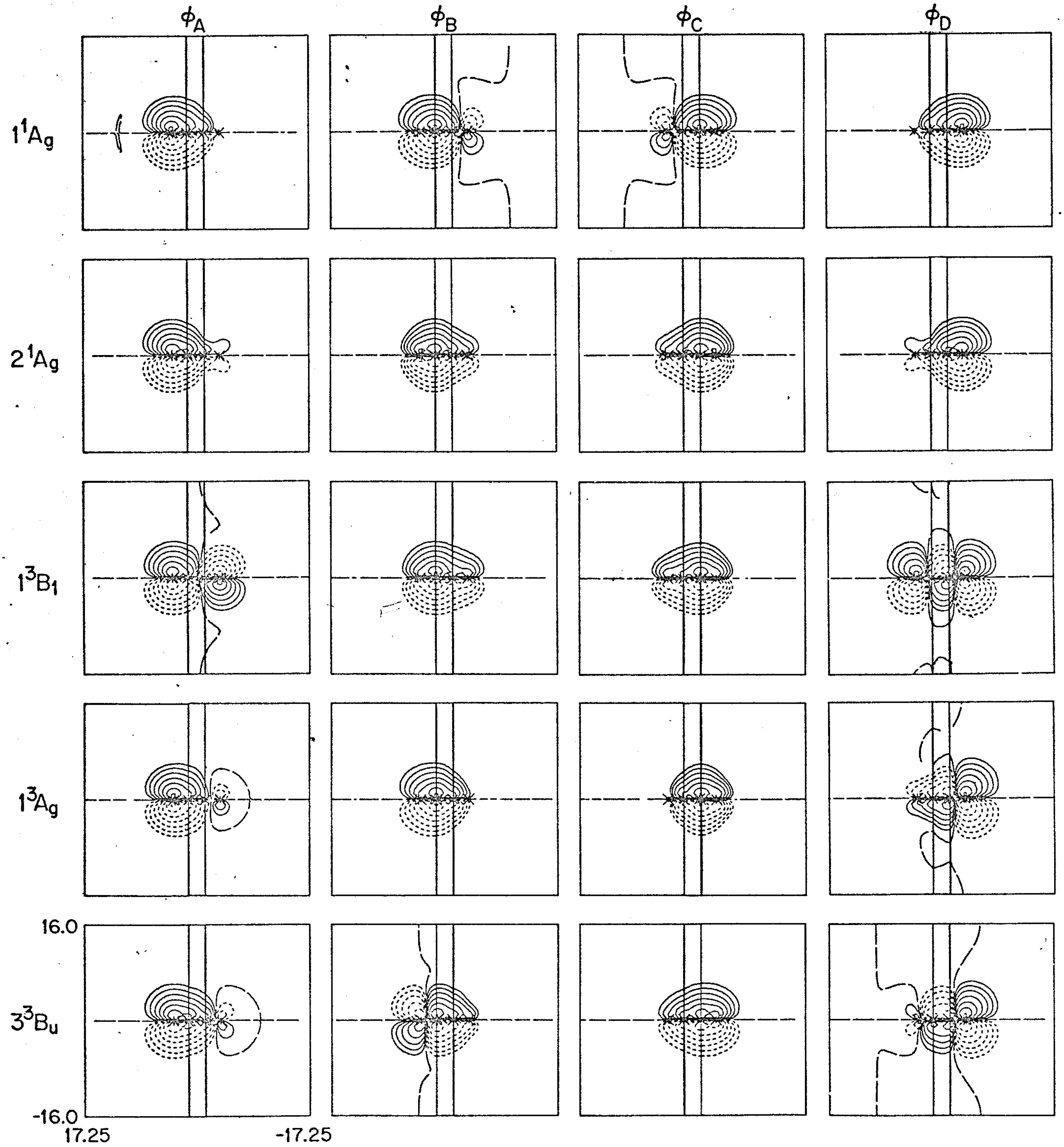


Figure 6

The GVB(SP) pi orbitals for the Rydberg-like states of butadiene. The order of orbitals is as in Figure 5. The figure in the upper right corner indicates the planes in which the orbitals have been plotted. The amplitudes are identical to those in Figure 5.

# RYDBERG - LIKE STATES OF BUTADIENE
# GVB(SP) PI ORBITALS

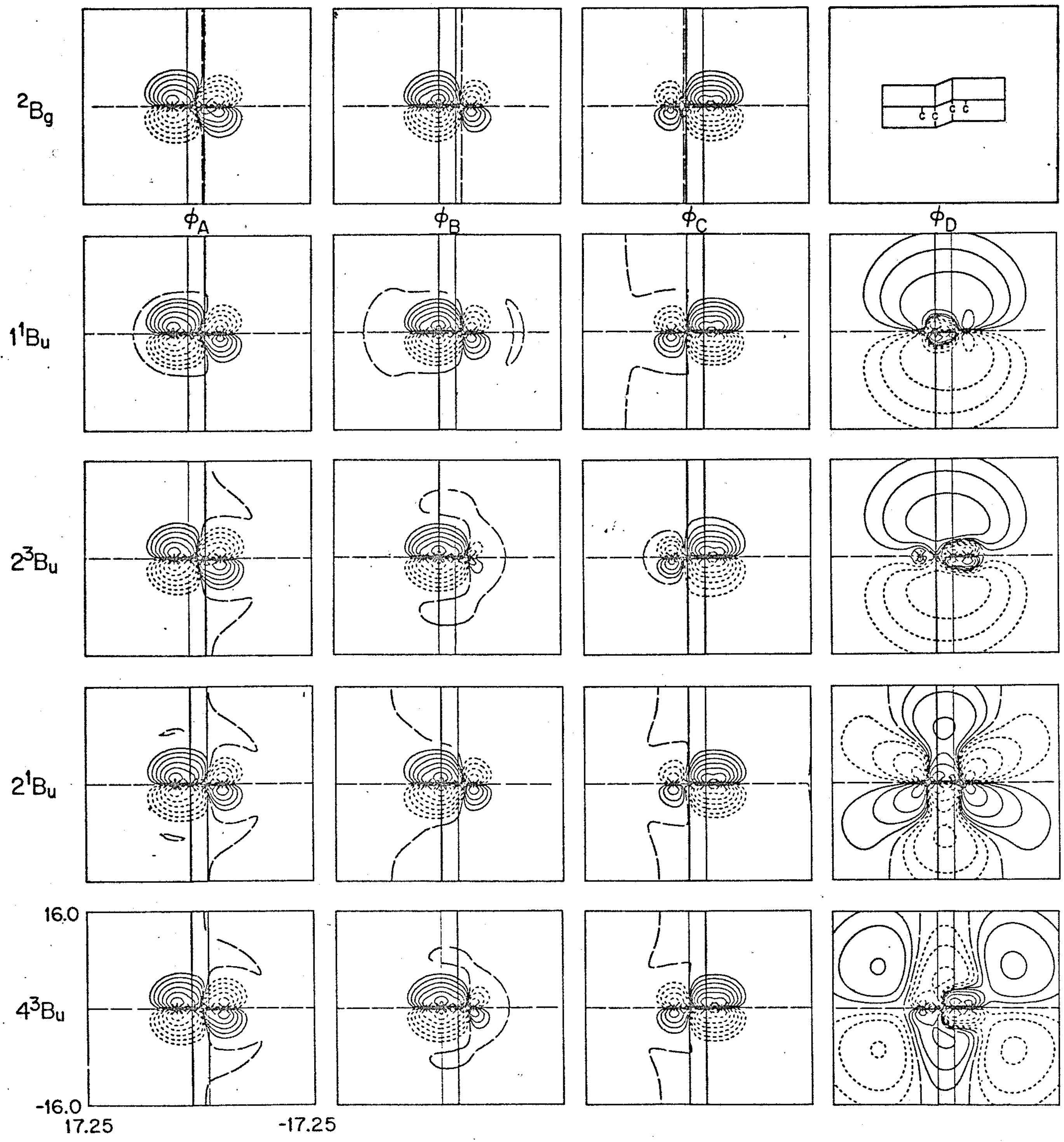


Figure 7

The GVB pi orbitals of various states of allyl radical. The ordering of orbitals is such that orbitals 1 and 2 are singlet coupled. The most diffuse contour has an amplitude of 0.003. The amplitude increases by a factor of 2.1544 at each contour corresponding to a factor of 10 for three contours.

ALLYL RADICAL GVB PI ORBITALS

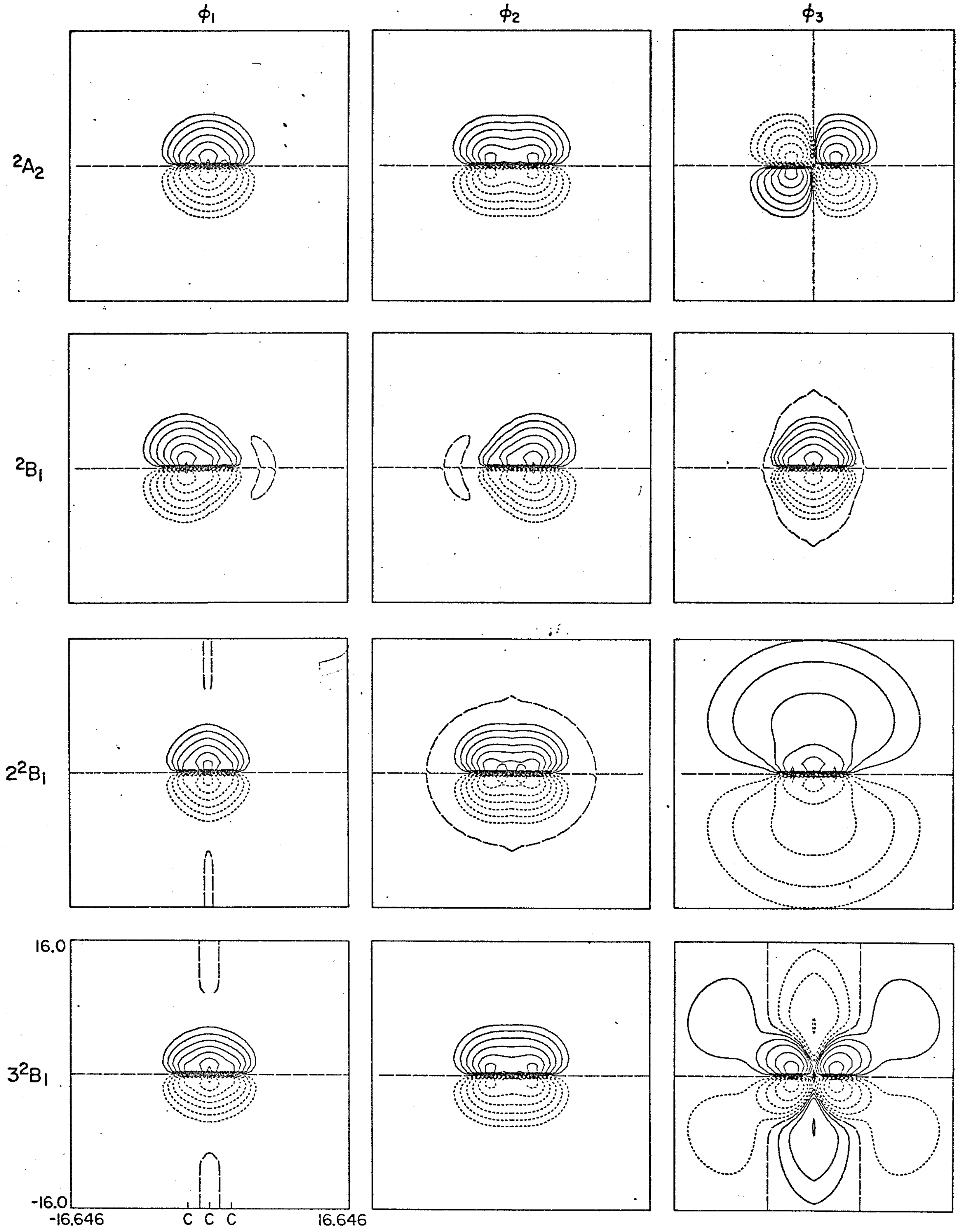
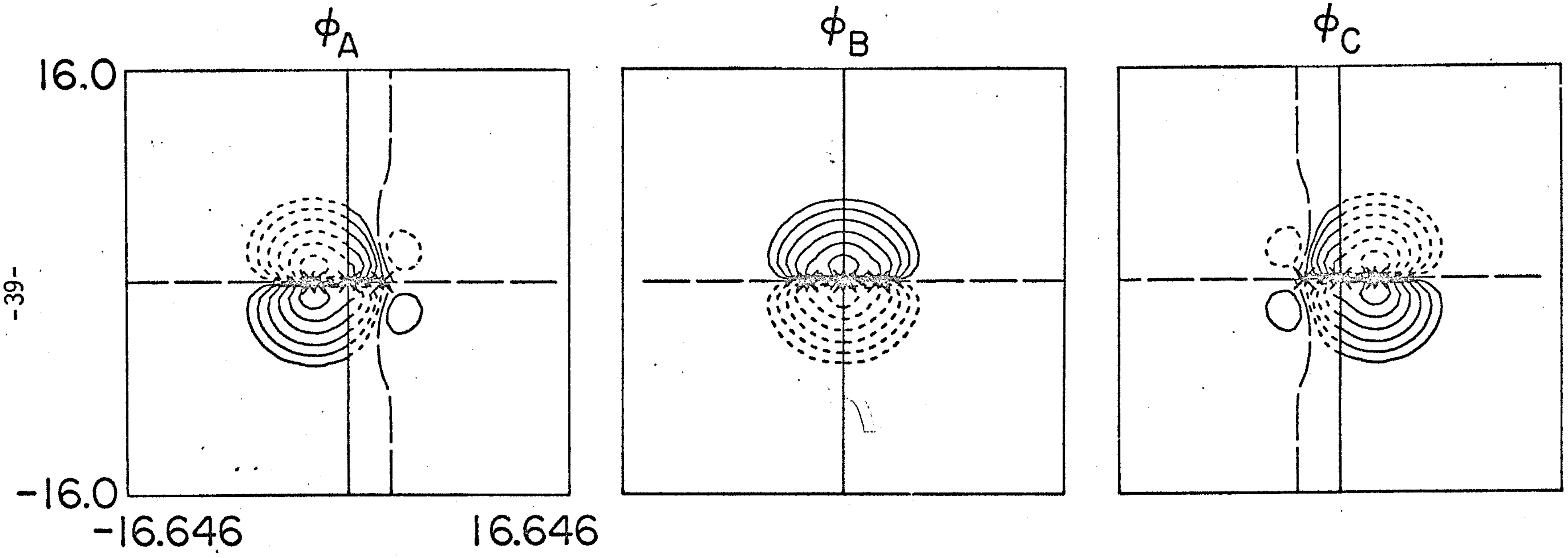


Figure 7a

The localized GVB pi orbitals of the ground state of allyl radical. The amplitudes are the same as Figure 7.

GVB PI ORBITALS FOR
1 $^2A_2$ STATE OF ALLYL RADICAL



orbitals, while the GVB(SP) orbitals for the ground state of allyl radical are localized each about a different carbon atom. Extremely diffuse Rydberg-like orbitals tend to be so large in spatial extent that these orbitals extend over the entire system. However, the GVB(SP) diffuse Rydberg orbitals have a tight part about one particular center and tend to be slightly more concentrated in one side or about one particular center. In the case of butadiene, the GVB orbitals for the valence-like $1^3A_g$ state (see Figure 8) are delocalized symmetry orbitals and the GVB orbitals for the Rydberg-like states (see Figure 9) are also delocalized symmetry orbitals. However, the GVB(SP) orbitals for all the states we examined are localized, although very diffuse Rydberg orbitals tend to extend across the entire system.

As discussed in Section III.A, and as can be seen from Tables II through IV, the GVB(SP) energies for all the states agree quite well with full CI energies, the difference in energies being less than 0.01 Hartrees. Without exception, the GVB(SP) energies are less than the GVB energies for all of those states in ethylene, allyl cation, allyl radical and butadiene studied by both methods.

Since the GVB(SP) wave function will generate an energy closer to the full CI energy than any other independent particle wave function (where the basis set is the same for all calculations) the GVB(SP) description of a system may be considered as the "best" independent particle description. Further, since there are no restrictions imposed upon individual orbitals in the GVB(SP) wave function, the GVB(SP) orbitals should be the "best" orbitals. All applications

Figure 8

The GVB pi orbitals for the valence states of butadiene. The ordering of orbitals in each state is such that the first two are uniquely coupled in the predominate spin coupling. The amplitude of the most diffuse contour is 0.003. The amplitude of each succeeding contour is a factor of 2.154 greater or a factor of 10 for each three contours.

VALENCE STATE OF BUTADIENE
GVB PI ORBITALS

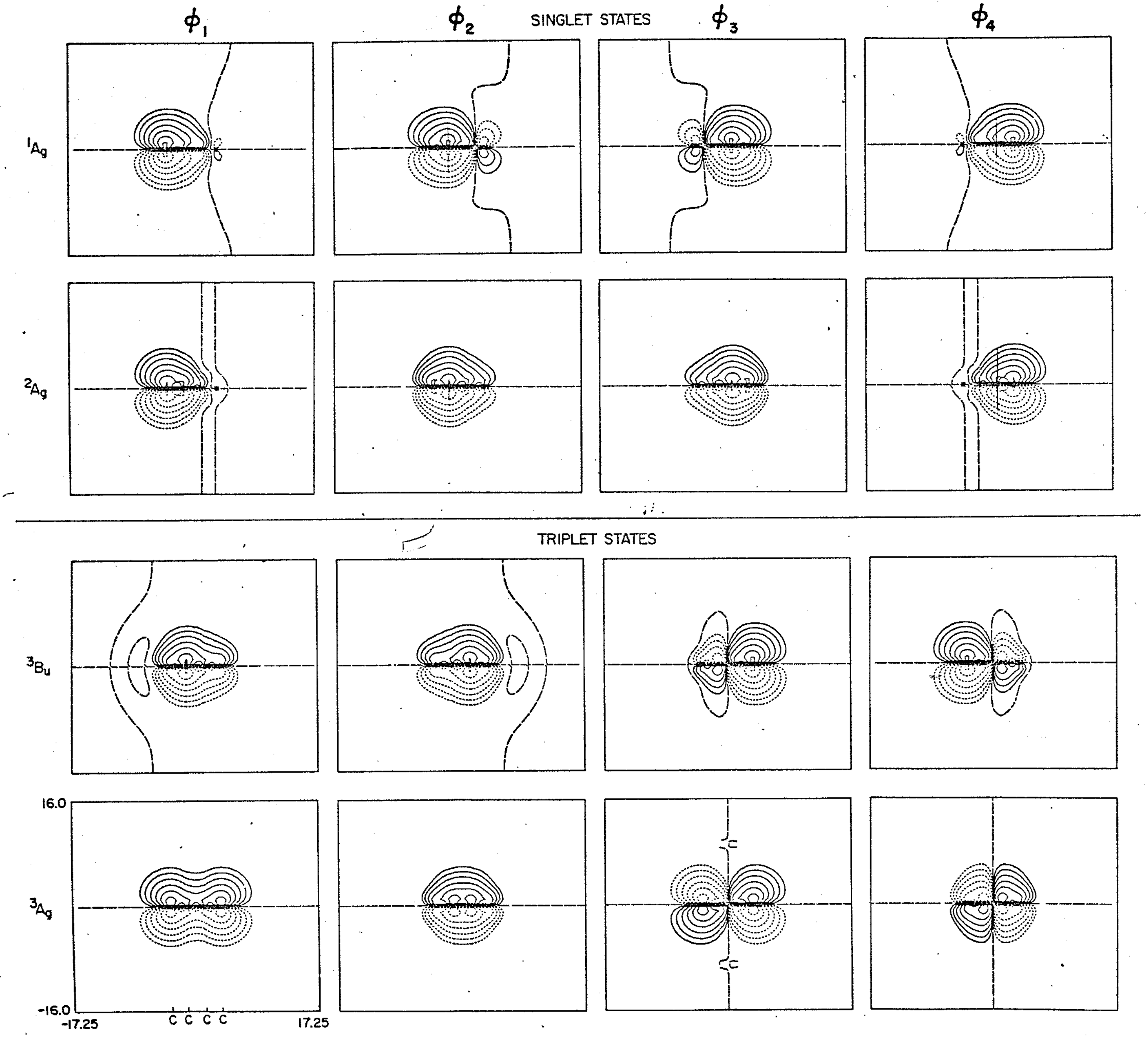
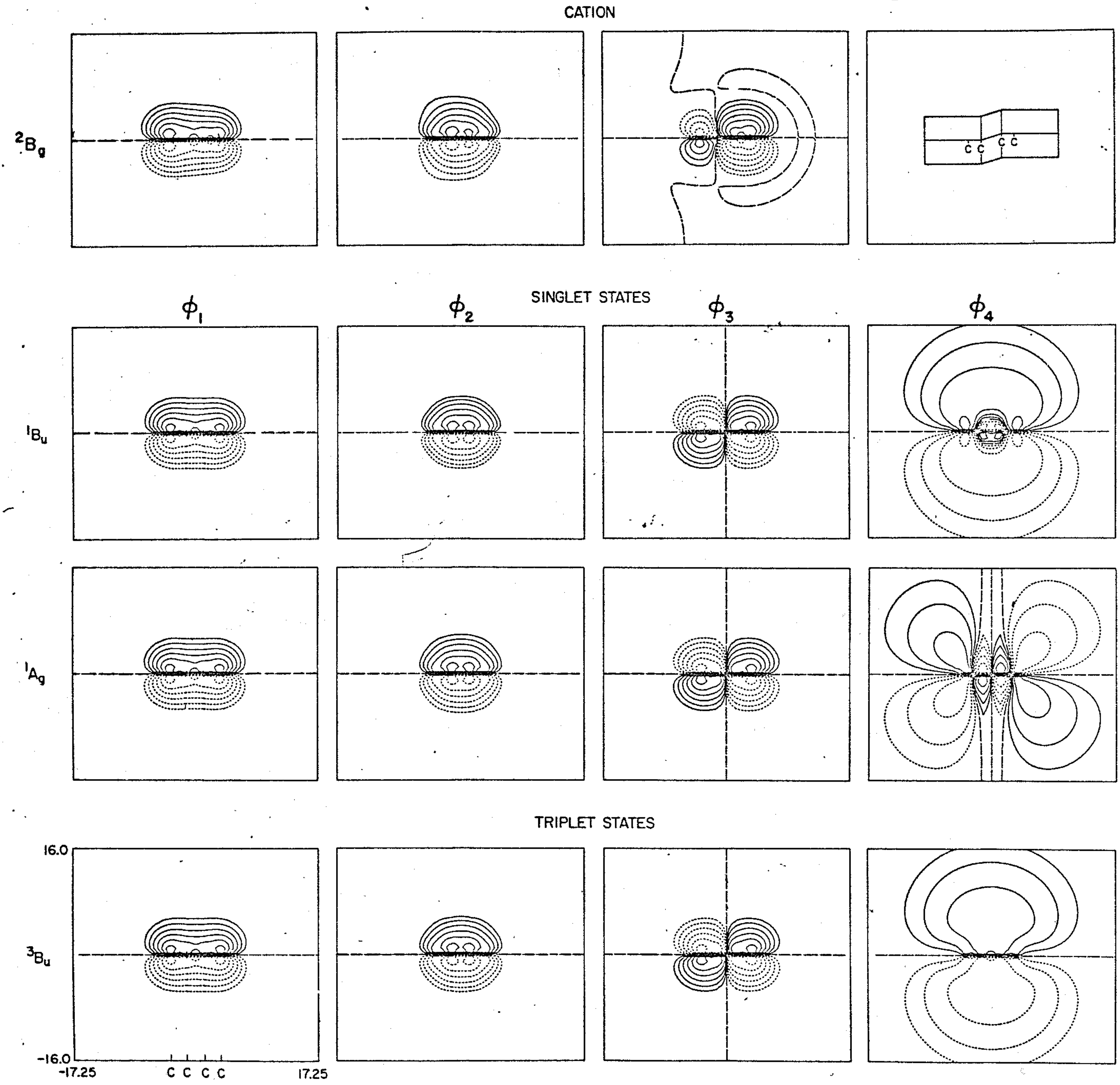


Figure 9

The GVB pi orbitals for the Rydberg-like states of butadiene. The order of orbitals is as in Figure 8. The figure in the upper right corner indicates the planes in which the orbitals have been plotted. The amplitudes are identical to Figure 8.

RYDBERG LIKE STATES OF BUTADIENE
GVB PI ORBITALS



of the GVB(SP) wave function have yielded localized orbitals, particularly for tight valence-like orbitals. Thus, we conclude that localized models for systems are to be preferred as these represent more accurate models. Localized orbital descriptions of systems appear to be the most fundamental description and should be used in models of systems.

## C. Resonance

The additional stability of the benzene pi electron system over that expected from comparison with ethylene pi bonds has long been a subject of interest and speculation for chemists. There have been many models and rationales proposed for the additional energy lowering in benzene. Simple MO theory[6] attributes the additional stability of the benzene pi electron system to delocalized pi orbitals extending uniformly over all six carbon atoms. The additional stability of the pi electron system is referred to as the delocalization energy. Simple VB theory[11] describes benzene as an equal mixture of the two Kekule structures


(a) (b)

(1)

with a small amount of the three Dewar structures

(2)

This mixing of structures is referred to as resonance and imparts additional stability to the pi electron system. The amount of energy lowering resulting from the mixing of structures is called the resonance energy.

Of the pi electron systems examined, allyl radical, butadiene, and benzene display resonance stabilization. The GVB wave function is well suited to describe the stabilization in these systems because the orbitals are found self-consistently and are not restricted in form, and mixing of structures as in VB theory may be performed. The orbitals are free to be delocalized symmetry orbitals, as in MO theory, and reduce the energy in this manner. (Larger orbitals permit a reduction of the kinetic energy.) Alternatively the orbitals can be localized on one center and become atomic-like and reduce the total energy by mixing of structures as in VB theory. The GVB wave function has the freedom to adopt either form of some combination of the two. We find that the GVB wave function contains some delocalization of the individual orbitals, while still maintaining their basic localized nature and a spin coupling corresponding to the VB mixing of states. The GVB results are qualitatively similar to the VB model of these systems, so the VB model will be used in our discussion.

Resonance in allyl radical results from the mixing of the two degenerate structures

(3)

The VB description of the resonant state is

(4)

and the resonance energy is the difference in the energies of (4) and (3a). The GVB description of the ground ($1^2A_2$) state of allyl radical is equivalent to (4) but the mixing of form is described as a mixing of spin couplings and the orbitals are found self consistently. The GVB wave function for the $1^2A_2$ state of allyl radical may be represented as

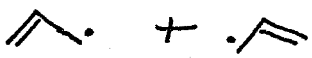
$$\begin{array}{|c|c|} \hline \phi_L & \phi_C \\ \cline{2-2} \phi_R & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} \qquad (5)$$

where $\phi_L$ ,$\phi_C$, and $\phi_R$ are pi orbitals localized about the left, center and right carbon atoms and the vertical box denotes the orbitals are triplet coupled. The resonance energy is calculated as the difference in energies of (5) and the GVB wave function for (3a) which is

$$\begin{array}{|cc|} \hline \phi_L & \phi_C \\ \hline \multicolumn{1}{|c|}{\phi_R} & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} \qquad (6)$$

where the horizontal box denotes the orbitals are singlet coupled, and the same spatial orbitals are used in both wave functions.

The VB description of the antiresonant ($1^2B_1$) state of allyl radical is



(7)

The GVB wave function may be represented as

$$\begin{array}{|cc|} \hline \phi_L & \phi_R \\ \hline \multicolumn{1}{|c|}{\phi_C} & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} \qquad (8)$$

which is the spin coupling orthogonal to (5) (provided $\phi_L$ and $\phi_R$

are identical in shape which is true in these cases). The antiresonant energy may then be calculated by comparison with (3a) or (6) as appropriate. The resonance and antiresonance energies are contained in Table VI.

From Figure 1 we see that the allyl radical ground state pi orbitals are somewhat delocalized as compared to the ethylene pi orbitals. However, experimental estimates of resonance energy are based upon ethylene[7]. Further, in VB theory, (3a) is an ethylene pi bond plus an electron, since atomic orbitals are used throughout in VB theory. To measure the effect of delocalization of the allyl radical, we used the GVB ethylene orbitals for $\phi_L$ and $\phi_C$ and a GVB methylene $^3B_1$ state[12] orbital for $\phi_R$ in (6). The energy of this state was 1.01 eV (23.1 Kcal) greater than the energy of (6) with the optimum orbitals (which are depicted in Figure 1). Two of the three orbitals have delocalized; the center orbital has delocalized relative to the ethylene orbitals and the methylene orbital has delocalized to be like an ethylene orbital.

Thus, we have found that in going from an allyl radical, which is an ethylene pi bond plus a pi electron, to a resonant allyl radical, two effects take place to reduce the energy. The orbitals spread out while staying basically localized. This reduces the energy about 23 Kcal [13]. The mixing of the two spin couplings to form (5) reduces the energy by 11.4 Kcal. The second effect is directly analogous to the VB picture of resonance.

Resonance in VB description of butadiene arises by a mixture of the two unequal structures

(9)

Since the two structures are not equivalent, the resonance effect is small. These structures may be denoted as

$$\begin{array}{|cc|}\hline \chi_{1R} & \chi_{2R} \\ \hline \chi_{2L} & \chi_{1L} \\ \hline \end{array} \qquad \begin{array}{|cc|}\hline \chi_{2L} & \chi_{2R} \\ \hline \chi_{1L} & \chi_{1R} \\ \hline \end{array} \tag{10}$$

where the $\chi$'s are atomic orbitals located at various centers. The optimum VB wave function is basically (10a) with a small mixture of (10b). The energy lowering due to incorporation of (10b) in the VB wave function is 2.27 Kcal.

The GVB wave function for the pi electrons of butadiene is formally the same as the VB wave function but the individual orbitals are found self-consistently and the spin coupling simultaneously optimized. There are two independent ways to couple four electrons to a singlet state. These may be chosen in many ways, such as (10), but for convenience, we use orthogonal spin functions denoted as

$$\begin{array}{|cc|}\hline \phi_a & \phi_b \\ \hline \phi_c & \phi_d \\ \hline \end{array} \tag{11}$$

and

$$\begin{array}{|c|c|}\hline \phi_a & \phi_c \\ \phi_b & \phi_d \\ \hline \end{array} \qquad (12)$$

The optimum mixture of (11) and (12) is $c_1 = 0.991$ and $c_2 = -0.131$, where $c_1$ is the coefficient of (11) and $c_2$ is the coefficient of (12). The calculated resonance energy found by comparing the energy of the optimum wave function with the energy of (11), using the optimum orbitals in both is 0.7 Kcal, while the experimental value is 3.6 Kcal [8].

Since the experimental estimate of the butadiene resonance energy is based upon a comparison with ethylene, the optimum GVB orbitals for ethylene were used in (11). The resulting energy is 0.37 eV (8.47 Kcal) greater than the energy of (11) using the optimum orbitals. The major part[13] of this energy difference is due to the more localized nature of the ethylene orbitals relative to the butadiene orbitals.

Resonance in benzene results from the mixing of the five canonical structures, (1) and (2). The Kekule structure constitutes about 90% of the VB wave function[11] and the dominant part of the VB wave function of the ground ($^1A_{1g}$) state is

(13)

As can be seen from Table VIII, the GVB wave function for the $^1A_{1g}$ is almost identical to the VB wave function. The first excited singlet

## Table VIII

## SINGLET VALENCE STATES OF BENZENE

| States | ΔE(eV)[b] | Spin Coupling | | | | |
|---|---|---|---|---|---|---|
| | | 1(a) | 1(b) | 2c | 2a | 2b |
| VB States | | | | | | |
| $^1A_{1g}$ | 0[a] | 0.42 | 0.42 | -0.17 | -0.17 | -0.17 |
| $^1B_{2u}$ | 3.96 | -0.82 | 0.82 | 0.00 | 0.00 | 0.00 |
| $^1E_{2g}$ | 7.21 | 0.00 | 0.00 | 0.20 | 0.70 | -0.90 |
| $^1E_{2g}$ | 7.23 | -0.00 | 0.00 | 0.92 | -0.64 | -0.29 |
| $2\,^1A_{1g}$ | 11.46 | -1.35 | -1.35 | -1.04 | -1.04 | -1.04 |
| GVB States (using $1\,^1A_{1g}$ originals) | | | | | | |
| $^1A_{1g}$ | 0[a] | 0.50 | 0.50 | -0.11 | -0.11 | -0.11 |
| $^1B_{2u}$ | 5.32 | 0.82 | -0.82 | -0.00 | -0.00 | -0.00 |
| $^1E_{2g}$ | 8.90 | 0.00 | 0.00 | 0.94 | -0.44 | -0.50 |
| $^1E_{2g}$ | 8.91 | 0.00 | 0.00 | -0.03 | 0.83 | -0.80 |
| $2\,^1A_{1g}$ | 14.81 | -1.34 | -1.34 | -1.04 | -1.04 | -1.04 |

---

[a] Calculated total energies for the ground state are -230.54931h and -230.70988h for the VB and GVB($1\,^1A_{1g}$ orbitals)

[b] 1 hartree = 27.2117 eV

($^1B_{2u}$) state is the antiresonant state and is described in both the VB wave function and the GVB wave function as

(14)

The standard state used to calculate the resonance energy may be represented as

(15)

Since the VB orbitals for (13), (15), and ethylene are the same, the calculation is well defined. The GVB wave function for (15) was taken as the G1 wave function. In this wave function the orbitals are coupled into three singlet pairs. The optimum orbitals were used in (15). This led to a resonance energy of 20.9 Kcal.

The experimental estimate of 36 Kcal is found by comparing the heat of hydrogenation of cyclohexene and benzene[8]. The resonance energy is the difference between the heat of hydrogenation of benzene and three times the heat of hydrogenation of cyclohexene. The pi bond of cyclohexene should be similar to the pi bond of ethylene, that is, basically a two-center pi bond. However, the GVB orbitals used to represent (15) are delocalized over all six centers of the molecule. Delocalization of the orbitals over all six centers should reduce the energy by reducing the kinetic energy.

To measure the effect of delocalization of the orbitals, we have performed calculations using ethylene, allyl radical, and butadiene orbitals. The GVB wave function for (15) may be represented as

$$\begin{array}{|cc|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \phi_4 \\ \hline \phi_5 & \phi_6 \\ \hline \end{array} \qquad (16)$$

where $\phi_i$ denotes a pi orbital localized about center $i$ . The results are summarized in Table IX. From this, we see that using ethylene orbitals in (16) increases the energy by 2.12 eV over the G1 energy (or 3.02 eV over the optimum GVB energy). Allowing two orbitals to delocalize onto at least four centers by using one butadiene ground state and one ethylene ground state in (16) reduces the energy by 0.69 eV or 0.35 eV/orbital. If one assumes that allowing each orbital to delocalize onto six centers reduces the energy by 0.03-0.04 eV/orbital over the butadiene orbitals, then the full increase of 2.12 eV found in using ethylene orbitals is recovered.

Using the ethylene orbitals or the butadiene orbitals in (12) introduces some unfavorable interactions that are not present in cyclohexene. The overlap of pairs of orbitals is unfavorable and raises the energy of the system. However, these calculations on benzene, butadiene and allyl radical demonstrate that delocalization of the orbitals over more centers results in a significant lowering of the energy.

The experimentally measured resonance energy can be attributed to two effects. Delocalization of individual pi orbitals in benzene compared to the pi orbitals of cyclohexene contributes a significant reduction of the energy. Resonance in the VB sense contributes 20.9 Kcal to the energy reduction. Neither effect is able alone to

## Table IX

| System | Spin Coupling Optimum | Orbitals Optimum | E(h) | $\Delta E$(eV) |
|---|---|---|---|---|
| Allyl Radical | | | | |
| | G1 | Optimum | -116.414975<br>-116.396808 | 0<br>0.49 |
| | G1 | Ethylene and Methylene | -116.368228 | 1.27 |
| | G1 | Valence Bond | -116.330115 | 2.31 |
| Butadiene | | | | |
| | G1[b] | Optimum | -154.935750<br>-154.934441 | 0 |
| | G1 | Ethylene | -154.920969 | 0.40 |
| | G1 | Valence Bond | -154.850013 | 2.33 |
| Benzene | | | | |
| | Optimum | Optimum | -230.709915 | |
| | G1[c] | Optimum | -230.676690 | 0.90 |
| | G1 | Butadiene and Ethylene | -230.624443 | 2.33 |
| | G1 | Allyl Radical | -230.607156 | 2.79 |
| | G1 | Ethylene | -230.599031 | 3.02 |
| | G1 | Valence Bond | -230.498620 | 5.75 |

---

[a] Refer to equation 6

[b] Refer to equation 11

[c] Refer to equation 16

account for the energy reduction.

Thus, in the three system examined, the experimentally measured resonance energy arises from two effects. Individual orbitals are delocalized relative to ethylene pi orbitals, but still retain a basically localized nature. Mixing of spin couplings in a manner directly analogous to VB mixing of canonical structures provides additional stabilization. Neither effect alone accounts for the experimentally measured resonance stabilization (or delocalization) energy.

## D. Fused Ethylene Model

Dunning originally proposed[3] a fused ethylene mode for butadiene. This model considered butadiene as two fused ethylenes and the pi electrons states of butadiene were considered as arising from combinations of pi electron states of the ethylene. We have extended this model to allyl radical and to a limited degree to benzene. This model requires a localized orbital description of the pi electron system in order to be able to separate the ethylene entities. In Table X we summarize the states of allyl radical, butadiene, and benzene that we have been able to analyze using this model. Appendices II through VI discuss individual states with respect to the fused ethylene model.

In general, the fused ethylene model for linear polyenes is fully consistent with GVB or GVB(SP) results and the CI ordering of states. This model predicts the existence of low-lying valence states not found in the HF spectrum of state. First we will examine the valence-like states.

# Table X

## ANALYSIS OF STATES OF ALLYL RADICAL, BUTADIENE, AND BENZENE IN ETHYLENE COMBINATIONS

| Allyl Radical | | Butadiene | | Benzene | |
|---|---|---|---|---|---|
| $1^2A_2$ | N - $2p\pi$ | $1^1A_g$ | NN | $1^1A_{1g}$ | NNN+NNN |
| $1^2B_1$ | T - $2p\pi$ | $1^3B_u$ | NT-TN | $1^3B_{1u}$ | NNN-NNN |
| $2^2B_1$ | N - $3p\pi$ | $1^3A_g$ | NT+TN | $1^1B_{2u}$ | NTT |
| $2^2A_2$ | N - $3d\pi$ | $2^1A_g$ | TT | $1^1E_{2g}$ | NTT |
| $3^2B_1$ | N - $4p\pi$ | $1^1B_u$ | NR | $N^1A_{1g}$ | NTT |
| $4^2B_1$ | $2^3B_{1u}$-$2p\pi$ | $2^3B_u$ | $N^3Ag$ | | |
| $3^2A_2$ | T - $3p\pi$ | $2^1B_u$ | NV | | |
| $4^2A_2$ | R - $2p\pi$ | $3^3B_u$ | TT | | |
| | | $4^3B_u$ | N $2^3B_{1u}$ | | |

Symbols used:

N - Ethylene ground state $1^1A_g$

T - Ethylene lowest triplest state $1^3B_{1u}$

V - $1^1B_{1u}$ ethylene state

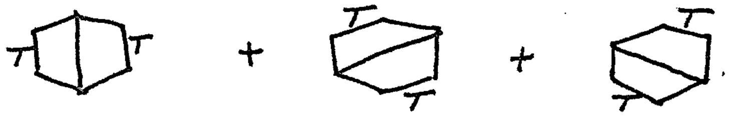
R - $2^1A_g$ ethylene state

There are two valence-like states of ethylene, the ground (N) state and the first triplet (T) state. The excitation energy for the T state from GVB(SP) result is 4.20 eV. From these states we shall build up all of the valence states of larger polyenes

There are two valence states of allyl radical. The ground ($^2A_2$) state is an N state ethylene plus a pi electron and the first excited ($1^2B_1$) state is a T state ethylene plus a pi electron. The GVB(SP) excitation energy of the $^2B_1$ state is 3.19 eV. The decrease in the excitation energy is due to favorable interaction possible in the $^2B_1$ state not possible in T state ethylene, such as overlap of a T state orbital with the third electron. The N state ethylene orbitals have unfavorable interactions with the third electron from the Pauli principle, bringing the two states closer together.

In butadiene there are two singlet valence states and three triplet valence states. The singlet valence states are the ground ($^1A_g$) state and the $2^1A_g$ state. The ground state is two ethylene N states. The $2^1A_g$ state is two ethylene T states coupled to a singlet. The GVB(SP) excitation energy of this state is 6.81 eV compared to 8.40 eV for two T states. Favorable interactions across the middle two carbons account for the reduction in the excitation energy. The three triplet valence states of butadiene are the $1^3B_u$, $1^3A_g$, and $3^3B_u$ states. These states are, respectively, the antisymmetric combination of N and T states ethylenes, the symmetric combination of N and T states ethylenes, and two T state ethylenes coupled to a triplet. The average excitation energy of the $1^3B_u$ and $1^3A_g$ states should be equal to the T state excitation energy and is found to be 4.21 eV using the GVB(SP) values. The excitation energy of the $3^3B_u$ state is 8.29 eV compared to 8.40 eV for two ethylene T states.

The benzene ground state is the symmetric combination of three N state ethylenes. The $^1B_{2u}$ state can be considered as the antisymmetric combination of three N state ethylenes. The remaining three valence states are combinations of two ethylene T states coupled to a singlet and an ethylene N state. The fifth ($^1A_g$) state would be



The $^1E_{2g}$ states would be the orthogonal combinations. The $^3B_{1u}$ state would be a T state of ethylene and two N state ethylenes. The other triplet states are more complicated combinations. The analysis of benzene pi states in terms of the fused ethylene model has not been developed or tested and may not prove to be useful.

For Rydberg-like states the analysis is similar to that used for the valence states. The results are summarized in Table 10. From Figures 3, 4, and 5, the shapes of the Rydberg-like orbitals are consistent with the designated ethylene state diffuse orbital.

For allyl radical and butadiene, the fused ethylene model provides a good model for valence-like and Rydberg-like states. This model yields an upper estimate to the excitation energy and a good qualitative description of the individual orbitals.

## E. GVB Orbitals

VB theory uses atomic orbitals to describe all valence states. The quantitative agreement between valence bond theory and experiment is quite poor, but the qualitative descriptions of the states of systems is consistent with GVB and CI results. We will explore the VB approach of using the same GVB orbitals to describe all valence states of a given pi electron system. Only localized orbitals will be considered as the shape of delocalized symmetry orbitals is determined mainly by the molecular symmetry.

In Figures 1 and 2, the GVB pi orbitals for the ground and some excited states of ethylene, allyl radical, butadiene, and benzene are depicted in a plane parallel to and 1 Bohr above the molecular plane. The minimum amplitude indicated is 0.05. The general shape of all the orbitals is quite similar and basically reflects the number of nearest neighbors each orbital can interact with in a favorable (bonding) manner. For example, each ethylene orbital and end orbital in allyl radical and butadiene have only one nearest neighbor. These orbitals are very similar in shape. The middle orbital in allyl radical, an inner orbital in butadiene, and the benzene orbitals each have two nearest neighbors and these orbitals are very similar in shape.

Although the basis sets used for the calculations differ slightly, the valence basis functions were the same in all cases. In Table XI we list the coefficients of the GVB orbitals on the valence basis functions for valence states described by localized orbitals. The similarity is obvious.

# Table XI

## GVB VALENCE ORBITALS

|  | Ethylene | Allyl Radical |  |  |  |
|---|---|---|---|---|---|
|  | $^1A_{1g}$ | $^2A_2$ |  | $^2B_1$ |  |
| Center |  | Left or right | Center | Left or right | Center |
| C 1 | 0.73210742 | 0.62651132 | 0.13434089 | 0.59762974 | 0.16875606 |
|  | 0.29673319 | 0.38718288 | 0.03262637 | 0.42090113 | -0.04603354 |
| 2 | 0.13454132 | 0.16353875 | 0.64104185 | 0.21863452 | 0.62718041 |
|  | 0.06518117 | 0.03212702 | 0.31449110 | -0.03260074 | 0.39530478 |
| 3 |  | 0.00457299 | 0.13434089 | 0.03428495 | 0.17002335 |
|  |  | -0.07101176 | 0.03262637 | -0.00460641 | -0.04469781 |

Table XI (continued)

GVB VALENCE ORBITALS

Butadiene

| | $^1A_{1g}$ | | $2^1A_g$ | | $^3B_u$ | |
|---|---|---|---|---|---|---|
| | outer | inner | outer | inner | outer | inner |
| 1 | 0.72719169 | 0.13502303 | 0.60733810 | 0.36938591 | 0.66935057 | 0.24203865 |
| | 0.29796164 | 0.03438053 | 0.27478009 | 0.04757594 | 0.35671195 | 0.09920208 |
| 2 | 0.14285856 | 0.72137246 | 0.37299595 | 0.58775088 | 0.24553249 | 0.65428600 |
| | 0.04998636 | 0.30572698 | 0.07585374 | 0.30102190 | 0.00223824 | 0.30819091 |
| 3 | 0.05269520 | 0.08244678 | 0.04473142 | 0.11307546 | -0.01050047 | 0.11044373 |
| | -0.00243165 | 0.02216648 | -0.03711687 | 0.03866268 | -0.05088063 | 0.02257073 |
| 4 | -0.00836648 | -0.04871290 | -0.00305814 | 0.01898838 | +0.0042011 | 0.05285339 |
| | -0.01816462 | 0.05010608 | 0.01709367 | 0.01903004 | 0.03701238 | 0.00360587 |

Table XI (continued)

Benzene

| | $^1A_{1g}$ | $^1B_{2u}$ | $^3B_{1u}$ |
|---|---|---|---|
| 1 | 0.70256023 | 0.67752589 | 0.68626015 |
| | 0.29943378 | 0.369649423 | 0.34476423 |
| 2 | 0.13239026 | 0.15594805 | 0.15016905 |
| | 0.03452430 | -0.01987728 | -0.02402999 |
| 3 | -0.00467753 | 0.00385420 | 0.03037260 |
| | -0.02794186 | -0.02306240 | -0.01487679 |
| 4 | -0.05299941 | -0.08505667 | 0.00626247 |
| | -0.04622635 | -0.01661531 | 0.02473011 |
| 5 | -0.00514493 | 0.00350809 | 0.02890368 |
| | -0.02816464 | -0.02317635 | -0.02011091 |
| 6 | 0.13231848 | 0.15534735 | 0.13927672 |
| | 0.03447428 | -0.02031669 | -0.02090541 |

From Figures 1 and 2, we see the orbitals for the two lowest states ($1^2A_2$ and $1^2B_1$) of allyl radical. Using the $1^2B_1$ state pi orbitals in the $^2A_2$ state wave function yields an energy only 2.62 Kcal above the $^2A_2$ energy, while using the $^2A_2$ state pi orbitals in the $^2B_1$ state wave function yields an energy only 6.58 Kcal above the $^2B_1$ . Small self-consistent adjustments reflecting the differences between spin couplings are the difference between these two sets of orbitals.

In benzene the energy of the $^1B_{2u}$ state with the $^1A_{1g}$ state orbitals is only 9.58 Kcal greater than the self-consistent value.

In general, the local nature of GVB pi orbitals is the same in all systems we have studied. The major change in the orbitals from state to state and system to system is delocalization onto more centers.

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# APPENDIX I

# THE GENERALIZED VALENCE BOND $\pi$ ORBITALS OF ETHYLENE AND ALLYL CATION

## 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 $\pi$ 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 states 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 [2-4]projection) of the $\pi$-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. Calculational Considerations

### A. The Hartree-Fock and Generalized Valence Bond Wavefunctions

The Hartree-Fock wavefunction for the ground state of ethylene is of the form:

$$\mathcal{A}[\phi_1\alpha\phi_1\beta \ldots \phi_q\alpha\phi_q\beta\phi_{\pi_1}\alpha\phi_{\pi_1}\beta] = \mathcal{A}[\Phi_\sigma\varphi_{\pi_1}\alpha\varphi_{\pi_1}\beta] \tag{1}$$

where there are seven doubly-occupied $\delta$-orbitals (orbitals that are symmetric under the operation of reflection through the molecular plane) and one doubly-occupied $\pi$ orbital (orbitals that are antisymmetric under the operation of reflection through the molecular plane). The many-electron product $\Phi_\sigma$ is used here to represent all of the $\sigma$-orbitals. Some of the important excited states of ethylene are obtained by replacing one $\pi$ orbital in (1) with an excited $\pi$ orbital, $\phi_{\pi_2}$. This produces wavefunctions of the form

$$\text{triplet:} \quad \mathcal{A}[\Phi_\sigma(\varphi_{\pi_1}\varphi_{\pi_2} - \varphi_{\pi_2}\varphi_{\pi_1})\alpha\beta] \tag{2}$$

$$\text{singlet:} \quad \mathcal{A}[\Phi_\sigma(\varphi_{\pi_1}\varphi_{\pi_2} + \varphi_{\pi_2}\varphi_{\pi_1})\alpha\beta] \tag{3}$$

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 $\pi$ 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 $\pi$ 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 $\pi$ orbital of (1) with

$$(\varphi_{\pi a}\varphi_{\pi b} + \varphi_{\pi b}\varphi_{\pi a}) \tag{4}$$

(the valence bond description of the $\pi$ 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 $\pi$-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., equation (4)] which are solved for self-consistently is called the generalized valence bond method.[1]

## B. The Core Hamiltonians

As demonstrated in the appendix,[5] the problem of solving for wavefunctions of the form

$$\mathcal{A}[\Phi_{\text{val}}(1,2)\,\Phi_\sigma(3,\ldots N)] \tag{5}$$

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

$$\mathcal{A}[\Phi_{\text{val}}(1,2)] \tag{6}$$

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

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

where

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

and h is the usual one-electron operator

$$h(i) = -\tfrac{1}{2}\nabla_i^2 - \sum_a{}' \frac{Z_a}{r_{ia}} \tag{9}$$

Although the eigenfunction $\Phi_{\text{val}}$ of (7) is a rigorous solution for (5) given a particular $\Phi_\sigma$, the resulting total wavefunction is useful only if $\Phi_\sigma$ is relatively insensitive to changes in $\Phi_{\text{val}}$. In this case a $\Phi_\sigma$ 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 $\Phi_\sigma$ from an <u>ab initio</u> HF calculation on the same state so that $\Phi_\sigma$ should be well described. For allyl cation, we used the $\Phi_\sigma$ from a self-consistent, <u>ab initio</u> HF calculation on the ground state of allyl cation. This $\Phi_\sigma$ should be a good description of the $\sigma$-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 $\Phi_\sigma$ 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.

## C. Spatially Projected Wavefunctions

The simple valence bond (VB) description of the $\pi$ electrons of the ground state of ethylene is

$$\boxed{\ell 2p_x \quad r2p_x} = (\phi_{\ell 2p_x}\phi_{r2p_x} + \phi_{r2p_x}\phi_{\ell 2p_x})(\alpha\beta - \beta\alpha) \qquad (10)$$

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 $\pi$ 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

$$\boxed{\ell 2p_x \quad r3p_x} \qquad (11)$$

or

$$\boxed{\ell 3p_x \quad r2p_x} \qquad (12)$$

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

$$\begin{aligned}\boxed{\ell 2p_x \quad r3p_x}_s &\equiv \boxed{\ell 2p_x \quad r3p_x} + \boxed{\ell 3p_x \quad r2p_x} \\ &= (\varphi_{\ell 2p_x}\varphi_{r3p_x} + \varphi_{r3p_x}\varphi_{\ell 2p_x})(\alpha\beta - \beta\alpha) + \\ &\quad (\varphi_{\ell 3p_x}\varphi_{r3p_x} + \varphi_{r2p_x}\varphi_{\ell 3p_x})(\alpha\beta - \beta\alpha)\end{aligned} \tag{13}$$

or

$$\boxed{\ell 2p_x \quad r3p_x}_a \equiv \boxed{\ell 2p_x \quad r3p_x} - \boxed{\ell 3p_x \quad r2p_x} \tag{14}$$

where the subscript 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 $\ell$ and r centers.[6]

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

$$\begin{aligned} x &\rightarrow x \\ y &\rightarrow y \\ z &\rightarrow -z \end{aligned}$$

where the z axis is perpendicular to the reflection plane. Thus

$$\hat{R}\,\boxed{\ell 3p_x \quad r2p_x} = \boxed{r3p_x \quad \ell 2p_x} = \boxed{\ell 2p_x \quad r3p_x}$$

and (13) may be written as

$$\boxed{\ell 2p_x \quad r3p_x}_s = \hat{P}_s\,\boxed{\ell 2p_x + r3p_x} \tag{15}$$

where

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

Similarly (14) is

$$\boxed{\ell 2p_x \quad r3p_x}_a = \hat{P}_a \boxed{\ell 2p_x \quad r3p_x .} \tag{17}$$

where

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

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

$$(\varphi_{\ell 2p_x} \varphi_{r2p_x} + \phi_{r2p_x} \phi_{\ell 2p_x}) = (1 + P_{12}) \phi_{\ell 2p_x} \phi_{r2p_x} \tag{19}$$

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

$$(1 \pm \hat{R})(1 + P_{12}) \varphi_{\ell a}(1) \varphi_{rb}(2) \tag{20}$$

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 for each orbital self-consistently. This is called the generalized valence bond (GVB) approach.[1-4] To indicate explicitly that a spatial projection operator has been included,[2-4] 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 $\phi_{rb}$ 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

$$\hat{R}\,\phi_{\ell a} = \varphi_{ra}$$
$$\hat{R}\,\phi_{rb} = \varphi_{\ell b}$$

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

$$\boxed{\begin{matrix}\varphi_{\ell a}\\ \varphi_{rb}\end{matrix}}_{a} = [(\varphi_{\ell a}\varphi_{rb} - \varphi_{rb}\varphi_{\ell a}) - (\varphi_{ra}\varphi_{\ell b} - \varphi_{\ell b}\varphi_{ra})](\alpha\beta+\beta\alpha) \qquad (21)$$

## D. The Basis and Other Details

For each state of ethylene we used the $\sigma$ orbitals from a Hartree-Fock calculation[9] on the same state to define the $h^{\text{core}}$ in (7) for use in the $\pi$-electron calculations for this state. One Hartree-Fock calculation was performed on allyl cation and the resulting $\sigma$ orbitals used to define $h^{\text{core}}$ in (7) for all of the allyl cation $\pi$ 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 (4s3p) 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 $\pi$ 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 $\pi$ orbitals of ethylene are depicted in Figure 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 I contains a summary of the calculated energies and includes HF results for comparison.

The allyl cation GVB $\pi$ orbitals are depicted in Figure 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 I contains a summary of the calculated results.

## 4. Discussion

### A. Ethylene

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

$$\begin{aligned} \text{N:}&\ \pi_u\pi_u \\ \text{T:}&\ \pi_g\pi_u - \pi_u\pi_g \\ \text{V:}&\ \pi_g\pi_u + \pi_u\pi_g \end{aligned}$$

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

From Figure 1, we see that the N state GVB $\pi$ 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

$$\phi_{\pi_\ell} = N[\phi_{2p\ell} + \lambda\phi_{2pr}]$$

$$\phi_{\pi_r} = N[\phi_{2pr} + \lambda\phi_{2p\ell}]$$

where $\lambda$ is approximately 0.14. If one of the $\pi$ orbitals is ionized, the remaining orbital becomes completely delocalized

$$\phi_{\pi g} = N(\phi_{2p\ell} + \phi_{2pr})$$

just as in the MO description (If readjustments are allowed in the $\sigma$ 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 ($\phi_r$) remains close enough to one of the nuclei so that the unexcited orbital ($\phi_\ell$) 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, Hunt, and Goddard[9] and has been discussed in detail elsewhere.[10, 11]

In Figure 1, we show the GVB(SP) orbitals for the N state, which should be compared to the GVB orbitals also in Figure 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.

## B. Allyl Cation

One would expect the allyl cation $\pi$ 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 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 Figures 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 I and II. 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.

### C. Comparison With Other Methods

In Table 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 $\sigma$ core.

The agreement between the GVB(SP) and full CI calculations is excellent, the largest disagreement being 0.017ev (0.4 kcal)[12] for the allyl cation ground state. In comparison the HF energy for this state is 0.028h (17.5 kcal) above the full CI energy. Thus the GVB(SP) method provides 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 [3s1p/1s] basis contracted from a (10s5p/5s) primitive basis. Our basis is considerably more extensive, (9s 5p/5s) contracted to [4s2p/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 $\pi$ system). The GVB (SP) wavefunction also yields a simple interpretation of the wavefunctions for the various states.

## Appendix A. The Core Potential [5]

Consider a wavefunction of the form

$$\mathcal{A}(\phi_1\alpha\phi_1\beta\phi_2\alpha\phi_2\beta\ldots\phi_q\alpha\phi_q\beta\phi_v\alpha) \qquad \text{(A-1)}$$

The variational equation for the optimum orbital $\phi_v$ is

$$H_v\phi_v = \epsilon_v\phi_v \qquad \text{(A-2)}$$

where $H_v$ has the form

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

if in solving (A-2) we restrict $\phi_v$ to be in the space orthogonal to the doubly-occupied orbitals

$$\{\phi_1, \ldots, \phi_q\}\ , \qquad \text{(A-4)}$$

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

$$\mathcal{A}(\Phi_{\text{core}}\Phi_{\text{val}})\ , \qquad \text{(A-5)}$$

where

$$\Phi_{\text{core}} = \phi_1\alpha\phi_1\beta\phi_2\alpha\phi_2\beta\ldots\phi_q\alpha\phi_q\beta \qquad \text{(A-6)}$$

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

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

$$\int \Phi_{\text{val}}(1, \ldots N') \phi_j(i)\, d^3r_i = 0 \qquad (j = 1, q) \tag{A-7}$$

As a result if $\Phi_{\text{val}}$ is solved for within the space orthogonal to the core orbitals (A-4), then the only surviving terms in the energy expression involving both the core and valence orbitals have the form

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

where $\mu$ and $\nu$ 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 $\Phi_{\text{val}}$ can be obtained by solving for the optimum wavefunction of the form

$$\mathcal{A}(\Phi_{\text{val}}) \tag{A-9}$$

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

$$\mathcal{H} = \sum_i^{N'} h^{\text{core}}(i) + \sum_{i>j}^{N'} \frac{1}{r_{ij}} \tag{A-10}$$

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 $\Phi_{\text{core}}$ 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 $h^{\text{core}}$ forms an effective potential for movement of the valence electrons. This differs from the various pseudopotential methods and the usual effective potential methods in that we do <u>not</u> approximate the way that the field terms due to $\Phi^{\text{core}}$ enter the wavefunction.

## Table I

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 $\phi_\ell$ | Orbital Energy $\phi_r$ | Excitation Energy (eV) |
|---|---|---|---|---|---|
| $N(^1A_g)^a$ | 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 |

[a] The overlap $\langle\phi_\ell|\phi_r\rangle$ 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) |
|---|---|---|---|---|---|
| | | | $\phi_\ell$ | $\phi_r$ | |
| $1^1A_1$ | GVB[a] | -116.163675 | -0.712930 | -0.712930 | --- |
| | GVB(SP)[a] | -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 |

[a] For the $^1A_1$ state the overlap $\langle \phi_\ell | \phi_r \rangle$ 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 energies (in hartrees) is given in each case.

| Ethylene | State | HF | GVB | GVB(SP) | Full CI |
|---|---|---|---|---|---|
| | 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 | -116.163675 | -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[a] |
|---|---|---|---|---|
|  | GVB | GVB(SP) | Full CI | 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 |

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

## References

[1] W.A. Goddard III, T.H. Dunning Jr., P.J. Hay, and W.J. Hunt Accts. Chem. Res. 6, (1973) 358.

[2] D.L. Huestis and W.A. Goddard III, Chem. Phys. Lett. 16 (1972) 157.

[3] D.L. Huestis, PhD Thesis, Calif. Inst. of Tech., Sept. 1972.

[4] S.L. Guberman and W.A. Goddard Chem. Phys. Lett -14, (1972) 460. See also S.L. Guberman PhD Thesis, Calif. Inst. of Tech. Nov., 1972.

[5] Based on unpublished work by W.A. Goddard III, T.H. Dunning, and P.J. Hay. See for example T.H. Dunning Ph.D. Thesis, Caltech, Sept. 1969.

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

$$\overset{2p}{C}-\overset{3p}{C}\longleftrightarrow\overset{3p}{C}-\overset{2p}{C}$$

[7] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293.

[8] T.H. Dunning, Jr., J. Chem. Phys. 53 (1970) 2823.

[9] T.H. Dunning, Jr., W.J. Hunt, and W.A. Goddard III, Chem. Phys. Lett. 4 (1969) 147.

[10] C.B. Bender, T.H. Dunning, H.F. Schaefer III, W.A. Goddard III and W.J. Hunt, Chem. Phys. Letters, 15, (1972) 171.

[11] W.J. Hunt, W.A. Goddard III, T.H. Dunning Jr., Chem. Phys. Lett., to be published. See W.J. Hunt, Ph.D. Thesis, Caltech, Sept. 1971.

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

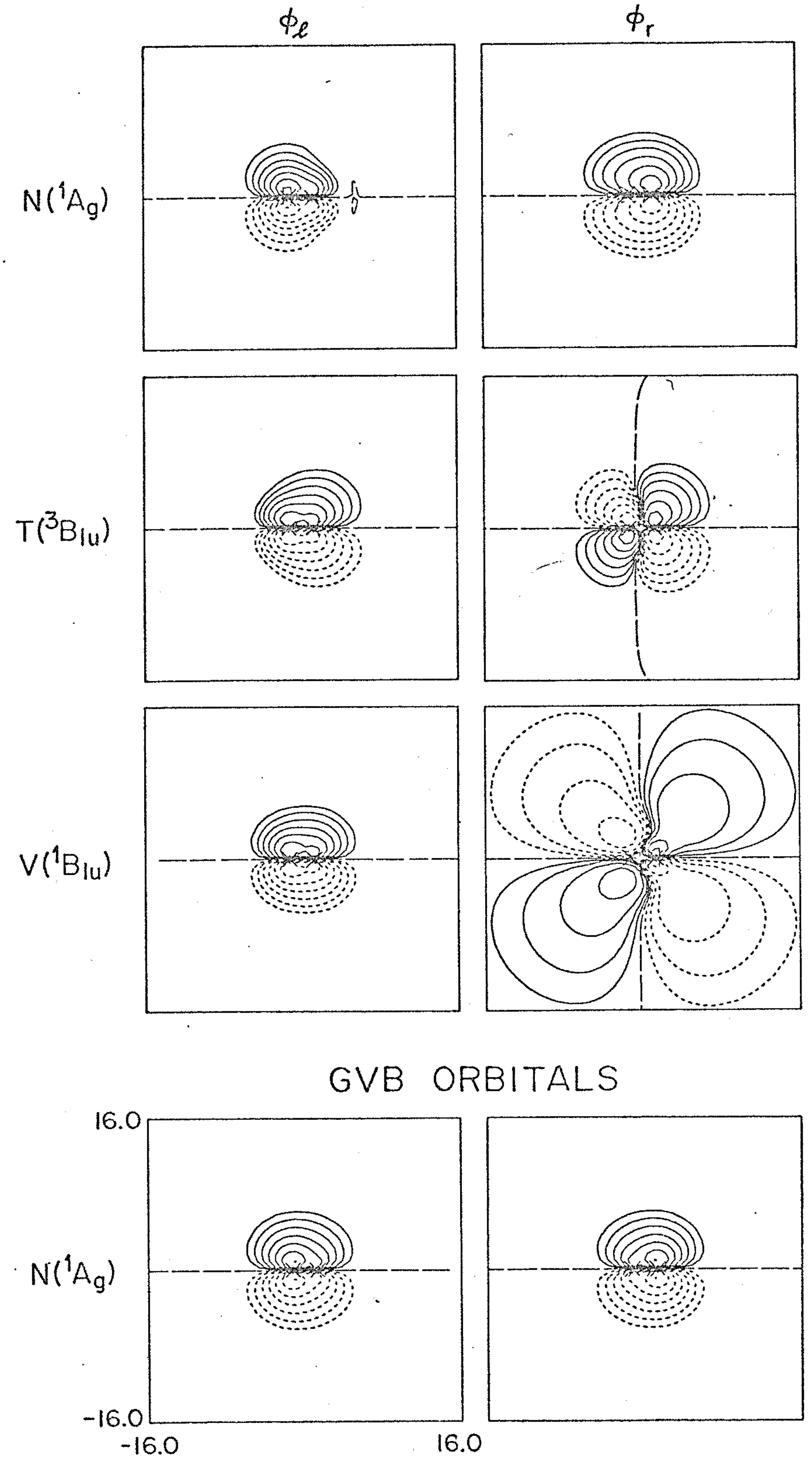
[13] S.D. Peyerimhoff and R.J. Buenker, J. Chem. Phys., 51 (1969) 2528.

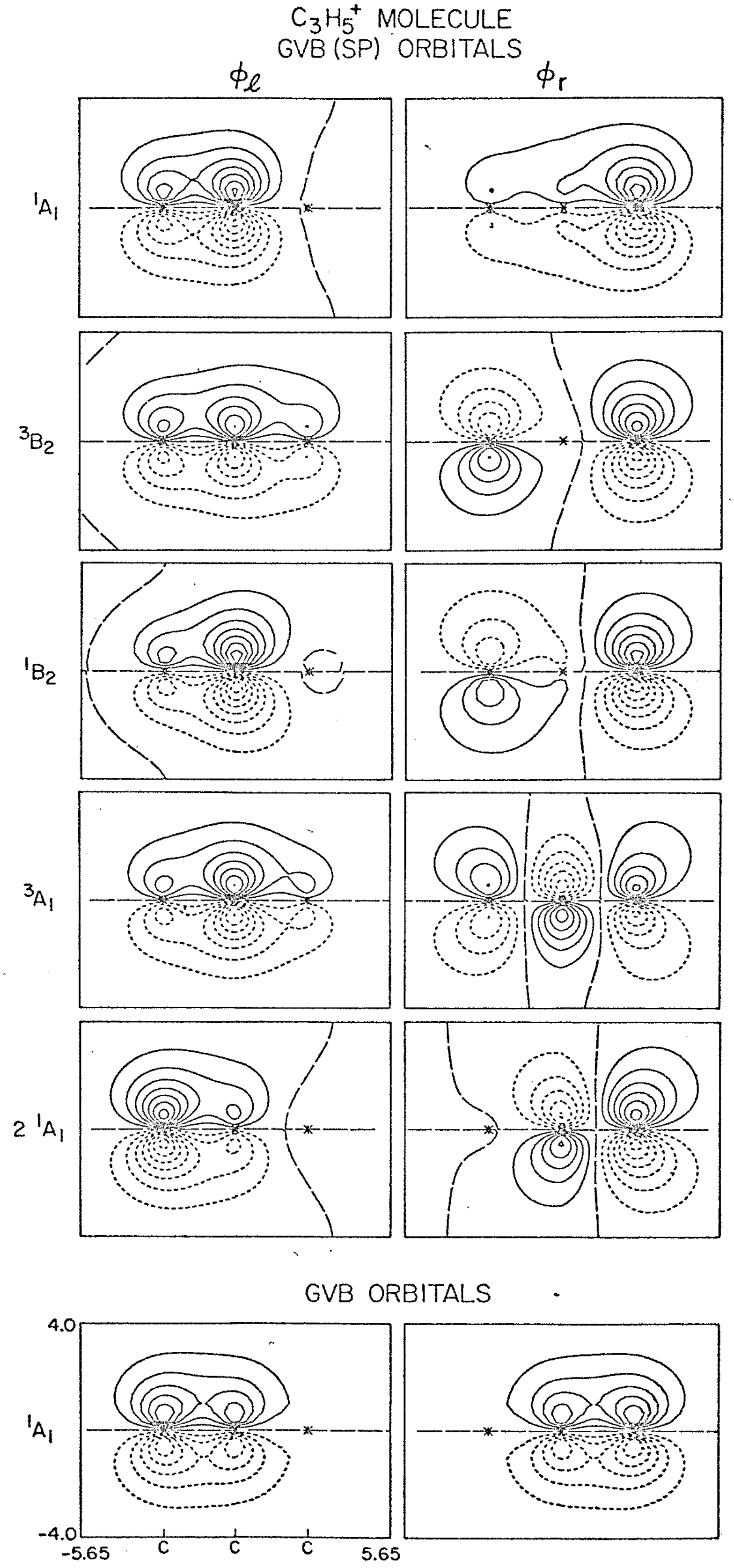
## Figure Captions

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. The GVB(SP) orbitals of allylcation. 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 of 120°.

## $C_2H_4$ MOLECULE
## GVB(SP) ORBITALS




$C_3H_5^+$ MOLECULE
GVB (SP) ORBITALS
$\phi_\ell$
$\phi_r$
$^1A_1$
$^3B_2$
$^1B_2$
$^3A_1$
$2\ ^1A_1$
GVB ORBITALS
$^1A_1$
4.0
-4.0
-5.65
C
C
C
5.65

# APPENDIX II

# THE GENERALIZED VALENCE BOND DESCRIPTION OF ALLYL RADICAL

## 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]

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 as the wavefunction may be expressed as 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). We find that the ground and first-excited states are well described as the resonant and antiresonant states,

thus, providing a more rigorous quantum mechanical basis for the concept of resonance.

## II. Calculational considerations

### A. The wavefunctions

#### a. Hartree Fock

The Hartree-Fock (HF) wavefunction for the ground state of allyl radical may be written in the form[4]

$$\mathcal{A}\,[\varphi_1\alpha\varphi_1\beta\cdots\varphi_q\alpha\varphi_q\beta\varphi_{\pi_1}\alpha\varphi_{\pi_1}\beta\varphi_{\pi_2}\alpha]\,, \qquad (1)$$

where for allyl radical there are ten 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 wavefunctions of the form

$$\mathcal{A}\,[\Phi_\sigma\varphi_{\pi_1}\alpha\varphi_{\pi_2}\beta\varphi_{\pi_2}\alpha] \qquad (2a)$$

$$\mathcal{A}\,[\Phi_\sigma\varphi_{\pi_1}\alpha\varphi_{\pi_1}\beta\varphi_{\pi_3}\alpha] \qquad (2b)$$

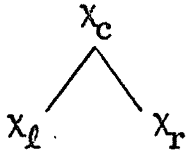
or

$$\mathcal{A}\,[\Phi_\sigma\varphi_{\pi_1}\alpha\varphi_{\pi_2}\beta\varphi_{\pi_3}\alpha] \qquad (3)$$

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 wavefunction

In the valence bond (VB) wavefunction of allyl there is a singly-occupied atomic $\pi$ orbital on each carbon atom. We will denote these orbitals as $\chi_\ell$, $\chi_c$, and $\chi_r$ as indicated in (4)



(4)

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

$$= \begin{array}{|c|c|}\hline \chi_\ell & \chi_c \\ \hline \chi_r & \\ \cline{1-1}\end{array} = \Psi_1 \tag{5}$$

$$= \begin{array}{|c|c|}\hline \chi_r & \chi_c \\ \hline \chi_\ell & \\ \cline{1-1}\end{array} = \Psi_2 \tag{6}$$

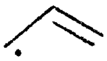
where orbitals in the same row of the tableau in (5) or (6) are singlet paired (i.e., paired in a bonding manner). The wavefunctions corresponding to (5) and (6) are

$$\begin{aligned}\Psi_1 &= \mathcal{A}[\Phi_\sigma(\chi_\ell\chi_c + \chi_c\chi_\ell)\chi_r\,\alpha\beta\alpha] \\ &= \mathcal{A}[\Phi_\sigma\chi_\ell\chi_c\chi_r(\alpha\beta - \beta\alpha)\alpha] \qquad (7a) \\ &= \mathcal{A}[\Phi_\sigma\chi_r\chi_\ell\chi_c\,\alpha(\alpha\beta - \beta\alpha)]\end{aligned}$$

$$\begin{aligned}\Psi_2 &= \mathcal{A}[\Phi_\sigma(\chi_r\chi_c + \chi_c\chi_r)\chi_\ell\,\alpha\beta\alpha] \\ &= \mathcal{A}[\Phi_\sigma(\chi_r\chi_c\chi_\ell\,(\alpha\beta - \beta\alpha)\,\alpha] \qquad (7b) \\ &= \mathcal{A}[\Phi_\sigma\chi_r\chi_\ell\chi_c\,(\beta\alpha\alpha - \alpha\alpha\beta)]\end{aligned}$$

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

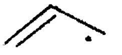
Allowing the wavefunction for the system to be a superposition of $\Psi_1$ and $\Psi_2$, leads to an optimum wavefunction of the form

$\Psi_a = \Psi_1 - \Psi_2 \equiv$  $-$  (8a)

with an energy lower than $E_1$ (the energy of $\Psi_1$ or $\Psi_2$),

$$E_a < E_1 ,$$

and a second wavefunction

$\Psi_s = \Psi_1 + \Psi_2 \equiv$  $+$  (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 wavefunctions (5) and (6). The energy change

$$E_{res} = E_1 - E_a \qquad (9a)$$

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 wavefunctions in (8) can both be written as

$$\Psi_i = \mathcal{A}[\Phi_\sigma \chi_r \chi_\ell \chi_c \Theta_i] \tag{10}$$

where the spin functions $\Theta_i$ are

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

$$\Theta_s = -(\alpha\beta - \beta\alpha)\alpha\ . \tag{11b}$$

Thus proceeding from the simple valence bond wavefunction 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 wavefunction

The generalized valence bond (GVB) wavefunction is formally the same as the VB wavefunction

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

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 wavefunction). 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 $\phi_\ell$, $\varphi_c$, $\varphi_r$ (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 (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

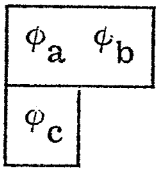
$$\theta_1 = (\alpha\beta - \beta\alpha)\,\alpha \tag{14}$$

$$\theta_2 = 2\,\alpha\alpha\beta - (\alpha\beta + \beta\alpha)\,\alpha \ ,$$

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

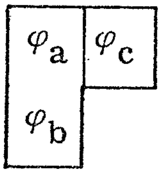
$$\Theta = C_1\theta_1 + C_2\theta_2 \tag{15}$$

In discussing such wavefunctions it is often convenient to use the diagram



(16)

to indicate the wavefunction $\mathcal{A}[\Phi_\sigma \phi_a \phi_b \phi_c \theta_1]$ (that is, singlet coupling of $\phi_a$ and $\phi_b$) and



(17)

to indicate the wavefunction $\mathcal{A}[\Phi_\sigma \phi_a \phi_b \phi_c \theta_2]$ (that is, triplet coupling of $\phi_a$ and $\phi_b$).

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

$$\begin{array}{|c|c|}\hline \chi_r & \chi_c \\ \hline \chi_\ell & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = \begin{array}{|c|c|}\hline \chi_\ell & \chi_c \\ \hline \chi_r & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} - \begin{array}{|c|c|}\hline \chi_r & \chi_c \\ \hline \chi_\ell & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \qquad (18)$$

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

$$\begin{array}{|c|c|}\hline \chi_r & \chi_\ell \\ \hline \chi_c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = - \begin{array}{|c|c|}\hline \chi_\ell & \chi_c \\ \hline \chi_r & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} - \begin{array}{|c|c|}\hline \chi_r & \chi_c \\ \hline \chi_\ell & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \qquad (19)$$

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

### d. The core Hamiltonian

As discussed in reference 2, the problem of finding a wave function of the form

$$\mathcal{A}[\Phi_{\text{core}} \Phi_{\text{val}}]$$

may be reduced to that of finding the wave function

$$\mathcal{A}[\Phi_{\text{val}}] \qquad (20)$$

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

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

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

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

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 wavefunction, 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.

### e. 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[6] on each carbon with orbital exponents of 0.382 and 0.0127. All calculations used the following geometry:[7] $R_{CC} = 1.40$ 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 to the energy for full CI the energy in the GVB wavefunction is 0.13 eV $\underset{\sim}{=}$ 2.9 kcal, the error in the HF wavefunction is nine times as great (27.2 kcal) and the error in the VB wavefunction 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 wavefunctions are in Table II.

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 in Figure 1 contain 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 $\phi_c$ are symmetric ($b_1$) and $\phi_b$ is antisymmetric ($a_2$). We shall consider why this occurs.

## A. 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 $\underset{\sim}{C}_{2v}$ symmetry group of allyl. To determine which we must find how the wavefunction changes upon reflection in the symmetry plane interchanging the terminal groups of allyl. Denoting this reflection as $\sigma$, then

$$\begin{aligned} \sigma \Phi_{B_1} &= +\Phi_{B_1} \\ \sigma \Phi_{A_2} &= -\Phi_{A_2} \quad . \end{aligned} \tag{23}$$

Mixing the $\chi_\ell$ and $\chi_r$ orbitals as

$$\begin{aligned} \phi_a &= \cos\theta\, \chi_\ell + \sin\theta\, \chi_r \\ \phi_b &= -\sin\theta\, \chi_\ell + \cos\theta\, \chi_r \end{aligned} \qquad (27)$$

we find that

$$\begin{array}{|c|c|}\hline \phi_a & \phi_c \\ \hline \phi_b \\ \cline{1-1}\end{array} = (\cos^2\theta + \sin^2\theta) \begin{array}{|c|c|}\hline \chi_\ell & \chi_c \\ \hline \chi_r \\ \cline{1-1}\end{array} \qquad (28)$$

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

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

$$\begin{array}{|c|c|}\hline \phi_a & \phi_b \\ \hline \phi_c \\ \cline{1-1}\end{array} = -\sin\Theta\cos\Theta \begin{array}{|c|c|}\hline \chi_\ell & \chi_\ell \\ \hline \chi_c \\ \cline{1-1}\end{array} + \sin\Theta\cos\Theta \begin{array}{|c|c|}\hline \chi_r & \chi_r \\ \hline \chi_c \\ \cline{1-1}\end{array} + (\cos^2\Theta - \sin^2\Theta) \begin{array}{|c|c|}\hline \chi_\ell & \chi_r \\ \hline \chi_c \\ \cline{1-1}\end{array} \qquad (29)$$

and hence a real change in the wavefunction and hence in the energy. However (29) is still of $B_1$ symmetry.

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

$$C_1 \begin{array}{|c|c|}\hline \chi_\ell & \chi_r \\ \hline \chi_c \\ \cline{1-1}\end{array} + C_2 \begin{array}{|c|c|}\hline \chi_\ell & \chi_c \\ \hline \chi_r \\ \cline{1-1}\end{array} \qquad (30)$$

or

$$C_1 \begin{array}{|c|c|}\hline \varphi_a & \varphi_b \\ \hline \varphi_c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + C_2 \begin{array}{|c|c|}\hline \phi_a & \phi_c \\ \cline{1-2} \phi_b & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \tag{31}$$

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

$$\begin{aligned} \phi_a &= \frac{1}{\sqrt{2}} (\chi_\ell + \chi_r) \\ \phi_b &= \frac{1}{\sqrt{2}} (-\chi_\ell + \chi_r) \end{aligned} \tag{32}$$

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

$$\underset{(33a)}{\begin{array}{|c|c|}\hline \phi_a & \varphi_c \\ \cline{1-2} \varphi_b & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}} \quad \text{and} \quad \underset{(33b)}{\begin{array}{|c|c|}\hline \varphi_a & \varphi_b \\ \hline \varphi_c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}}$$

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 wavefunction (28) leads to the same energy for all (nonsingular) choices of the coefficients and since the choice (32) allows an additional term (33b) of proper symmetry,

$$\Psi = C_1 \begin{array}{|c|c|}\hline \phi_a & \phi_b \\ \hline \varphi_c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + C_2 \begin{array}{|c|c|}\hline \phi_a & \varphi_c \\ \cline{1-2} \varphi_b & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \tag{34}$$

not allowed for other choices of the coefficients, we expect the optimum wavefunction 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 wavefunction for the ground state. 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 wavefunction so that $C_1 = 0$ and solving for the optimum orbitals leads to an increase in the energy of 0.91 kcal.[8] However with $C_1 = 0$ we can recombine the GVB orbitals into localized orbitals, as

$$\begin{aligned} \phi_\ell &= (\varphi_a - \varphi_b)/\sqrt{2} \\ \phi_r &= (\varphi_a + \varphi_b)/\sqrt{2} \end{aligned} \tag{35}$$

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

$$\begin{array}{|c|c|}\hline \varphi_\ell & \varphi_c \\ \hline \varphi_r \\ \cline{1-1}\end{array} \equiv \begin{array}{|cc|}\hline \varphi_c & \varphi_\ell \\ \hline \multicolumn{1}{|c|}{\varphi_r} \\ \cline{1-1}\end{array} - \begin{array}{|cc|}\hline \varphi_c & \varphi_r \\ \hline \multicolumn{1}{|c|}{\varphi_\ell} \\ \cline{1-1}\end{array} \tag{36}$$

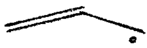
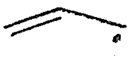
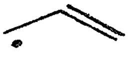
and

$$\begin{array}{|cc|}\hline \varphi_\ell & \varphi_r \\ \hline \multicolumn{1}{|c|}{\varphi_c} \\ \cline{1-1}\end{array} \equiv \begin{array}{|cc|}\hline \varphi_c & \varphi_\ell \\ \hline \multicolumn{1}{|c|}{\varphi_r} \\ \cline{1-1}\end{array} + \begin{array}{|cc|}\hline \varphi_c & \varphi_r \\ \hline \multicolumn{1}{|c|}{\varphi_\ell} \\ \cline{1-1}\end{array} \quad , \tag{37}$$

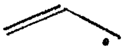
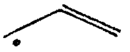
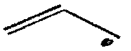
using for $\varphi_\ell$, $\varphi_c$, and $\varphi_r$ either the atomic orbitals (i.e. VB) or the localized orbitals from self consistent GVB calculations on either the ground or excited states. From (36) we will define the resonance energy(of the ground state) of allyl as the energy stabilization of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

$$\begin{array}{|cc|}\hline \varphi_c & \varphi_\ell \\ \hline \multicolumn{1}{|c|}{\varphi_r} \\ \cline{1-1}\end{array} \tag{38}$$

using the same orbitals. That is

$E_{res} = E($  $) - E($  $-$  $).$ (39)

Similarly from (37) we define the antiresonance (of the excited state) of allyl as the destabilization energy of the antiresonant wavefunction (37) as compared to the same single configuration wavefunction (38)

$E_{antires} = E($  $+$  $) - E($  $)$ (40)

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

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

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

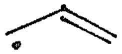
$$E_{res} = 9.4 \text{ kcal}$$

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

(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 wavefunction yields a ground state energy 38.3 kcal higher than that of the GVB wavefunction).

This theoretical estimate of 11.4 kcal for the resonance energy is in reasonable agreement with the value of 10 ± 1.5 kcal from thermochemical considerations.[9]

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

 and  (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 (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) wavefunction (38); $S$ is the overlap between the two wavefunctions of (41) and $H_{12}$ is the matrix element between the wavefunction os (41). From (42) we see that

$$\frac{E_{res}}{E_{antires}} = \frac{1-S}{1+S} \tag{43}$$

The orbitals of the VB, GVB ($^2A_2$), and GVB ($^2B_1$) wavefunctions lead to $S = .57$, $S = .72$, and $S = .71$ respectively.

## 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. 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

$$\text{N:} \quad \boxed{\phi_\ell \quad \phi_c} \tag{44}$$

$$\text{T:} \quad \boxed{\begin{matrix}\phi_\ell \\ \phi_c\end{matrix}} \tag{45}$$

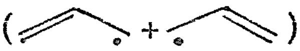
in terms of localized orbitals on the left and center carbons. These states are found to be separated by 4.2 eV = 97 kcal[8] in the GVB description. Fusing on the $\phi_r$ orbital leads then to zero order (doublet) states of the form

$$\begin{array}{|c|c|}\hline \phi_\ell & \phi_c \\ \hline \phi_r & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \tag{46}$$

and

$$\begin{array}{|c|c|}\hline \phi_\ell & \phi_r \\ \cline{2-2} \phi_c & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \tag{47}$$

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. Defining the destabilization energy as

$E_{destab} = E\,($  $) - E_{(47)}$ (48)

we find that

$$E_{destab} = 30.1 \text{ kcal}$$

(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 → 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 $\phi_\ell$ and $\phi_c$ while (47) involves bonding interactions between $\phi_r$ and the ethylene T state orbitals.[11] Thus the energy separation between (46) and (47) is only 2.5 eV. The stabilization and destabilization effects attendent to the relaxation of the wavefunctions (46) and (47) to obtain the optimum wavefunctions 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

$$^2A_2\text{:}\ \ (1b_1)^2(1a_2) \tag{49}$$

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

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

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

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

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 description. However since the model in (49) - (52) is clearly only capable of describing valence excited states, we will compare these methods using wavefunctions based on just three valence-like orbitals,[12] $1b_1$, $1a_2$, and $2b_1$. The results are indicated in Figure 4 and Table V.

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 wavefunction for the antiresonant state (37) in terms of MO's requires both the $(1b_1)(1a_2)^2$ and $(1b_1)^2(2b_1)$ configurations with roughly equal coefficients. The first excited state of allyl is simply not described by any one 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 wavefunctions for the excited states. As shown in Table IV this does not eliminate the problem with the HF description of the first $^2B_1$ state. This difficulty is intrinsic to the single states determinant nature of the wavefunction 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[13] and benzene finding exactly the same situation. The valence excited states involve essentially a recoupling of the spin functions and are well described with the GVB wavefunctions but very poorly described with MO's.

## D. Excitation energies

In Table IV 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 h = 0.127 eV. This close agreement with the full CI wavefunction justifies interpreting the wavefunction in terms of GVB orbitals.

In Table VI, excitation energies from various sources are compared. Experimental results[12] are not definitive, placing the $^2A_2 \rightarrow {}^2B_1$ vertical excitation energy at 3.04 to 5.0 eV, in reasonable agreement with our value of 3.2 eV. The best previous theoretical studies[7] 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 an

$$(2^2B_1) \quad 1a_2 \rightarrow 3pb_1 \tag{53}$$

excitation while the $3^2B_1$ state should correspond to a

$$(3^2B_1) \quad 1a_2 \rightarrow 3db_1 \tag{54}$$

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 0.006eV lower than the $3^2B_1$ state. This is consistent with the description (54) for $3^2B_1$ since

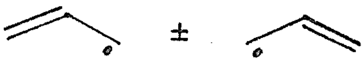
$$(2^2A_2) \quad 1a_2 \rightarrow 3da_2 \tag{55}$$

would be expected to be close to (54).

Our calculated quantum defects are $\zeta(2^2B_1) = 0.40$ and $\zeta(3^2B_1) = -0.29$. The value for the 3p orbital is consistent with the typical value of 0.50 (e.g. $\zeta_{3p} = 0.50$ for butadiene[15]) for np Rydberg orbitals. Usual nd Rydberg orbitals have $\zeta \sim 0$. Our negative value reflects the inadequacy 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 kcal from full configuration interaction calculations. Qualitatively the GVB wavefunctions 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.

Table I: Comparison of Ground State Energies for Allyl

| | Energy (h) | Error (eV) | Error (kcal) |
|---|---|---|---|
| VB | -116.35544 | 1.79 | 41.2 |
| HF | -116.377697 | 1.18 | 27.2 |
| GVB-GF | -116.41497 | 0.17 | 3.8 |
| GVB | -116.416438 | 0.13 | 2.9 |
| CI | -116.421089 | 0.00 | 0.0 |

Table II. Energy Quantities for the GVB Wavefunctions of Allyl Radical (all using the same basis)

| State | Total Energy (h) | Spin Coupling$^{(a)}$ $c_1$ | $c_2$ | Excitation Energy (eV) |
|---|---|---|---|---|
| $1^2A_2$ | -116.416438 | $0.118^{c}$ | -0.928 | 0 |
| | -116.41499 | $0.0^{c}$ | 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 |

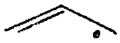
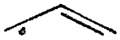
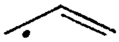
(a) Refer to Equation 15.

(b) In this calculation the spin coupling was restricted so that $c_1 = 0$.

(c) The orbitals are ordered as $\phi_\ell \phi_r \phi_c$ or in terms of Figure 1 as $\phi_a \phi_c \phi_b$.

(d) The orbitals are ordered as $\phi_a \phi_b \phi_c$.

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

| | | Orbitals Used | |
|---|---|---|---|
| | Atomic | 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 |
| $\begin{array}{\|c\|c\|}\hline \phi_\ell & \phi_r \\ \hline \phi_c & \\ \cline{1-1}\end{array}$ [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 Eqn. 15). This wavefunction leads to an energy 0.88 kcal above the optimum energy of the $^2A_2$ state.

[b] This wavefunction has orbitals $\phi_\ell$ and $\phi_c$ coupled into a triplet state and then $\phi_r$ is coupled to yield a doublet.

[c] Using ethylene $\pi$ orbitals for $\phi_\ell$ 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 wavefunctions.

Table IV. Energies for Allyl Radical (Hartree Atomic Units).

| State | GVB | CI-Full[a] | $E_{CI}-E_{GVB}$ | CI-Singles[b] |
|---|---|---|---|---|
| $^2A_2$ | -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.

Table V. 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 |
| $3\ ^1B_1$ | -115.855376 | $(1a_2)^2(2b_1)$ | -115.817880 |
| | (-116.219937)[b] | $(1b_1)(2b_1)^2$ | -115.769586 |

[a] Using the natural orbitals from the GVB wavefunction.

[b] Energies from the full CI calculations using the full basis.

[c] Solving self consistently for the HF wavefunction in the full basis leads to -116.377697.

Table V. Excitation Energies for Allyl Radical (all values in eV)

| State | Present Work | | Peyerimhoff & Buenker (Ab initio CI) (Ref. 7) | Hirst and Linnett (Semi-empirical CI)[a] |
|---|---|---|---|---|
| | GVB | Full CI | | |
| $^2A_2$ | 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 | | |

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

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5. (a) S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).
   (b) T. H. Dunning, Jr., J. Chem. Phys. **53**, 2823 (1970).

6. 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 → 3p excitation of C atom.

7. S. D. Peyerimhoff and R. J. Buenker, J. Chem. Phys. **51**, 2528 (1969).

8. The conversions between various units of energy are 1h = 27.2117 eV = 627.526 kcal and hence 1 kcal = 0.0016 h. Note that we use the abbreviation kcal to indicate kilocalories per molecule.

9. D. M. Golden and S. W. Benson, Chem. Rev. **69**, 125 (1969).

10. This is analogous to the approach suggested by Dr. T. H. Dunning, Jr. (private communications, April, 1971) for considering the excited states of butadiene. See for example the discussion in H. F. Schaffer III *The Electronic Structure of Atoms and Molecules, A Survey of Rigorous Quantum Mechanical Results,* Addison-Wesley (Reading, Mass.) 1972.

11. W. A. Goddard III and C. W. Wilson, Jr., Theor. Chem. Acta. **26**, 211(19

12. 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 GVB wavefunction. The results are summarized in Table IV. The energies for the first two states are 0.009 h and 0.022 h 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 h (1.0 kcal) higher than the self consistent HF energy for the full basis (see Table I).

13. G. Levin and W. A. Goddard III, "The GVB Description of the Low Lying Electronic States of 2-*trans*-1, 3-butadiene," to be published.

14. (a) C. L. Currie and D. A. Ramsay, J. Chem. Phys. **45**, 488 (1966).

    (b) D. A. Ramsay, J. Chem. Phys. **43**, 518 (1965).

    (c) D. M. Bodily and M. Dole, J. Chem. Phys. **44**, 2821 (1966).

    (d) A. B. Callear and H. K. Lee, Trans. Faraday Soc. **64**, 308 (1968).

15. G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrand Company, Inc. (Princeton, New Jersey) 1967.

# FIGURE CAPTIONS

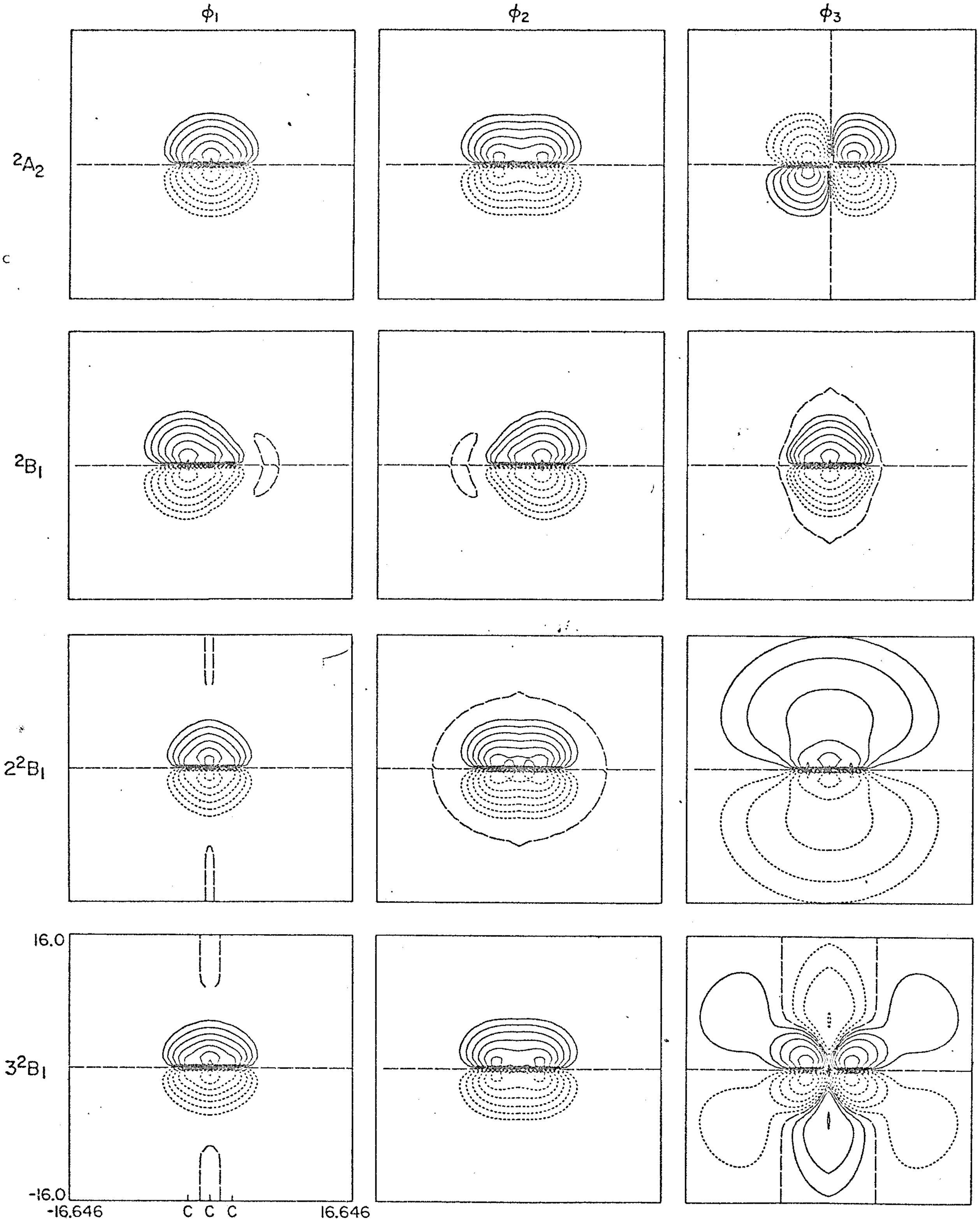
Figure 1: The GVB orbitals of various states of allyl radical. The ordering of orbitals is such that orbitals 1 and 2 are singlet coupled in the first term of Equation (4) and orbitals 2 and 3 are singlet coupled in the second term. The most diffuse contour has an amplitude of 0.003. The amplitude increases by a factor of 2.1544 at each contour corresponding to a factor of 10 for three contours.

Figure 2: The GVB orbitals of the ground state of allyl radical obtained using $c_1 = 0$ in Equation (34) while optimizing the orbitals and then transforming using Equation (35).

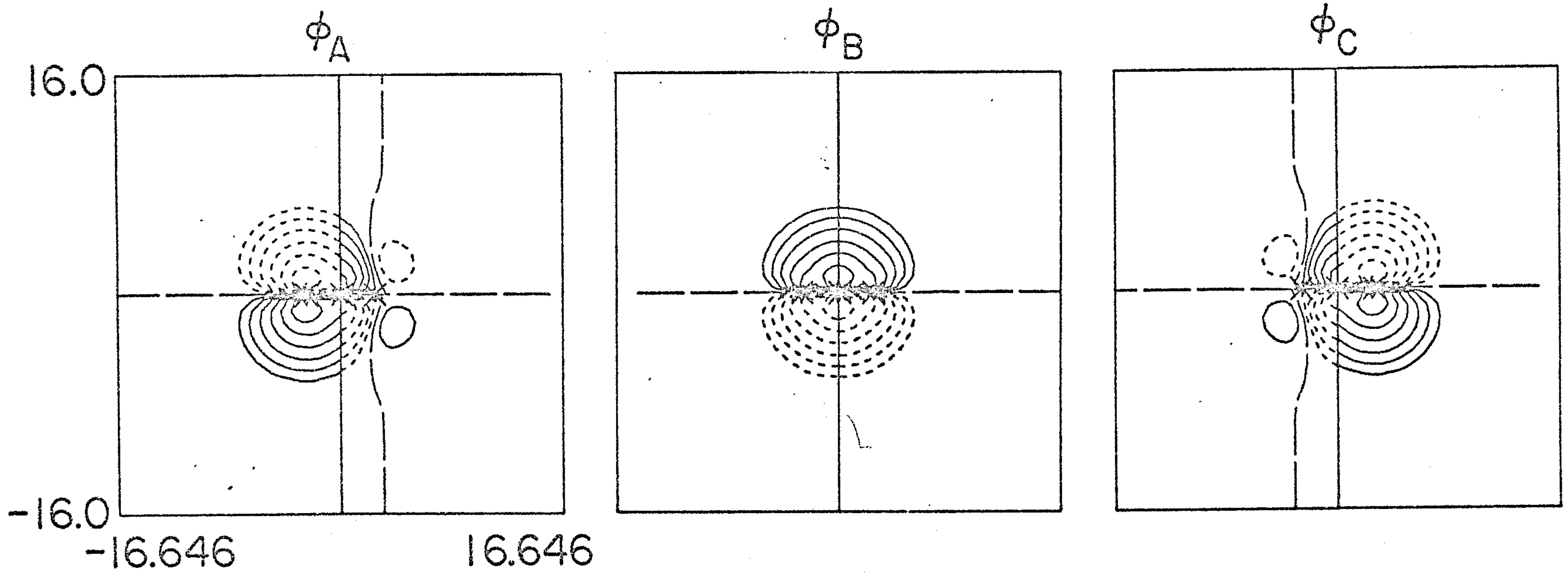
Figure 3: The valence states of allyl radical in the VB and GVB pictures.

Figure 4: The relative energies of the MO, GVB, and CI wavefunctions. All energies are relative to the full CI wavefunction.

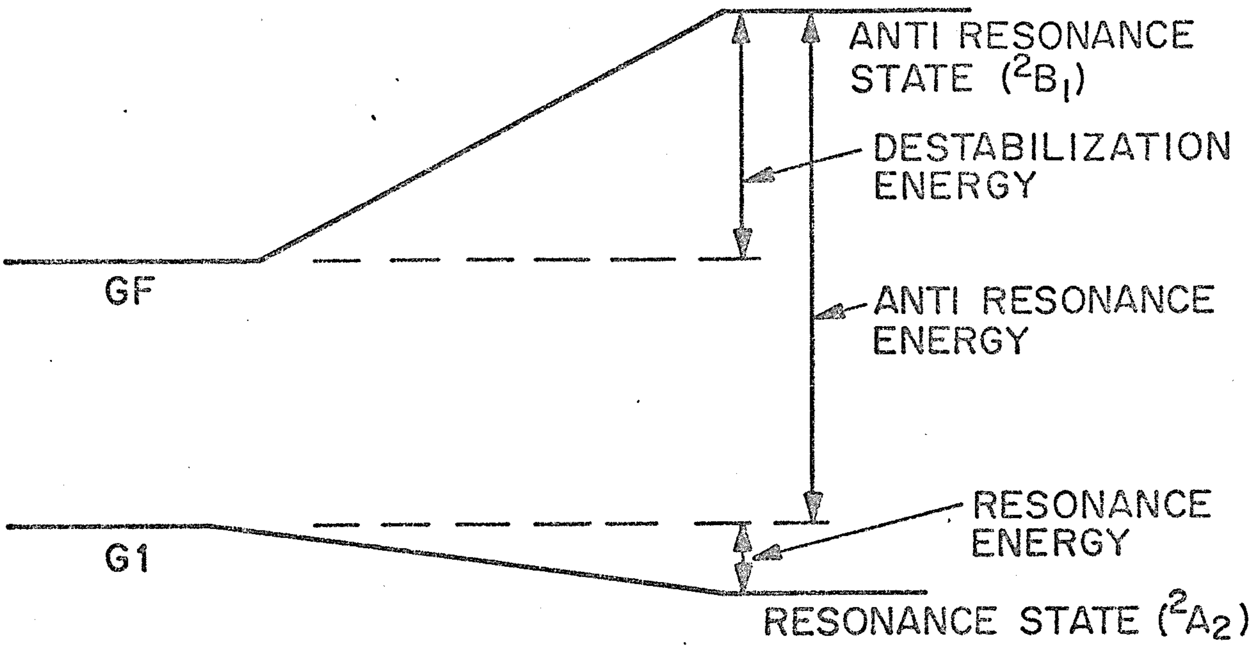
ALLYL RADICAL GVB PI ORBITALS



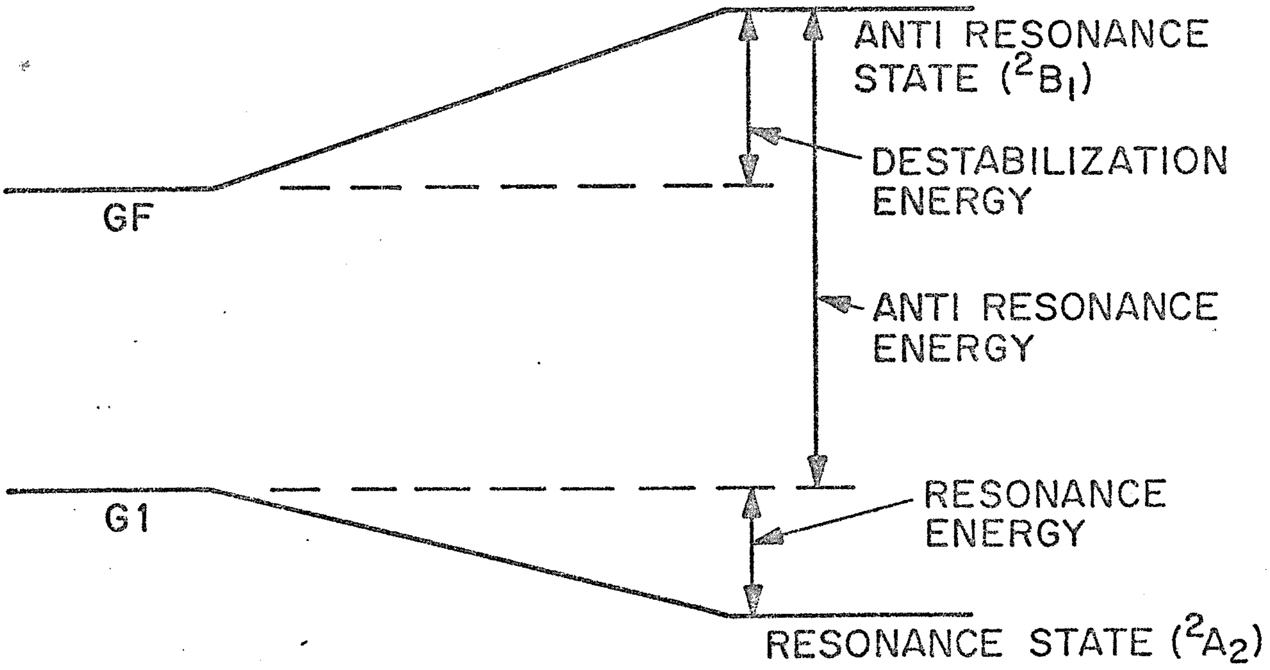
GVB PI ORBITALS FOR
$1\ ^2A_2$ STATE OF ALLYL RADICAL



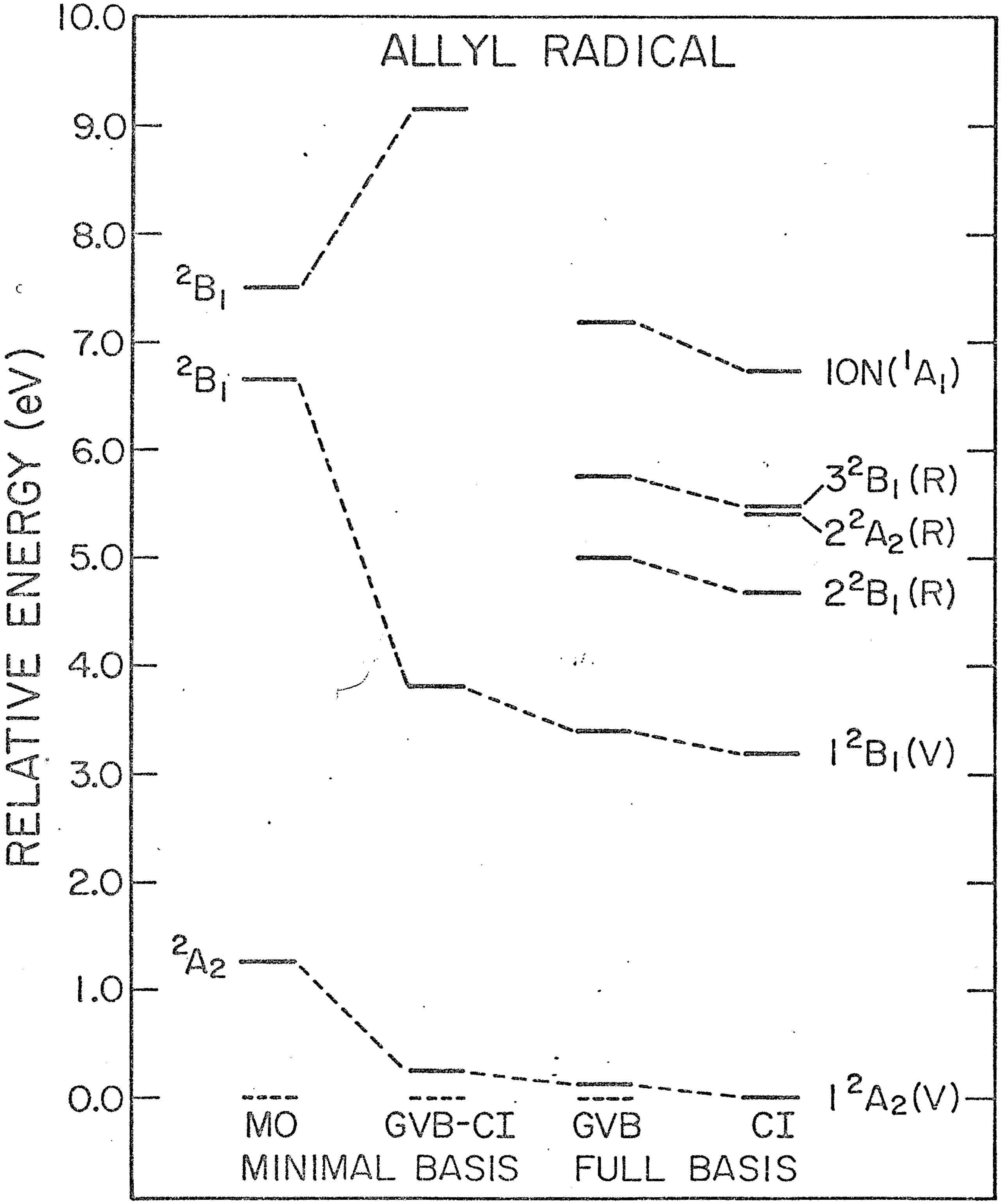
# ALLYL RADICAL



GENERALIZED VALENCE BOND



VALENCE BOND


ALLYL RADICAL
RELATIVE ENERGY (eV)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
$^2B_1$
$^2B_1$
$^2A_2$
ION($^1A_1$)
$3^2B_1$(R)
$2^2A_2$(R)
$2^2B_1$(R)
$1^2B_1$(V)
$1^2A_2$(V)
MO
GVB-CI
GVB
CI
MINIMAL BASIS
FULL BASIS

# APPENDIX III

## SPATIALLY PROJECTED GENERALIZED VALENCE BOND DESCRIPTION OF THE PI-STATES OF ALLYL RADICAL

## I. 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 the permutation symmetry and spin symmetry so that the total wavefunction will have the proper symmetries for arbitrary shapes of the orbitals. It was considered that removing all restrictions on the orbitals (but ensuring that the total wavefunction have the proper spin symmetry) would result in the shapes of the orbitals having physical significance and thereby lead to useful chemical concepts. This has proved to be the case for many systems; however an examination of the results for allyl radical and butadiene suggested that 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 that ensures the total wavefunction has the correct spatial symmetry for an arbitrary set of spatial orbitals. 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 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.

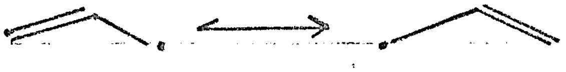
In section II, we shall develop the GVB(SP) wavefunction by examining the valence bond (VB) wavefunction and generalizing this wavefunction while retaining the basic form of VB wavefunction. Section III presents the results of our calculations. Section IV includes our interpretations of the results and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

## II. 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 to the pi-electron systems of allyl radical.

### A. 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



(1)

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

Let $\chi_r$, $\chi_c$, and $\chi_\ell$ denote atomic orbitals located on the right, center, and left centers respectively. The VB wavefunction for a three-electron doublet may be represented as

$$\psi^{VB} = c_1\psi_1 + c_2\psi_2 \tag{2a}$$

$$\psi^{VB} = c_1 \begin{array}{|c|c|}\hline \chi_c & \chi_\ell \\ \hline \chi_r & \\ \cline{1-1} \end{array} + c_2 \begin{array}{|c|c|}\hline \chi_c & \chi_r \\ \hline \chi_\ell & \\ \cline{1-1} \end{array} \tag{2b}$$

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

$$c_1 = -c_2 \tag{3a}$$

$$c_1 = c_2 \tag{3b}$$

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

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

$$\psi_1 = \mathcal{A}[\Phi_\sigma(\chi_\ell\chi_c + \chi_c\chi_\ell)\chi_r\alpha\beta\alpha] \tag{4a}$$

$$= \mathcal{A}[\Phi_\sigma \chi_\ell\chi_c\chi_r(\alpha\beta - \beta\alpha)\alpha]$$

$$\psi_2 = \mathcal{A}[\Phi_\sigma(\chi_r\chi_c + \chi_c\chi_r)\chi_\ell\alpha\beta\alpha] \tag{4b}$$

$$= \mathcal{A}[\Phi_\sigma \chi_r\chi_c\chi_\ell(\alpha\beta - \beta\alpha)\alpha]$$

$$= \mathcal{A}[\Phi_\sigma \chi_\ell\chi_c\chi_r(\alpha\beta\alpha - \alpha\alpha\beta)]$$

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

$$\psi^{VB} = \mathcal{A}[\Phi_\sigma\chi_\ell\chi_c\chi_r\Theta] \tag{5}$$

where

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

## B. Generalized Valence Bond Wavefunction

The GVB wavefunction is formally the same as the VB wavefunction

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

except the orbitals $\varphi_a$, $\varphi_b$, and $\varphi_c$ are solved for self-consistently (rather than being taken as atomic orbitals as in the VB wavefunction) and the spin coupling $\Theta$ 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 $\phi_\ell$, $\phi_c$, $\phi_r$ indicating the location of the maximum amplitude of each orbital.

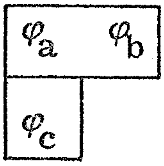
There are two independent ways of coupling three electrons into a doublet. We find it convenient to use orthogonal spin functions denoting them as

$$\begin{aligned}\theta_1 &= (\alpha\beta - \beta\alpha)\,\alpha \\ \theta_2 &= 2\alpha\alpha\beta - (\alpha\beta + \beta\alpha)\,\alpha\end{aligned} \tag{8}$$

referred to as the G1 and G2 (or GF) spinfunctions. Note that electrons 1 and 2 are singlet coupled in $\theta_1$ and triplet coupled in $\theta_2$. The spin function for (7) is

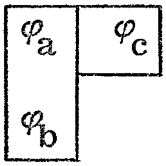
$$\Theta = c_1\theta_1 + c_2\theta_2 \tag{9}$$

It is often convenient to use the diagram



(10)

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

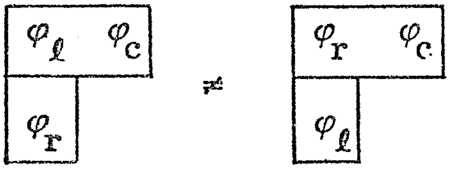


(11)

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

## C. Spatially Projected Generalized Valence Bond Wavefunction

If in the GVB wavefunction, we have localized orbitals $\varphi_r$, $\varphi_c$, $\varphi_\ell$ such that $\varphi_r$ and $\varphi_\ell$ are not identical in form, then the two VB canonical structures are not equivalent



The ground state GVB wavefunction will not be an equal mixture of these two structures as we expect from VB theory, or 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 posesses the correct spatial symmetry, 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 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 is formed by letting P operate on the GVB wavefunction

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

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

To determine the affect 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 $\sigma$ the reflection through the plane bisecting the system. Generalization to larger spatial symmetry groups is mathematically straight forward, but interpretations become more complicated.

Let us first consider the affect 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

$$\begin{aligned} e\,\chi_\ell &= \chi_\ell & \qquad \sigma\,\chi_\ell &= \chi_r \\ e\,\chi_c &= \chi_c & \qquad \sigma\,\chi_c &= \chi_c \\ e\,\chi_r &= \chi_\ell & \qquad \sigma\,\chi_r &= \chi_\ell \end{aligned} \tag{13}$$

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

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

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

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

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

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

Defining two spatial projection operators by

$$P_A = e - \sigma \tag{17}$$

$$P_S = e + \sigma \tag{18}$$

we see that

$$\psi_A^{VB} = P_A \left( \begin{array}{|c|c|}\hline \chi_c & \chi_r \\ \hline \chi_\ell & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \right) \tag{19}$$

$$\psi_S^{VB} = P_S \left( \begin{array}{|c|c|}\hline \chi_c & \chi_r \\ \hline \chi_\ell & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \right) \tag{20}$$

We note that the antisymmetric spatially projected VB wavefunction (15) or (19) is identical to the resonant state wavefunction and that 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

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

$$= P\ c_1 \left[ \begin{array}{|c|c|} \hline \varphi_a & \varphi_b \\ \hline \varphi_c \\ \cline{1-1} \end{array} + c_2 \begin{array}{|c|c|} \hline \varphi_a & \varphi_c \\ \hline \varphi_b \\ \cline{1-1} \end{array} \right] \qquad (21)$$

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

$$\Psi^{\mathrm{GVB(SP)}} = P\ \ c_1 \left[ \begin{array}{|c|c|} \hline \varphi_\ell & \varphi_c \\ \hline \varphi_r \\ \cline{1-1} \end{array} + c_2 \begin{array}{|c|c|} \hline \varphi_\ell & \varphi_r \\ \hline \varphi_c \\ \cline{1-1} \end{array} \right] \qquad (22)$$

Since $\varphi_r$ is not identical in general with $\varphi_\ell$,

$$\sigma\varphi_r \neq \varphi_\ell$$

as was true for the 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 $\varphi_r$ and $\varphi_\ell$ to be quite similar and one spin coupling component to be the primary component of each wavefunction.

## D. The Core Hamiltonian

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

$$\mathcal{A}[\Phi_{core}\Phi_{val}] \tag{23}$$

may be reduced to finding the wave function

$$\mathcal{A}[\Phi_{val}] \tag{24}$$

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 $\Phi_{core}$. The Hamiltonian for the valence orbitals will have the form

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

where

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

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

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

in the usual one-electron Hamiltonian, and $n_\pi$ is the number of pi electrons. For allyl radical, the sigma-electron core was formed from an <u>ab-initio</u> HF calculation on the ground state of allyl cation.

### E. 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.[5] This was contracted to a double-zeta basis (4s, 2p) on each carbon and (2s) on each hydrogen, as suggested by Dunning.[6] 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: $R_{CC} = 1.40\ \mathring{A}$, $R_{CH} = 1.08°\ A$ and all bond angles = 120°.

## III. 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 I. Figure 1 depicts the orbitals for the $A_2$ states and Figure 2 the orbitals for the $B_1$ states. In Figure 1, the orbitals in the first two columns, $\phi_a$ and $\phi_b$, are singlet coupled except for the $3^2A_2$ state, for which $\phi_a$ and $\phi_b$ are triplet coupled. In Figure 2, the orbitals in the first two columns $\phi_a$ and $\phi_b$ are singlet coupled except for the $4^2B_1$ state, for which $\phi_a$ and $\phi_b$ are triplet coupled.

From Figures 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 antiresonant 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 the 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.

## IV. Discussion

### A. 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 Figures 1 and 2 we see that the orbitals for these states are very similar, and from Table I, 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 $\varphi_a$ and $\varphi_c$ 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

$$\Psi = p_{A_2}\left(\begin{array}{|c|c|}\hline \varphi_\ell & \varphi_c \\ \hline \varphi_r & \multicolumn{1}{|c}{} \\ \cline{1-1}\end{array}\right) \tag{28a}$$

$$\Psi = \begin{array}{|c|c|}\hline \varphi_\ell & \varphi_c \\ \hline \varphi_r & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \; - \; \begin{array}{|c|c|}\hline \varphi_r & \varphi_c \\ \hline \varphi_\ell & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \qquad (28b)$$

This is the same form as the VB resonance state and the GVB $1^2A_2$ (resonance) state.[1] Resonance in the GVB(SP) description arises from the symmetry of the state. To the extent $\varphi_\ell$ and $\varphi_r$ differ, the second tableau in (22) is required, but we see from Table I, that $C_2$ is very small and the second tableau does not contribute.

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

$$\Psi = p_{B_1}\left( \begin{array}{|c|c|}\hline \varphi_\ell & \varphi_c \\ \hline \varphi_r & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \right) \qquad (29a)$$

$$\Psi = \begin{array}{|c|c|}\hline \varphi_\ell & \varphi_c \\ \hline \varphi_r & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \; + \; \begin{array}{|c|c|}\hline \varphi_r & \varphi_c \\ \hline \varphi_\ell & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \qquad (29b)$$

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, $\varphi_\ell$ and $\varphi_r$ will not have the same form and the second (GF) tableau must be included in the wavefunction. From Table I, 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-consistant orbitals are used in lieu of atomic orbitals. The GVB model, however, describes the resonant state as the optimum spin coupling associated with the set of spatial orbitals, and the antiresonant state is formed using the same spatial orbitals and the orthogonal spin coupling. However, the optimum GVB description of the $1^2A_2$ state includes delocalized orbitals, but using localized orbitals, the GVB combination of tableaux is identical to the VB combination and only slightly (0.88 kcal) higher in energy.[1] The GVB combination of tableaux for the $1^2B_1$ state is identical to the VB combination of bonding structures.[1] The GVB orbitals for the $1^2A_2$ and $1^2B_1$ states are not identical, but are quite similar in form.

We have three qualitative descriptions of the $1^2A_2$ and $1^2B_1$ states of allyl radical and have found these to have the same form, essentially

(28b) and (29b) respectively. However, the individual orbitals used in these wavefunctions differ. The VB wavefunction uses atomic orbitals. The GVB wavefunction uses self-consistant orbitals, but spatial symmetry considerations restrict the individual orbitals to be delocalized symmetry functions or, if the orbitals are localized, restrict the spin coupling to the resonant (or anti-resonant) combinations and require the shapes of $\varphi_r$ and $\varphi_\ell$ be identical.[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 of the GVB G1(10) wavefunction,[1] we obtain the GVB(SP) estimate of the resonance energy. We find 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.[8] 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 57.9kcal for the GVB wavefunction.

## B. The Fused Ethylene Model

Dunning[7] 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 worked 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 ground (N) state and the lowest triplet (T) state. The $1^2A_2$ state of allyl radical may be considered as arising from a combination of a N state of ethylene with a 2p like pi orbital on the third carbon, i.e. a $^3B_1$ methylene. The $1^2B_1$ state of allyl radical would then be the combination of the T state of ethylene and the same third orbitals. The excitation energy of the $1^2B_1$ state is 3.25eV as compared to 4.20 eV for the T state of ethylene.[4]

The $2^2A_2$ state may be considered as a combination of an N state of ethylene with an excited pi orbital. Because of the diffuse nature of excited pi orbitals, this third orbital will be almost orthogonal to the N state ethylene core and the dominant term in the GVB(SP) wavefunction will be

$$\begin{array}{|c|c|}\hline \varphi_{1\ell} & \varphi_{2c} \\ \hline \varphi_{3r} & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} \quad - \quad \begin{array}{|c|c|}\hline \varphi_{1r} & \varphi_{2c} \\ \hline \varphi_{3\ell} & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array}$$

where $\varphi_1$ and $\varphi_2$ are the ethylene N state orbitals. Since $\varphi_3$ is spread over the entire molecule, it must have $A_2$ symmetry and therefore is a $3d\pi$ orbital. Similarly the $2^2B_1$ state may be considered as an N state ethylene with a diffuse pi orbital, which here must have $B_1$ symmetry and is therefore a $3p\pi$ orbital. Since a $3p\pi$ orbital is lower than a $3d\pi$ orbital, we expect the $2^2B_1$ state to be lower in energy than the $2^2A_2$ state.

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 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.

The $3^2B_1$ state may be considered as an ethylene N state core and a diffuse pi orbital. As discussed earlier for the $2^2B_1$ state, the diffuse orbital must have $B_1$ symmetry and may be identified as a $4p\pi$ orbital.

The $4^2A_2$ and $4^2B_1$ states are more complicated consisting of an excited ethylene core combined with a valence-like pi orbital. In the $4^2A_2$ state, the first two orbitals are singlet coupled and may be considered as the $2^1A_g$( state of ethylene orbitals. The third orbital should be the same as in the $1^2A_2$ state. In the $4^2B_1$ state, the first two orbitals are triplet coupled and may be identified as the $2^3B_{1u}$. Since one orbital is diffuse the two orbitals can be orthogonal without the introduction of any nodes.

## C. Rydberg Like Excited States

Table II 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 agreement 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, $\zeta$, 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 reference 1, and $\zeta$ the quantum defect. We obtain

$2^2B_1$: $\zeta = 0.38$ $(3p\pi)$

$3^2B_1$: $\zeta = 0.65$ $(4p\pi)$

$2^2A_2$: $\zeta = -0.21$ $(3d\pi)$

For p like Rydberg states, $\zeta$ is typically 0.50.[9] The $2^2B_1$ state corresponds then to a $2p\pi \rightarrow 3p\pi$ excitation and the $3^2B_1$ state to a $2p\pi \rightarrow 4p\pi$ excitation. For d and f like Rydberg orbitals $\zeta$ is typically $<0.10$. From the symmetry of the diffuse orbital we identify the $2^2A_2$ state as a $2p\pi \rightarrow 3d\pi$ excitation. Since our basis set only includes $p\pi$ functions, a $3d\pi$ orbital is poorly described accounting for the negative sign of $\zeta$ for the $2^2A_2$ state.

The $3^2A_2$ should ionized to the $1^3B_2$ state of allyl cation since the two tight 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). The $3^2A_2$ state corresponds to a $2p\pi \rightarrow 3p\pi$ excitation. 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.

In the $4^2B_1$ and $4^2A_2$ the nature of the spin coupling is such that it is not to identify the states of allyl cation that would result from ionization of the diffues orbital. Thus, quantum defects cannot be calculated for these states.

Table III contains a comparison with other results. The GVB(SP) results compare very favorably. The basis set used by Peyerimhoff and Buenker[10] did not contain diffuse function accounting for their poor description of the $2^2B_1$ state.

Table I. GVB(SP) Energies for Ground and Excited States of Allyl Radical

| State | Total Energy(h) | Spin Coupling Coefficients | |
|---|---|---|---|
| | | $c_1$ | $c_2$ |
| $1^2A_2$ | -116.418612 | 1.00 | 0.00 |
| $1^2B_1$ | -116.301432 | -0.938 | 0.345 |
| $2^2B_1$ | -116.2458977 | 0.999 | -0.027 |
| $2^2A_2$ | -116.221249 | 0.999 | 0.003 |
| $3^2B_1$ | -116.217433 | 0.999 | -0.032 |
| $4^2B_1$ | -116.140243 | 0.089 | 0.996 |
| $3^2A_2$ | -116.136173 | 0.858 | 0.514 |
| $4^2A_2$ | -116.135127 | 0.973 | -0.231 |
| Cation[a] | 116.172189 | - | - |

[a] Reference 4.

Table II. Comparison of GVB, GVB(SP), and CI Energies for the Ground and Excited States of Allyl Radical.

| State | GVB[a,b] Total Energy (hartrees) | GVB[a,b] Excitation Energy (eV)[d] | GVB(SP) Total Energy (hartrees) | GVB(SP) Excitation Energy (eV)[d] | Full CI[a,b] Total Energy (hartrees) | Full CI[a,b] 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[c] | -116.157899 | 7.04 | -116.172789 | 6.69 | -116.173420 | 6.74 |

[a] Reference 1.

[b] All calculations were performed using the same basis set.

[c] Reference 4.

[d] 1h = 27.2117 eV

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

| State | GVB(SP) | GVB[1] | CI[1] | Peyerimhoff[10] and Buenker (*Ab initio* CI) | Semi-Empirical CI[11] |
|---|---|---|---|---|---|
| $^2A_2$ | 0 | 0 | 0 | 0 | 0 |
| $^2B_1$ | 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 |

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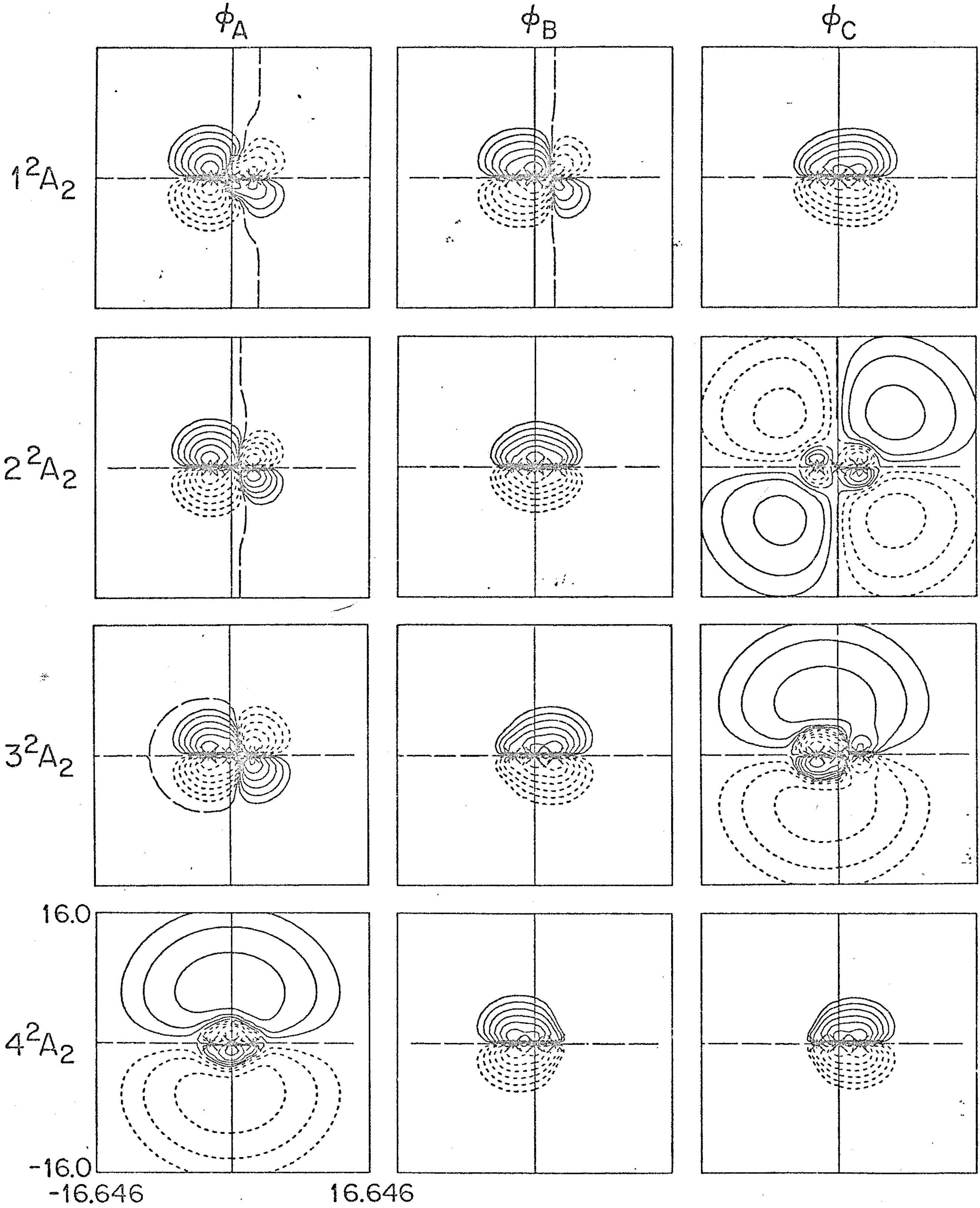
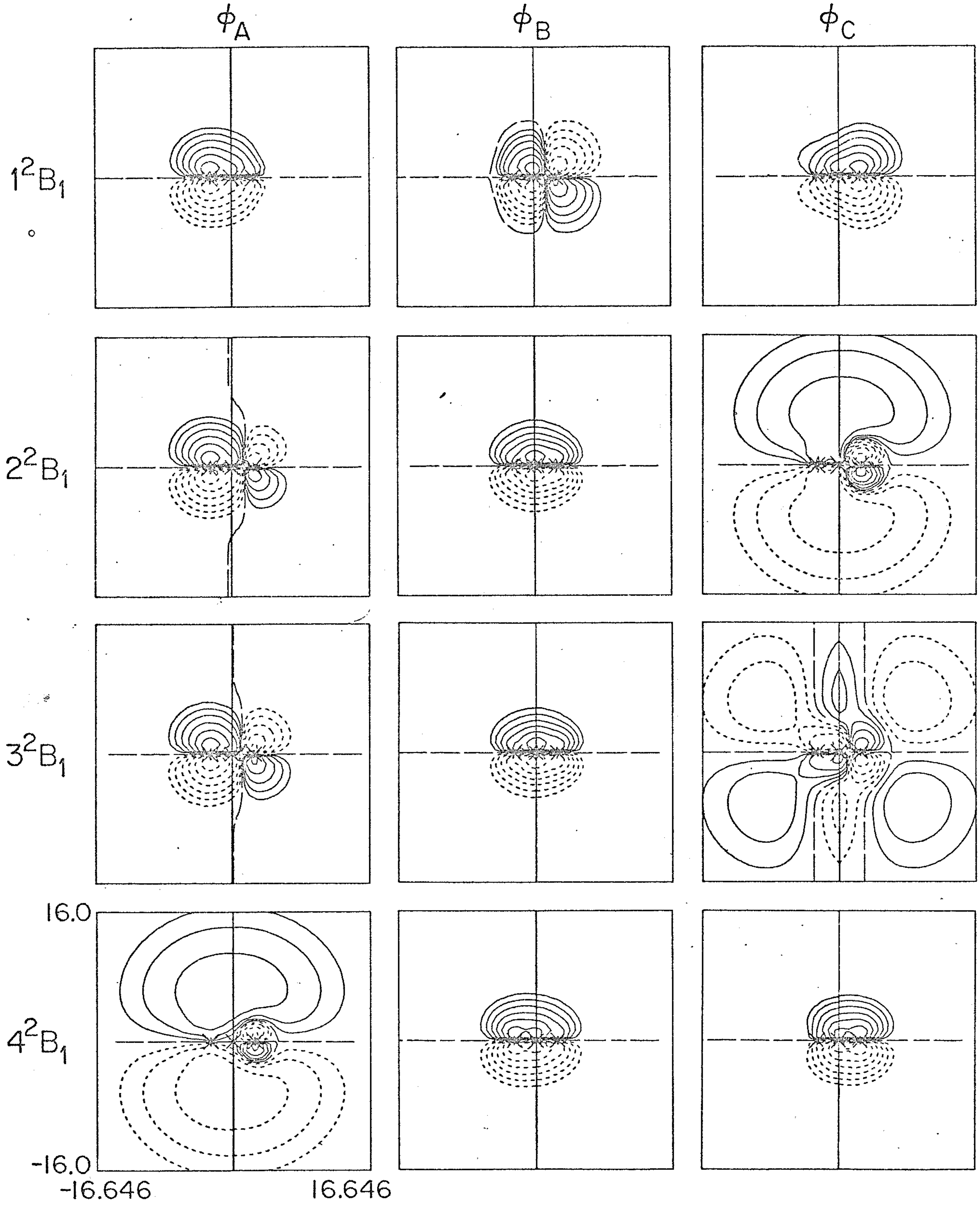
# Figure Captions

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.
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 Figure 1.

# ALLYL RADICAL
# GVB(SP) PI ORBITALS FOR $A_2$ STATES



# ALLYL RADICAL
# GVB(SP) PI ORBITALS FOR $B_1$ STATES



# APPENDIX IV

# THE GENERALIZED VALENCE BOND DESCRIPTION OF THE LOW-LYING ELECTRONIC STATES OF S-*TRANS*-1,3 BUTADIENE

## I. INTRODUCTION

The generalized valence bond (GVB) method is a generalization of the valence bond (VB) method in which each singly occupied orbital is solved for self-consistently. This is analogous to the Hartree-Fock procedure except that each doubly occupied orbital of the HF wavefunction is allowed to split into two singly occupied orbitals.

This paper is one of a series examining the GVB wavefunctions of the ground and excited states of conjugated molecules. Previously we considered ethylene,[1] allyl cation,[1] and allyl radical[2] and now we turn our attention to s-<u>trans</u>-1, 3-butadiene (hereafter referred to as butadiene). As with the other papers in this series only the $\pi$ system is described in the GVB formalism, the $\sigma$ orbitals are taken as doubly occupied and obtained from HF calculations.

Details concerning the wavefunctions and calculations are presented in Section II. Section III presents the results of the GVB calculations and a comparison with energies of extensive configuration interaction (CI) calculations. Here we find that the GVB energies are quite close to the CI energies. Section III also includes our interpretations of the GVB wavefunctions.

## II. THE WAVEFUNCTIONS

### A. The Wavefunctions

The Hartree-Fock (HF) description of the ground state of butadiene is

$$\mathcal{A}[\varphi_1^2\varphi_2^2\cdots\varphi_q^2\varphi_{\pi_1}^2\varphi_{\pi_2}^2(\alpha\beta\alpha\beta\cdots\alpha\beta\alpha\beta\alpha\beta)]. \quad (1)$$

Low-lying excited states are obtained, for example, by exciting an electron from the $\pi_2$ orbital of (1) to an empty $\pi_3$ orbital, obtaining either a singlet state

$$\begin{aligned}&\mathcal{A}[\Phi_\sigma\phi_{\pi_1}\phi_{\pi_1}(\phi_{\pi_2}\phi_{\pi_3}+\phi_{\pi_3}\phi_{\pi_2})\alpha\beta\alpha\beta]\\ =\ &\mathcal{A}[\Phi_\sigma\phi_{\pi_1}\phi_{\pi_1}\phi_{\pi_2}\phi_{\pi_3}\ \alpha\beta(\alpha\beta-\beta\alpha)]\end{aligned} \quad (2)$$

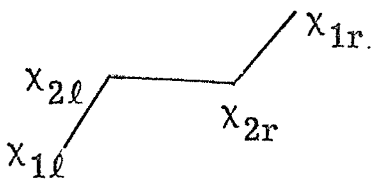
or a triplet state

$$\begin{aligned}&\mathcal{A}[\Phi_\sigma\phi_{\pi_1}\phi_{\pi_1}(\phi_{\pi_2}\phi_{\pi_3}-\phi_{\pi_3}\phi_{\pi_2})\alpha\beta\alpha\beta]\\ &\mathcal{A}[\Phi_\sigma\phi_{\pi_1}\phi_{\pi_1}\phi_{\pi_2}\phi_{\pi_3}\ \alpha\beta(\alpha\beta+\beta\alpha)]\end{aligned} \quad (3)$$

where $\Phi_\sigma$ denotes the product of a sigma spin orbitals from (1). In the HF method all orbitals are solved for self-consistently.

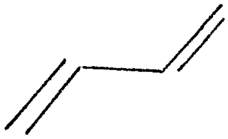
## B. The VB Wavefunction

In the valence bond (VB) method, one electron is placed in an atomic $\pi$ orbital on each carbon. We will denote these orbitals as $\chi_{1\ell}$, $\chi_{2\ell}$, $\chi_{1r}$, $\chi_{2r}$, as indicated in (4)



(4)

These orbitals can be coupled into singlet states as



$$\equiv \begin{array}{|c|}\hline \chi_{1\ell}\,\chi_{2\ell} \\ \hline \chi_{1r}\,\chi_{2r} \\ \hline \end{array} \equiv \Psi_1 \qquad (5)$$

or as

$$\equiv \begin{array}{|c|}\hline \chi_{2\ell}\,\chi_{2r} \\ \hline \chi_{1\ell}\,\chi_{1r} \\ \hline \end{array} \equiv \Psi_2 \qquad (6)$$

where orbitals in the same row of the tableaux in (5) and (6) are singlet paired. For example the wavefunction $\Psi_1$ can be written as

$$\begin{aligned} \Psi_1 &= \mathcal{A}[\Phi_\sigma(\chi_{1\ell}\chi_{2\ell} + \chi_{2\ell}\chi_{1\ell})(\chi_{1r}\chi_{2r} + \chi_{2r}\chi_{1r})\alpha\beta\alpha\beta] \\ &= \mathcal{A}[\Phi_\sigma\chi_{1\ell}\chi_{2\ell}\chi_{1r}\chi_{2r}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)] \end{aligned} \qquad (7)$$

The simple VB wavefunction is often taken to be either $\Psi_1$ of (5) or the combination

$$\Psi^{VB} = C_1\Psi_1 + C_2\Psi_2 \qquad (8)$$

in which the coefficients $C_1$ and $C_2$ are optimized.

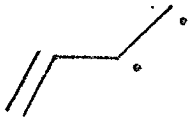
The wavefunction (8) can be rewritten as

$$\Psi^{VB} = \mathcal{A}[\Phi_\sigma\chi_{1\ell}\chi_{2\ell}\chi_{1r}\chi_{2r}\Theta] \qquad (9)$$

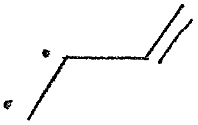
where the spin function $\Theta$ is

$$\Theta = C_1(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) + C_2[\beta\beta\alpha\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha + \alpha\alpha\beta\beta]$$

For a triplet state there are three linearly independent valence bond functions, which can be taken as

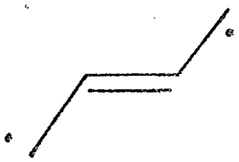


$$\equiv \begin{array}{|c|c|}\hline \chi_{1\ell} & \chi_{2\ell} \\ \hline \chi_{1r} \\ \cline{1-1} \chi_{2r} \\ \cline{1-1}\end{array} \equiv \Psi_3 \qquad (10)$$



$$\equiv \begin{array}{|c|c|}\hline \chi_{1r} & \chi_{2r} \\ \hline \chi_{1\ell} \\ \cline{1-1} \chi_{2\ell} \\ \cline{1-1}\end{array} \equiv \Psi_4 \qquad (11)$$

and



$$\equiv \begin{array}{|c|c|}\hline \chi_{2\ell} & \chi_{2r} \\ \hline \chi_{1\ell} \\ \cline{1-1} \chi_{1r} \\ \cline{1-1}\end{array} \equiv \Psi_5 \qquad (12)$$

For example,

$$\begin{aligned}\Psi_5 &= \mathcal{A}[\Phi_\sigma(\chi_{2\ell}\chi_{2r} + \chi_{2r}\chi_{2\ell})(\chi_{1\ell}\chi_{1r} - \chi_{1r}\chi_{1\ell})\alpha\beta\alpha\beta] \\ &= \mathcal{A}[\Phi_\sigma\chi_{2\ell}\chi_{2r}\chi_{1\ell}\chi_{1r}(\alpha\beta - \beta\alpha)(\alpha\beta + \beta\alpha)]\end{aligned} \qquad (13)$$

The simple VB wavefunction for a triplet state is taken to be either any one of the functions (10), (11), or (12), or alternatively as the linear combination

$$\Psi^{VB} = C_3\Psi_3 + C_4\Psi_4 + C_5\Psi_5 \qquad (14)$$

in which the coefficients $C_3$, $C_4$, and $C_5$ are optimized.

### C. The generalized valence bond wavefunction

The generalized valence bond (GVB) method[3, 4] is a generalization of the valence bond method in which the electron orbitals are solved for self-consistently (in a manner analogous to that in the HF method) rather than taken to be atomic orbitals (as in the VB method).

For a singlet state the GVB wavefunction can be written as

$$\Psi^{GVB} = \mathcal{A}[\Phi_\sigma \phi_{1\ell}\phi_{2\ell}\phi_{2r}\phi_{1r}\Theta] \qquad (15)$$

where

$$\Theta = C_1\theta_1 + C_2\theta_2, \qquad (16)$$

$$\theta_1 = \tfrac{1}{2}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)$$

and

$$\theta_2 = \frac{1}{\sqrt{3}}\left[\alpha\alpha\beta\beta + \beta\beta\alpha\alpha - \tfrac{1}{2}(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)\right].$$

so that $\theta_1$ and $\theta_2$ are orthogonal spin functions. In the GVB method the coefficients $C_1$ and $C_2$ are referred to as the spin coupling coefficients and are solved for simultaneously with the optimization of the individual electron orbitals.

We find that the optimum GVB orbitals are each localized near a different carbon atom just as in the VB wavefunction and hence the orbitals in the GVB wavefunction (15) are denoted in a manner comparable to that of the VB wavefunction.

If $C_1 = 1$ and $C_2 = 0$ the wavefunction (15) is said to have G1 spin coupling and is denoted as

$$\begin{array}{|c|} \hline \phi_{1\ell}\ \phi_{2\ell} \\ \hline \phi_{1r}\ \phi_{2r} \\ \hline \end{array} \tag{17}$$

If $C_1 = 0$ and $C_2 = 1$ the wavefunction (15) is said to have GF (or G2) spin coupling and is denoted as

$$\begin{array}{|c|c|} \hline \phi_{1\ell} & \phi_{1r} \\ \phi_{2\ell} & \phi_{2r} \\ \hline \end{array} \tag{18}$$

In (17) orbitals $\phi_{1\ell}$ and $\phi_{2\ell}$ are coupled into a singlet (bonding) pair, orbitals $\phi_{1r}$ and $\phi_{2r}$ are also coupled into a singlet pair and then the whole wavefunction is coupled into a singlet state. In (18) orbitals $\phi_{1\ell}$ and $\phi_{2\ell}$ are coupled into a triplet pair, orbitals $\phi_{1r}$ and $\phi_{2r}$ are also coupled into a triplet pair and then the whole wavefunction is coupled into a singlet state. [Two triplet states ($S = 1$) combine to yield $S = 2$, 1, and 0 states, that is quintet, triplet, and singlet states.]

Using the same orbitals in (17) and in (18) leads to two orthogonal many-electron wavefunctions. Below we will find that the ground state of butadiene corresponds closely to (17) while an excited singlet state corresponds closely to (18).

For a triplet state the GVB wavefunction has the form

$$\Psi^{\mathrm{GVB}} = \mathcal{A}[\Phi_\sigma \phi_{1\ell}\phi_{2\ell}\phi_{2r}\phi_{1r}\Theta] \tag{19}$$

where

$$\Theta = C_1\theta_1 + C_2\theta_2 + C_3\theta_3 \tag{20}$$

$$\theta_1 = \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\alpha\alpha$$

$$\theta_2 = \sqrt{\frac{2}{3}}[\alpha\alpha\beta - \tfrac{1}{2}(\alpha\beta + \beta\alpha)\alpha]\alpha$$

$$\theta_3 = \frac{\sqrt{3}}{2}[\alpha\alpha\alpha\beta - \tfrac{1}{3}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)\alpha]$$

$\theta_1$, $\theta_2$, and $\theta_3$ are mutually orthogonal spin functions. Special cases of (20) are: the G1 wavefunction

$$\begin{array}{|c|c|}\hline \phi_{1\ell} & \phi_{2\ell} \\ \hline \phi_{2r} & \multicolumn{1}{c}{} \\ \phi_{1r} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \tag{21}$$

($C_1 = 1$, $C_2 = C_3 = 0$) in which orbitals $\phi_{1\ell}$ and $\phi_{2\ell}$ are coupled into a singlet state while orbitals $\phi_{1r}$ and $\phi_{2r}$ are coupled into a triplet state; the G2 wavefunction

$$\begin{array}{|c|c|}\hline \phi_{1\ell} & \phi_{2r} \\ \hline \phi_{2\ell} \\ \cline{1-1} \phi_{1r} \\ \cline{1-1} \end{array} \tag{22}$$

($C_2 = 1$, $C_1 = C_3 = 0$) in which $\phi_{1\ell}$ and $\phi_{2\ell}$ are coupled into a triplet state; and the GF or G3 wavefunction

$$\begin{array}{|c|c|}\hline \phi_{1\ell} & \phi_{1r} \\ \hline \phi_{2\ell} \\ \cline{1-1} \phi_{2r} \\ \cline{1-1} \end{array} \tag{23}$$

($C_3 = 1$, $C_1 = C_2 = 0$) in which orbitals $\phi_{1\ell}$, $\phi_{2\ell}$, $\phi_{2r}$ are coupled into a quartet state.

None of the wavefunctions (21) - (23) corresponds to a state analogous to (18) [where the two $S = 1$ pairs were coupled into an overall $S = 0$ state] in which orbitals $\phi_{1\ell}$ and $\phi_{2\ell}$ are coupled into a triplet state, orbitals $\phi_{1r}$ and $\phi_{2r}$ are coupled into a triplet state, and then the whole wavefunction coupled into a triplet many-electron state. This would require a spin function of the form

$$\begin{aligned} \Theta &= \tfrac{1}{2}[\alpha\alpha(\alpha\beta + \beta\alpha) - (\alpha\beta + \beta\alpha)\alpha\alpha] \\ &= \frac{1}{\sqrt{3}}\,\theta_3 + \sqrt{\frac{2}{3}}\,\theta_2 \end{aligned} \tag{24}$$

## D. The Sigma Core

As discussed elsewhere[1, 5] the problem of finding a wavefunction of the form

$$\mathcal{A}[\,\Phi_{\text{core}}\ \ \Phi_{\text{val}}\,] \tag{25}$$

may be reduced to that of finding the wavefunction

$$\mathcal{A}[\,\Phi_{\text{val}}\,] \tag{26}$$

if (i) the core is a product of doubly-occupied orbitals and (ii) if the orbitals of $\Phi_{\text{val}}$ are taken to be orthogonal to those of $\Phi_{\text{core}}$. The result is a four-electron Hamiltonian for the pi-electron system of butadiene having the form

$$\mathcal{H} = \sum_{i=1}^{n_\pi} h^{\text{core}}(i) + \sum_{i>j}^{n_\pi} 1/r_{ij} \tag{27}$$

where $n_\pi$ is the number of electrons in $\pi$ orbitals and the one-electron operator

$$h^{\text{core}}(i) = h(i) + \sum_{j=1}^{q} (2J_j - K_j) \tag{28}$$

contains both the usual kinetic energy and nuclear attraction terms

$$h(i) = \tfrac{1}{2}\nabla_i^2 - \sum_a \frac{Z_a}{r_{ia}} \tag{29}$$

plus the Coulomb and exchange terms due to the interation with the q doubly-occupied core orbitals.

The sigma core for butadiene was obtained from an ab initio HF calculation on the ground state.[5] This core should provide a good description of the ground state and valence-like excited states. Excited states involving a diffuse orbital may not be as well described since the core orbitals would be expected to contract when solved for self-consistently. Using the ground state core for these excited states should result in an overestimation of excitation energies.

### E. The Basis and Other Details

The geometrical parameters used are the same as used in other work[5, 6] and were : $R_{CH} = 1.08°A$, $R_{C=C}=1.337°A$, $R_{C-C} = 1.438°A$, $\measuredangle$ HCH = 120° and $\measuredangle$ CCC = 120°.

The basis set used in these calculations consisted of a (9s, 5p) set of primitive Gaussian functions on each carbon and a (4s) set on each hydrogen as determined by Huzinaga.[7] This was contracted to a double-zeta basis (4s, 2p) on each carbon and (2s) on each hydrogen as suggested by Dunning.[8] To permit the description of Rydberg-like excited states, it is necessary to also include diffuse basis functions and consequently the above basis was supplemented by two additional diffuse $p\pi$-Gaussian functions on each carbon (orbital exponents of 0.03477 and 0.01075 were used).

## III. RESULTS AND DISCUSSION

### A. Valence States

In the VB description of butadiene, there is one electron in the atomic $\pi$ orbital centered on each carbon. Pairing these orbitals in different ways leads to two singlet states, three triplet states, and one quintet state. The singlet states would be linear combinations of $\Psi_1$ and $\Psi_2$ in (5) and (6) and the triplet states linear combinations of $\Psi_3$, $\Psi_4$, and $\Psi_5$ in (10) - (12). Any other excited state formed using only atomic $\pi$ orbitals would contain doubly-occupied orbitals corresponding to ionic-like configurations. States consisting mainly of such ionic configurations should be at higher energies than the covalent valence states of (5), (6), (10) - (12). Thus among the low-lying $\pi$ states butadiene, there should be two valence-like singlet states, three triplet states, and one quintet state.

Other excited covalent states of the $\pi$ electron system must have dominant configurations corresponding to exciting an electron from $2p\pi$ orbital to $3p\pi$, $3d\pi$ or higher-lying $\pi$ orbitals. Those states should lead to Rydberg series and will be referred to as Rydberg states.

#### 1. Valence singlet states

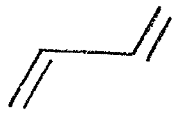
From the GVB calculations we find two valence-like singlet states as anticipated from the VB analysis. Extensive CI calculations[5] confirm this.

## 2. The $X^1A_g$ state

The GVB orbitals for the ground state of butadiene are shown in Figure 1. The energy and spin-coupling coefficients are given in Table I. As indicated in Table I, the GVB wavefunction has an energy only 3 kcal (0.0046 h.) higher then the full CI energy for this basis set, while the GVB energy is 36.7 kcal below the HF energy (with the same basis set).[5] Thus the GVB wavefunction includes 93% of the $\pi$ correlation error in the HF wavefunction. Since the GVB energy is so near the exact (full CI) energy, it is reasonable to assume that the GVB wavefunction includes all important bonding effects involving the $\pi$ system and that nature of the states may be understood on the basis of interpretation of the GVB orbitals.

From Figure 1, we see that the orbitals for the ground ($X^1A_g$) state are each localized near a different carbon atom, qualitatively similar to simple VB orbitals. However, each GVB orbital has delocalized onto neighboring centers. A similar delocalization of GVB orbitals has been seen for numerous system, for example $H_2$,[9] ethylene,[1] and ozone,[9] and is associated with the formation of covalent bonds.

In the simplest VB picture the bonding in butadiene would be represented by the single configuration



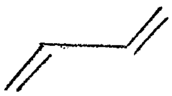
(5)

However allowing the long-bond structure (6) to mix with (5) as in (8) leads to

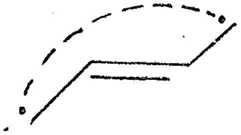
$$C_1 = 1.074 \quad \text{and} \quad C_2 = -0.170$$

and an energy lowering of 0.0036 h (2.2 kcal). [Note that (5) and (6) are not orthogonal so that $C_1^2$ and $C_2^2$ are not the relative contributions of (5) and (6).]

In the GVB description we make use of orthogonal configuration as in (15) - (18). Here we find that the configuration corresponding to

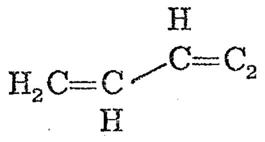


contributes about 98% of the wavefunction. The difference in energy between the optimum wavefunction of the form (5) and the full GVB wavefunction is 0.63 kcal. The incorporation of this other spin-coupling can be considered as arising from the incorporation of some bonding between orbitals $\phi_{2\ell}$ and $\phi_{2r}$ (carbons 2 and 3)



in addition to the bonding between carbons 1 and 2 and carbons 3 and 4. The delocalization of orbital $\phi_{2\ell}$ onto carbon 3 and $\phi_{2r}$ onto carbon 2 also indicates $\pi$ bonding between carbons 2 and 3.

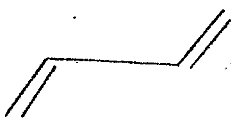
It has been noted that the heat of formation of butadiene is slightly lower than would be expected on the basis of two CC double bonds and one CC single bond as in



The extra stability is estimated as about 3.6 kcal[10] and is often referred to as the resonance stabilization energy [due to incorporation of (6)]. We calculate the energy lowering due to incorporation of (6) to be 2.27 kcal for the VB wavefunction and the corresponding energy lowering due to incorporation of (18) into (17) to be 0.7 kcal (see Table III). Thu these theoretical estimates of the resonance stabilization are in fair agreement with the experimentally based estimates.

### 3. The 2 $^1A_g$ state

Taking the ground state of butadiene as



$$= \begin{array}{|cc|}\hline \chi_{1\ell} & \chi_{2\ell} \\ \hline \chi_{1r} & \chi_{2r} \\ \hline \end{array}\,, \tag{5}$$

then the orthogonal excited state wavefunction would be

$$\begin{array}{|c|c|}\hline \chi_{1\ell} & \chi_{1r} \\ \chi_{2\ell} & \chi_{2r} \\ \hline \end{array} \; . \qquad (29)$$

The $\pi$ orbitals of (5) are just the same as if two ethylene molecules each in the ground electronic state $\boxed{\chi_{1\ell}\ \ \chi_{2\ell}}$ and $\boxed{\chi_{1r}\ \ \chi_{2r}}$ has been fused together. Similarly (29) can be considered as the fusion of two ethylene molecules each in its triplet excited states

$$\begin{array}{|c|}\hline \chi_{1\ell} \\ \chi_{2\ell} \\ \hline \end{array} \quad \text{and} \quad \begin{array}{|c|}\hline \chi_{1r} \\ \chi_{2r} \\ \hline \end{array}$$

For this reason we denote these states as NN for (5) and TT for (29) where N and T refer to the ground and lowest triplet states of ethylene. Neglecting any interactions between these ethylene groups, we would expect the NN and TT states to be separated by about twice the N to T excitation energy, i.e., by about 8.4 eV. The VB wavefunctions (5) and (29) are actually separated by much less (6.44 eV) since the ethylene-ethylene interactions in (5) are repulsive while those in (29) are attractive.[11] Allowing (5) and (29) to mix in the VB description leads to

$$C_5 = 0.989 \quad C_{29} = -0.147$$

for the X $^1A_g$ state and

$$C_9 = +0.147 \quad C_{29} + 0.989$$

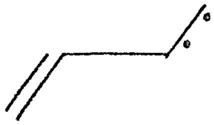
for the 2 $^1A_g$ state with an energy separation of 6.77 eV. Solving for the orbitals self-consistently, we find the 2 $^1A_g$ state to be 6.96 eV above the X $^1A_g$ state with spin-coupling coefficients as in Table I. From Figure 1 we see that the orbitals of the TT state have modified from those of the ground state reflecting the presence in the TT wavefunction of antibonding character in the terminal CC pi bonds and bonding character in the central pi bond.

The extensive CI calculations of Dunning et al.[5] show quite clearly the valence character of the 2 $^1A_g$ state expected from the TT description and indeed Dunning[12] suggested the TT interpretation of this state before the GVB calculations were carried out.[13] This state cannot be described as a linear combination of singly-excited configurations from the ground HF wavefunction.[5] The CI wavefunctions for the $2^1A_g$ include numerous important doubly-occupied configurations.[5]

## 3. The valence triplet states

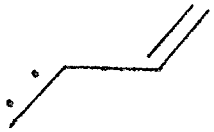
Based on the results of the previous section we would expect three valence triplet states. In zeroth order

$$\text{NT:} \quad \begin{array}{|cc|}\hline \chi_{1\ell} & \chi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\chi_{1r}} & \\ \multicolumn{1}{|c|}{\chi_{2r}} & \\ \cline{1-1} \end{array} \quad = \tag{30}$$



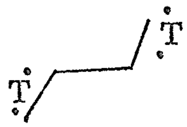
and

$$\text{TN:}\quad \begin{array}{|cc|}\hline \chi_{1r} & \chi_{2r} \\ \hline \multicolumn{1}{|c|}{\chi_{1\ell}} & \\ \multicolumn{1}{|c|}{\chi_{2\ell}} & \\ \cline{1-1}\end{array} \quad =$$



would be expected near 4.4 eV while the other state

$$\text{TT:}\ \sqrt{\frac{2}{3}}\ \begin{array}{|c|c|}\hline \chi_{1\ell} & \chi_{1r} \\ \cline{2-2} \chi_{2\ell} & \multicolumn{1}{c}{} \\ \cline{1-1} \chi_{2r} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \ + \sqrt{\frac{1}{3}}\ \begin{array}{|c|c|}\hline \chi_{1\ell} & \chi_{1r} \\ \cline{2-2} \chi_{2\ell} & \multicolumn{1}{c}{} \\ \cline{1-1} \chi_{2r} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \ =$$



would be at about 8.8 eV. Indeed from VB calculations we find the TT triplet state at 7.22 eV. Of course, NT and TN are degenerate and the optimum wavefunctions for these states would be the combinations,

$^3B_u$: NT - TN

$^3A_g$: NT + TN

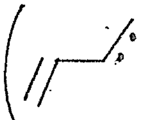
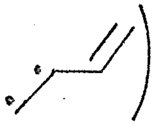
or in terms of tableaux

$$^3B_u \quad \begin{array}{|cc|}\hline \varphi_{2\ell} & \varphi_{1\ell} \\ \hline \multicolumn{1}{|c|}{\varphi_{2r}} & \\ \multicolumn{1}{|c|}{\varphi_{1r}} & \\ \cline{1-1}\end{array} \ - \ \begin{array}{|cc|}\hline \varphi_{2r} & \varphi_{1r} \\ \hline \multicolumn{1}{|c|}{\varphi_{2\ell}} & \\ \multicolumn{1}{|c|}{\varphi_{1\ell}} & \\ \cline{1-1}\end{array} \tag{31}$$

and

$$^3A_g \quad \begin{array}{|cc|}\hline \varphi_{2\ell} & \varphi_{1\ell} \\ \hline \multicolumn{1}{|c|}{\varphi_{2r}} & \\ \multicolumn{1}{|c|}{\varphi_{1r}} & \\ \cline{1-1}\end{array} \ + \ \begin{array}{|cc|}\hline \varphi_{2r} & \varphi_{1r} \\ \hline \multicolumn{1}{|c|}{\varphi_{2\ell}} & \\ \multicolumn{1}{|c|}{\varphi_{1\ell}} & \\ \cline{1-1}\end{array} \tag{32}$$

The optimum spin coupling of the $^3B_u$ state (see Table I) may be reexpressed as

$\Phi = C_A$ (  +  ) + $C_B$ 

where the coefficients are $C_A = 0.363$ and $C_B = -0.318$. Each term individually possesses the correct spatial symmetry.

The GVB orbitals of the $^3B_u$ state are localized on different centers much as in the VB description except that orbitals delocalize somewhat onto neighboring centers. The $^3B_u$ state orbitals are essentially identical to the ground state as can be seen in Figure 1. It should be noted that the orbitals are reordered in the $^3B_u$ state so that in the G1 tableaux (21) the orbitals localized near the center carbon atoms are coupled to a singlet. We find that the orbitals for the $^3A_g$ states are, however, symmetry orbitals and cannot be readily analyzed by a model of fused ethylenes. The average (calculated) vertical excitation energies of the $^3A_g$ and $^3B_u$ states is 4.33 eV while the N → T vertical excitation energy of ethylene is calculated to be 4.2 eV.[1] These results are consistent with the simple model assumed in (31) and (32). The stabilization of the $^3B_u$ states by 0.43 eV (9.9 kcal/mole) with respect to the energy of (30) may be considered as the resonance stabilization energy for this state.

There should be another valence excited state, the state formed by coupling two T state ethylenes to a triplet state giving a $^3B_u$ state. We anticipate that this state will have an excitation energy of about 8.4 eV.

## B. The Rydberg States

All of the states depicted in Figure 2 involve one orbital with diffuse Rydberg-like character. As the orbitals are quite delocalized, it is not easy or useful to delineate the origin of these states in terms of ethylene states. We have written a version of the GVB program which determines the optimum orbital for a spatially projected GVB wavefunction and are presently in the process of calculating the pi states of butadiene. This wavefunction should generate fully localized orbitals and thereby permit analysis of the Rydberg states in terms of coupled ethylene-like states.

Included in Table 1 are the energies from full CI calculations on the pi-orbitals of butadiene using the identical basis set. The GVB energies are in good agreement with the CI results, the largest error being 0.018 hartree or 0.50 eV.

Table II summarizes various theoretical and experimental results for the excitation energies of the pi-electron states of butadiene. For the Rydberg states, the discrepancies between the GVB and experimental results are larger than for the valence states. Allowing the sigma core to relax for Rydberg states would reduce the excitation energy by 0.5 to 1 eV bringing these states into reasonable agreement with experimental results.

To further test the designation of the states as Rydberg-like, we have calculated the quantum defect, $\zeta$, using the orbital energies for the diffuse orbital. GVB orbital energies must be used with care because removel of an orbital can lead to states without a well defined spin. For example for four electron triplets removing $\varphi_{1r}$ from (22) and (23) leads to

$$\begin{array}{|c|c|}\hline \varphi_{1\ell} & \varphi_{2r} \\ \hline \varphi_{2\ell} \\ \cline{1-1} \end{array} \tag{33}$$

$$\begin{array}{|c|}\hline \varphi_{1\ell} \\ \varphi_{2\ell} \\ \varphi_{2r} \\ \hline \end{array} \tag{34}$$

respectively a doublet and a quartet state. For four electron singlets no such problems arise and we find

$1^1Bu$: $\zeta = 0.50$ $(3p\pi)$

$3^1A_g$: $\zeta = 0.03$ $(3d\pi)$

For the $2^3Bu$, the small coefficient of the GF tableau (23) results in a negligible quartet state contamination and we find

$2^3Bu$: $\zeta = 0.41$ $(3p\pi)$

Typical experimental values for the quantum defect for butadiene are 0.50 for 3p like orbitals and 0.10 for d like orbitals.[15]

TABLE I. Energies for ground and excited states of <u>trans</u> butadiene

All quantities in atomic units (1 hartree = 27.2117 eV)

| State | GVB Wavefunction | | | | Full CI Energy[a] | $E_{CI} - E_{GVB}$ |
|---|---|---|---|---|---|---|
| | Spin Coupling Coefficient[b] | | | Total Energy | | |
| | $C_1$ | $C_2$ | $C_3$ | | | |
| Valence | | | | | | |
| $1^1A_g$ | 0.991 | -0.131 | --- | -154.93555 | -154.94015 | 0.00460 |
| $1^3B_u$ | -0.906 | 0.244 | -0.345 | -154.80627 | -154.81327 | 0.00700 |
| $1^3A_g$ | 0.710 | 0.411 | -0.571 | -154.74673 | -154.75489 | 0.00816 |
| $2^1A_g$ | 0.486 | 0.873 | --- | -154.67994 | -154.69123 | 0.01242 |
| Rydberg | | | | | | |
| $1^1B_u$ | 0.912 | -0.411 | --- | -154.66360 | -154.68093 | 0.01733 |
| $2^3B_u$ | 0.919 | -0.395 | -0.004 | -154.65961 | -154.67775 | 0.01814 |
| $3^1A_g$ | 0.913 | -0.409 | | -154.64026 | -154.65270 | 0.01244 |
| Cation $^2B_u$ | 0.944 | -0.329 | | -154.59576 | | |

[a] Reference 5b.

[b] Refer to equations (16) or (20) for the definitions.

TABLE II. Butadiene Excitation Energies (all values in eV)

| | VB | GVB | CI | | Experimental Mosher et al. (ref. 14) |
|---|---|---|---|---|---|
| | | | Dunning et al. (ref. 5) | Shih et al. (ref. 6) | |
| Valence States | | | | | |
| $1^1A_g$ | 0 | 0 | 0 | 0 | 0 |
| $1^3B_u$ | 3.13 | 3.52 | 3.45 | 3.24 | 3.22 |
| $1^3A_g$ | 4.66 | 5.14 | 5.04 | 4.95 | 4.92 |
| $2\ ^1A_g$ | 6.77 | 6.96 | 6.77 | 6.67 | |
| $3\ ^3B_u$ | 7.68 | | 8.08 | 7.92 | |
| Rydberg-like States | | | | | |
| $1^1B_u$ | | 7.40 | 7.05 | 6.60 | 5.96 |
| $2^3B_u$ | | 7.51 | 7.14 | 7.55 | 7.25 |
| $3^1A_g$ | | 8.04 | 7.82 | 7.79 | |
| Cation $^2B_u$ | | 9.25 | | | 9.08 |

[a] Ground state energy is -154.9181 h.

Table III. Resonance Energies

| | Orbitals Used | | |
|---|---|---|---|
| | Atomic | GVB($1^1A_g$) | GVB($2^1A_g$) |
| $\begin{array}{\|cc\|}\hline \phi_{1\ell} & \phi_{2\ell} \\ \hline \phi_{1r} & \phi_{2r} \\ \hline \end{array}$ | -154.85001 | -154.93444[a] | -154.90082 |
| $\begin{array}{\|c\|c\|}\hline \phi_{1\ell} & \phi_{1r} \\ \phi_{2\ell} & \phi_{2r} \\ \hline \end{array}$ | -154.61317 | -154.603975[a] | -154.71352 |
| $1^1A_g$ | -154.85362 | -154.93555 | -154.90488 |
| $2^1A_g$ | -154.60474 | -154.60042 | -154.67994 |
| Excitation Energy(eV) | 6.77 | 9.11 | 6.12 |
| Resonance Energy ($1^1A_g$) (kcal) | 2.27 | 0.7 | 2.55 |
| Destabilization Energy ($2^1A_g$) (kcal) | 5.29 | 2.23 | 21.08 |

[a] Using ethylene orbitals for the G1 and GF configurations leads to energies of -154.92097 and -154.60977, respectively.

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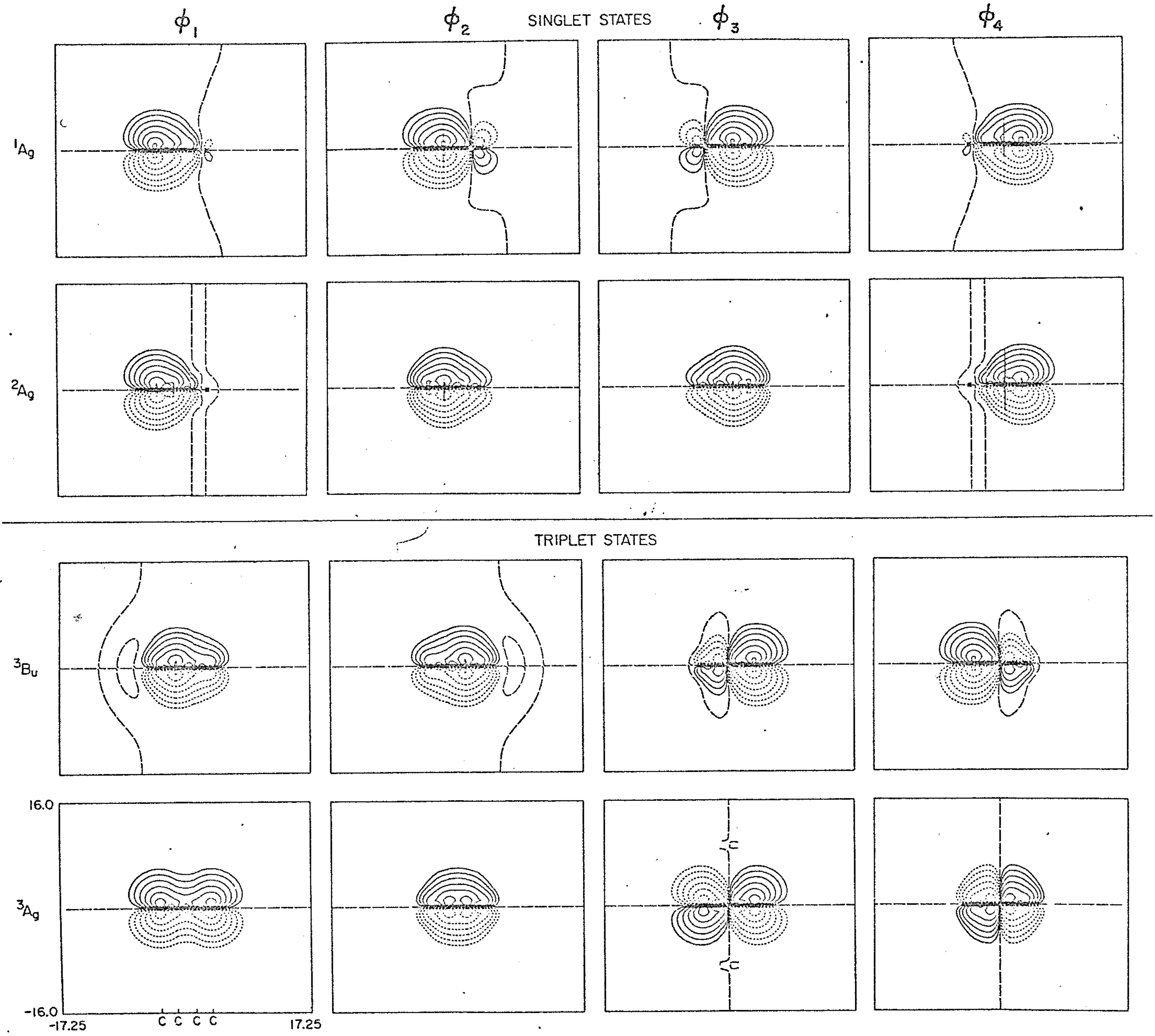
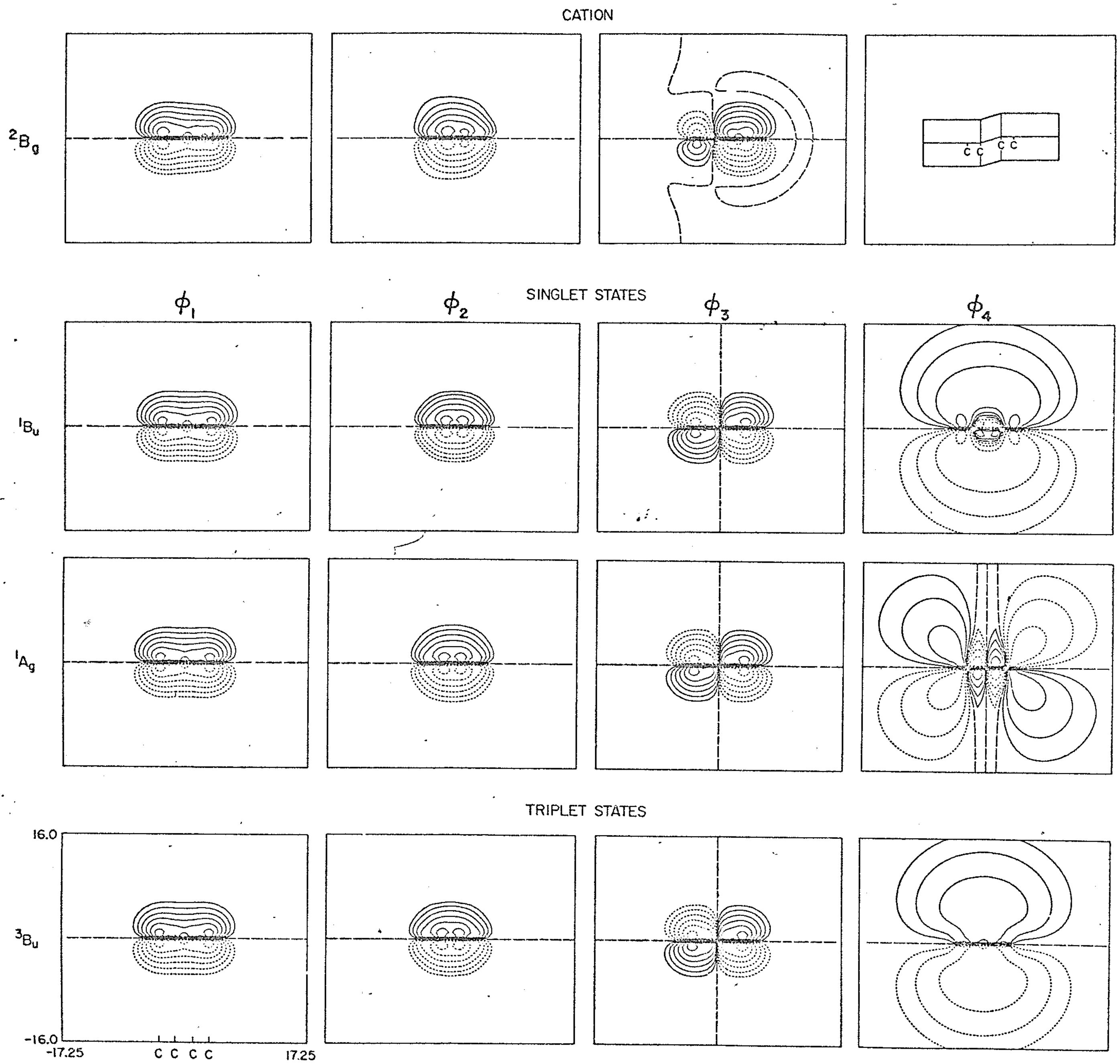
# LIST OF FIGURES

1. The Valence States of Butadiene. The ordering of orbitals in each state is such that the first two are uniquely coupled in the predominate spin coupling. 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.
2. The Rydberg-like States of Butadiene. The order of orbitals is as in Figure 1. The figure in the upper right corner indicates the planes in which the orbitals have been plotted. The amplitudes are identical to those in Figure 1.

VALENCE STATE OF BUTADIENE
GVB PI ORBITALS



RYDBERG LIKE STATES OF BUTADIENE
GVB PI ORBITALS



# APPENDIX V

## THE SPATIALLY PROJECTED GENERALIZED VALENCE BOND DESCRIPTION OF THE PI ELECTRONIC STATES OF S-TRANS-1,3-BUTADIENE

## I. Introduction

Previously[1] we reported the generalized valence bond (GVB) wavefunctions for the ground and excited pi-electron states of s-trans-1, 3-butadiene (hereafter referred to as butadiene). The GVB wavefunctions provided total energies and excitation energies in good agreement with full CI results. Although the individual orbitals which constitute the wavefunctions for the lowest two singlet ($^1A_g$ and $2^1A_g$) states and the lowest triplet ($^3B_u$) state were localized, the orbitals for all other states, both valence-like and Rydberg-like were delocalized. The GVB wavefunction includes self-consistent orbitals obtained at a particular spin coupling, and in some cases, this fact may impose restrictions upon the individual orbitals in the wavefunction. These restrictions were considered to be the reason that the optimum GVB description for the higher excited states involved delocalized orbitals, rather than being localized as, for example, were the GVB ground state orbitals.

The GVB wavefunction includes an operator which generates a spin eigenfunction and which explicitly builds in the Pauli principle.[2] To further generalize the GVB wavefunction, a spatial projection operator was incorporated into the GVB wavefunction(with the orbitals optimized after projection). The resulting wavefunction, called the spatially projected GVB wavefunction (denoted as GVB(SP)), imposes no restrictions upon the shapes of the individual orbitals. Previously, we have found that for the allyl radical pi electron system, states described by delocalized orbitals in the GVB wavefunction[3] were described by localized orbitals in the GVB(SP) wavefunction.[4] The GVB(SP) method was applied to the pi-electron system of butadiene with the expectation that all states would be described by localized orbitals, and indeed we found this to be the case.

In Section II we shall develop the GVB(SP) wavefunction by examining the valence bond (VB) wavefunction and generalizing this wavefunction. Section III presents the results of our calculations. Section IV includes our analysis of the results.

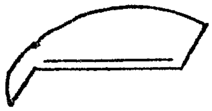
## II. Calculational Considerations

In this section we shall develop the GVB(SP) wavefunction by examining the valence bond (VB) wavefunction, the GVB wavefunction, and the GVB(SP) wavefunction to explicitly indicate the successive generalizations. Our discussion will be directed to the four pi electron system of butadiene. The other details of the calculations are also included in this section.

### A. The Valence Bond Wavefunction

The VB wavefunction may be represented as a linear combination of canonical structures each formed using an atomic orbital for each electron. Considering only the pi electrons, the singlet four electron system of butadiene has two inequivalent canonical structures usually represented as

(a)

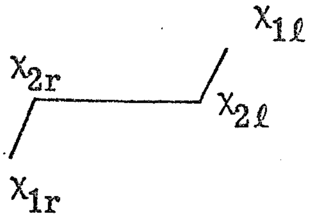


(b)

(1)

The two canonical structures are equivalent to the two independent ways of coupling four electrons to form a singlet state and are not orthogonal.

Let $\chi_{1r}$, $\chi_{2r}$, $\chi_{1\ell}$, $\chi_{2\ell}$ denote atomic orbitals located as indicated in (2).



(2)

The VB wavefunction for a four electron singlet may be represented as

$$\psi_S^{VB} = c_1\psi_1 + c_2\psi_2 \tag{3a}$$

$$\psi_S^{VB} = c_1 \boxed{\begin{array}{cc} \chi_{1r} & \chi_{2r} \\ \hline \chi_{1\ell} & \chi_{2\ell} \end{array}} + c_2 \boxed{\begin{array}{cc} \chi_{2r} & \chi_{2\ell} \\ \hline \chi_{1r} & \chi_{1\ell} \end{array}} \tag{3b}$$

where the orbitals within horizontal boxes are singlet coupled. The optimum VB description of the ground state is found by optimizing $c_1$ and $c_2$.

The wavefunctions corresponding to the individual terms in (3) are

$$\psi_1 = \mathcal{A}[\Phi_\sigma(\chi_{1r}\chi_{2r} + \chi_{2r}\chi_{1r})(\chi_{1\ell}\chi_{2\ell} + \chi_{2\ell}\chi_{1\ell})\alpha\beta\alpha\beta] \tag{4a}$$

$$= \mathcal{A}[\Phi_\sigma\chi_{1r}\chi_{2r}\chi_{2\ell}\chi_{1\ell}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)] \tag{4b}$$

$$\psi_2 = \mathcal{A}[\Phi_\sigma(\chi_{2r}\chi_{2\ell} + \chi_{2\ell}\chi_{2r})(\chi_{1r}\chi_{1\ell} + \chi_{1\ell}\chi_{1r})\alpha\beta\alpha\beta] \tag{5a}$$

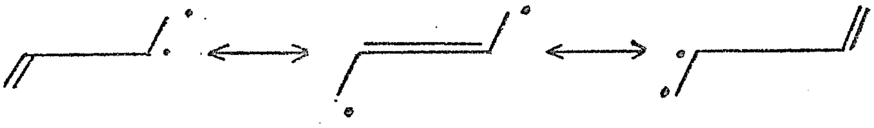
$$= \mathcal{A}[\Phi_\sigma\chi_{1r}\chi_{2r}\chi_{2\ell}\chi_{1\ell}(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \alpha\alpha\beta\beta - \beta\beta\alpha\alpha)] \tag{5b}$$

where $\mathcal{A}$ is the antisymmetrizer and $\Phi_\sigma$ is the product of all the doubly occupied sigma orbitals, including spin terms. Then (3) is equivalent to

$$\psi_s^{VB} = \mathcal{A}[\Phi_\sigma \chi_{1r}\chi_{2r}\chi_{2\ell}\chi_{1\ell}\,\Theta] \qquad (6)$$

$$\Theta_s = c_1[(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)] + c_2[\,\alpha\beta\alpha\beta+\beta\alpha\beta\alpha-\alpha\alpha\beta\beta-\beta\beta\alpha\alpha] \qquad (7)$$

The four atomic pi electrons of butadiene can also be coupled to form a triplet state. The three equivalent VB canonical structures for the four pi electron triplet are usually taken as



(8)

The three canonical structures are equivalent to the three ways of coupling four electrons to form a triplet state. (These three structures are not mutually orthogonal.)

Using the basis functions indicated in (2), the VB wavefunction for the four electron triplet state may be represented as

$$\Psi_t^{VB} = c_3\psi_3 + c_4\psi_4 + c_5\psi_5 \qquad (9a)$$

$$\psi_t^{VB} = c_3 \begin{array}{cc} \hline \multicolumn{1}{|c|}{\chi_{1r}} & \multicolumn{1}{c|}{\chi_{2r}} \\ \hline \multicolumn{1}{|c|}{\chi_{1\ell}} & \\ \multicolumn{1}{|c|}{\chi_{2\ell}} & \\ \cline{1-1} \end{array} + c_4 \begin{array}{cc} \hline \multicolumn{1}{|c|}{\chi_{2r}} & \multicolumn{1}{c|}{\chi_{2\ell}} \\ \hline \multicolumn{1}{|c|}{\chi_{1r}} & \\ \multicolumn{1}{|c|}{\chi_{1\ell}} & \\ \cline{1-1} \end{array} + c_5 \begin{array}{cc} \hline \multicolumn{1}{|c|}{\chi_{1\ell}} & \multicolumn{1}{c|}{\chi_{2\ell}} \\ \hline \multicolumn{1}{|c|}{\chi_{1r}} & \\ \multicolumn{1}{|c|}{\chi_{2r}} & \\ \cline{1-1} \end{array} \qquad (9b)$$

where the two orbitals within vertical boxes are triplet coupled. The optimum VB wavefunction is found by optimizing $c_3$, $c_4$, and $c_5$.

The wavefunctions corresponding to the individual terms of (9) are

$$\psi_3 = \mathcal{A}[\Phi_\sigma(\chi_{1r}\chi_{2r} + \chi_{2r}\chi_{1r})\chi_{1\ell}\chi_{2r}\,\alpha\beta\alpha\alpha] \qquad (10a)$$

$$= \mathcal{A}[\Phi_\sigma \chi_{1r}\chi_{2r}\chi_{2\ell}\chi_{1\ell}(\alpha\beta-\beta\alpha)\alpha\alpha] \qquad (10b)$$

$$\psi_4 = \mathcal{A}[\Phi_\sigma(\chi_{2r}\chi_{2\ell} + \chi_{2\ell}\chi_{2r})\chi_{1r}\chi_{1\ell}\,\alpha\beta\alpha\alpha] \qquad (11a)$$

$$= \mathcal{A}\,[\Phi_\sigma \chi_{1r}\chi_{2r}\chi_{2\ell}\chi_{1\ell}(\alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha)] \tag{11b}$$

$$\psi_5 = \mathcal{A}\,[\Phi_\sigma(\chi_{1\ell}\chi_{2\ell} + \chi_{2\ell}\chi_{1\ell})\chi_{1r}\chi_{2r}(\alpha\beta - \beta\alpha)\alpha\alpha] \tag{12a}$$

$$= \mathcal{A}\,[\Phi_\sigma \chi_{1r}\chi_{2r}\chi_{2\ell}\chi_{1\ell}(-\alpha\alpha\beta\alpha + \alpha\alpha\alpha\beta)] \tag{12b}$$

Then (9) may be written as

$$\Psi_t^{VB} = \mathcal{A}\,[\Phi_\sigma \chi_{1r}\chi_{2r}\chi_{2\ell}\chi_{1\ell}\Theta_t] \tag{13}$$

where

$$\Theta_t = c_3[(\alpha\beta - \beta\alpha)\alpha\alpha] + c_4[-\alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha] + c_5[-\alpha\alpha\beta\alpha + \alpha\alpha\alpha\beta] \tag{14}$$

## B. The Generalized Valence Bond Wavefunction

The form of the GVB wavefunction is the same as the VB wavefunction except that orbitals are solved for self-consistently (rather than being taken as atomic orbitals as in the VB wavefunction) and simultaneously the spin function $\Theta$ is optimized.

For a four pi electron system, the GVB wavefunction is

$$\psi^{GVB} = \mathcal{A}[\Phi_\sigma \varphi_a \varphi_b \varphi_c \varphi_d \Theta] \tag{15}$$

Although the GVB orbitals are allowed to have any form, frequently we find that each orbital is mainly concentrated near a particular carbon. In such cases, we shall indicate the location of each optimum GVB orbital with a label in accordance with (2).

There are two linear independent ways to couple four electrons into a singlet. There are many choices that may be used, for example (5b) and (6b), but we find it convenient to use the orthogonal spin functions

$$\theta_1 = (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \qquad (16)$$

$$\theta_2 = (2\,\alpha\alpha\beta\beta + 2\,\beta\beta\alpha\alpha - \alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha) \qquad (17)$$

referred to as the G1 and G2 (or GF) spinfunctions. The spinfunction in (15) for singlet states is

$$\Theta = c_1\theta_1 + c_2\theta_2$$

It is convenient to use the diagram

$$\begin{array}{|cc|}\hline \varphi_a & \varphi_b \\ \hline \varphi_c & \varphi_d \\ \hline \end{array} \qquad (18)$$

to represent $\mathcal{A}[\varphi_a\varphi_b\varphi_c\varphi_d\,\theta_1]$ and the diagram

$$\begin{array}{|c|c|}\hline \varphi_a & \varphi_c \\ \hline \varphi_b & \varphi_d \\ \hline \end{array} \qquad (19)$$

to represent $\mathcal{A}[\varphi_a\varphi_b\varphi_c\varphi_d\,\theta_2]$. (18) denotes that the orbitals are coupled into two singlet pairs, which are then coupled to a singlet. This is identical to the VB perfect pairing form (4). (19) denotes that two triplet coupled pairs are coupled to a singlet.

For a four electron triplet, there are three linear independent ways to couple the electron. We use orthogonal spinfunctions

$$\theta_3 = \sqrt{\tfrac{1}{2}}\,(\alpha\beta - \beta\alpha)\alpha\alpha \qquad (20)$$

$$\theta_4 = \frac{\sqrt{6}}{6}(2\alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha) \qquad (21)$$

$$\theta_5 = \frac{\sqrt{3}}{6}(3\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha) \qquad (22)$$

referred to as the G1, G2, and G3 (or GF) spinfunctions. The spinfunction for (15) for triplet states is

$$\Theta = c_3\,\theta_3 + c_4\,\theta_4 + c_5\,\theta_5 \tag{23}$$

Again the spinfunctions be represented by diagrams, which are corresponding to (20), (21), and (22)

$$\begin{array}{|c|c|}\hline \varphi_a & \varphi_b \\ \hline \varphi_c & \\ \varphi_d & \\ \cline{1-1}\end{array} \tag{24}$$

$$\begin{array}{|c|c|}\hline \varphi_a & \varphi_c \\ \cline{2-2} \varphi_b & \\ \cline{1-1} \varphi_d & \\ \cline{1-1}\end{array} \tag{25}$$

$$\begin{array}{|c|c|}\hline \varphi_a & \varphi_d \\ \cline{2-2} \varphi_b & \\ \varphi_c & \\ \cline{1-1}\end{array} \tag{26}$$

## C. The Spatially Projected Generalized Valence Bond Wavefunction

Let P denote a projection operator which operates only on spatial coordinates and which generates a state of a particular symmetry. The individual orbitals comprising this state need not possess any particular symmetry and in general will possess components of all possible symmetries. The GVB(SP) wavefunction is formed by operating with P on the GVB wavefunction

$$\Psi^{GVB(SP)} = P\Psi^{GVB} \tag{27}$$

To determine the effect of including a spatial projection operator in the wavefunction we will examine the four pi electron system of butadiene and a spatial symmetry group consisting of two elements, the identity and the reflection in the plane which is perpendicular to the molecule and which bisects the molecule. We first consider the effects of spatial projection on the VB wavefunction (3). Since the individual electron orbitals in (3) are identical atomic orbitals, the effect of the spatial reflection operator on the individual orbitals is

$$\begin{aligned} \sigma\chi_{1r} &= \chi_{1\ell} \\ \sigma\chi_{2r} &= \chi_{2\ell} \\ \sigma\chi_{2\ell} &= \chi_{2r} \\ \sigma\chi_{1\ell} &= \chi_{1r} \end{aligned} \tag{28}$$

and, of course, the identity operator leaves all orbitals unchanged.

The states which can be formed with these orbitals fall into two groups, those which are symmetric and those which are antisymmetric with respect to $\sigma$ (corresponding to $A_g$ and $B_u$, respectively of the molecular symmetry group of butadiene).

Examining the behavior of the two components of the singlet wavefunction, (4) and (5), under $\sigma$, we find[6]

$$\begin{aligned} \sigma \begin{array}{|cc|}\hline \chi_{1r} & \chi_{2r} \\ \hline \chi_{1\ell} & \chi_{2\ell} \\ \hline \end{array} &= \begin{array}{|cc|}\hline \chi_{1\ell} & \chi_{2\ell} \\ \hline \chi_{1r} & \chi_{2r} \\ \hline \end{array} \equiv \begin{array}{|cc|}\hline \chi_{1r} & \chi_{2r} \\ \hline \chi_{1\ell} & \chi_{2\ell} \\ \hline \end{array} \\ \sigma \begin{array}{|cc|}\hline \chi_{2r} & \chi_{2\ell} \\ \hline \chi_{1r} & \chi_{1\ell} \\ \hline \end{array} &= \begin{array}{|cc|}\hline \chi_{2\ell} & \chi_{2r} \\ \hline \chi_{1\ell} & \chi_{1r} \\ \hline \end{array} \equiv \begin{array}{|cc|}\hline \chi_{2r} & \chi_{2\ell} \\ \hline \chi_{1r} & \chi_{1\ell} \\ \hline \end{array} \end{aligned} \tag{29}$$

The spatial projection operator does not introduce any new features into the VB singlet wavefunction.

Similarly the three components of the triplet wavefunction (10), (11), and (12), behave under $\sigma$ as[7]

$$\sigma \begin{array}{|cc|}\hline \chi_{1r} & \chi_{2r} \\ \hline \multicolumn{1}{|c|}{\chi_{1\ell}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\chi_{2\ell}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = \begin{array}{|cc|}\hline \chi_{1\ell} & \chi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\chi_{1r}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\chi_{2r}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

$$\sigma \begin{array}{|cc|}\hline \chi_{2r} & \chi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\chi_{1r}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\chi_{1\ell}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = \begin{array}{|cc|}\hline \chi_{2\ell} & \chi_{2r} \\ \hline \multicolumn{1}{|c|}{\chi_{1\ell}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\chi_{1r}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = - \begin{array}{|cc|}\hline \chi_{2r} & \chi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\chi_{1r}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\chi_{1\ell}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \equiv \psi_4' \qquad (30)$$

$$\sigma \begin{array}{|cc|}\hline \chi_{1\ell} & \chi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\chi_{1r}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\chi_{2r}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = \begin{array}{|cc|}\hline \chi_{1r} & \chi_{2r} \\ \hline \multicolumn{1}{|c|}{\chi_{1\ell}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\chi_{2\ell}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

linear combination of $\psi_3$, $\psi_4$, and $\psi_5$ can be symmetric or antisymmetric under $\sigma$. Defining two spatial projection operators

$$P_a = e - \sigma \qquad (31)$$

$$P_s = e + \sigma \qquad (32)$$

using (30), we see that

$$P_s(\psi_3) = \psi_3 + \psi_5 \qquad (33)$$

$$P_a(\psi_3 + \psi_4) = \psi_3 - \psi_5 + \psi_4 - \psi_4' \qquad (34)$$

and we have generated wavefunctions each with a specific and different spatial symmetry.

Now we apply the same analysis to the GVB wavefunction (15). For the singlet case, the GVB(SP) wavefunction may be represented as

$$\Psi = P\left[ c_1 \begin{array}{|c|c|}\hline \phi_a & \phi_b \\ \hline \phi_c & \phi_d \\ \hline \end{array} + c_2 \begin{array}{|c|c|}\hline \phi_a & \phi_c \\ \phi_b & \phi_d \\ \hline \end{array} \right] \tag{35}$$

In general, $\phi_a$ and $\phi_d$ or $\phi_b$ and $\phi_c$ are not related by the symmetry operator. The projection operators will form linear combinations of orbitals and their projected form (not necessarily with the same coefficients) to form wavefunctions with a specific total symmetry. However, if the individual orbitals are localized and $\phi_a$ and $\phi_d$ and $\phi_b$ and $\phi_c$ have the same form, the GVB wavefunction will behave under spatial projection in the same manner as the VB wavefunction. We find that this occurs for the lowest singlet $({}^1A_g)$ state and we expect spatial projection to have very little effect.

For the triplet wavefunction the GVB(SP) wavefunction may be written

$$\Psi = P\left[ c_3 \begin{array}{|c|c|}\hline \varphi_a & \varphi_b \\ \hline \phi_c & \multicolumn{1}{c}{} \\ \phi_d & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} + c_4 \begin{array}{|c|c|}\hline \phi_a & \phi_c \\ \cline{2-2} \phi_b & \multicolumn{1}{c}{} \\ \cline{1-1} \phi_d & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} + c_5 \begin{array}{|c|c|}\hline \phi_a & \phi_d \\ \cline{2-2} \phi_b & \multicolumn{1}{c}{} \\ \phi_c & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} \right] \tag{36}$$

For the triplet wavefunction, if the individual orbitals are localized each about a different carbon atom, the spatial projection operator introduces new features in the wavefunction so that the GVB(SP) description of the triplet states will be different than the GVB description. For example, the GVB description of the $^3B_u$ state is

$$c_1\left(\begin{array}{|cc|}\hline \varphi_{1r} & \varphi_{2r} \\ \hline \multicolumn{1}{|c|}{\varphi_{2\ell}} & \\ \multicolumn{1}{|c|}{\varphi_{1\ell}} & \\ \cline{1-1} \end{array} + \begin{array}{|cc|}\hline \varphi_{1\ell} & \varphi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\varphi_{2r}} & \\ \multicolumn{1}{|c|}{\varphi_{1r}} & \\ \cline{1-1} \end{array}\right) - c_2 \begin{array}{|cc|}\hline \varphi_{2r} & \varphi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\varphi_{1\ell}} & \\ \multicolumn{1}{|c|}{\varphi_{1r}} & \\ \cline{1-1} \end{array}$$

where $c_1 = 0.363$ and $c_2 = -0.318$. All three tableaux are required in order for the state to have the correct spatial symmetry. The GVB(SP) description is predominately

$$P_{B_u}\left(\begin{array}{|cc|}\hline \varphi_{1\ell} & \varphi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\varphi_{2r}} & \\ \multicolumn{1}{|c|}{\varphi_{1r}} & \\ \cline{1-1} \end{array}\right)$$

where the spatial projection operator ensures that the state has the correct spatial symmetry.

## D. The Core Hamiltonian

As discussed elsewhere,[5] the problem of finding a wavefunction of the form

$$\mathcal{A}[\Phi_{\text{core}}\Phi_{\text{val}}] \tag{37}$$

may be reduced to finding the wavefunction

$$\mathcal{A}[\Phi_{\text{val}}] \tag{38}$$

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 $\Phi_{core}$. The Hamiltonian for the valence orbitals will have the form

$$\mathcal{H} = \sum_{i=1}^{n_\pi} h^{core}(i) + \sum_{j=1}^{n_\sigma} \frac{1}{r_{ij}} \tag{39}$$

where

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

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

$$h(i) = \tfrac{1}{2}\nabla_i^2 - \sum_a Z_a/r_{ia} \tag{40}$$

is the usual one-electron Hamiltonian, and $n_\pi$ is the number of electrons in $\pi$ orbitals. For butadiene, the sigma electron core was formed from an ab initio Hartree-Fock calculation on the ground state.

## E. 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.[8] This was contracted to a double-zeta basis (4s, 2p) on each carbon and (2s) on each hydrogen, as suggested by Dunning.[9] To permit the description of Rydberg-like excited states, it is necessary to include more diffuse functions and consequently the above basis was supplemented by two additional diffuse pi-Gaussian functions on each carbon with orbital exponents of 0.03477 and 0.01075. All calculations used the following geometry: $R_{C_1C_2} = R_{C_3C_4} = 1.337°A$; $R_{C_2C_3} = 1.438°A$; $R_{CH} = 1.08°A$ and all bond angles, 120°.

## III. Results

The two singlet valence states, the three triplet valence states, the cation, and several Rydberg-like excited states were examined. Table I contains a summary of the total energies, excitation energies, and spin coupling for these states. Figure 1 depicts the orbitals for the valence states and Figure 2 the orbitals for the cation and the Rydberg-like states.

From Figures 1 and 2, we see that all of the orbitals are basically localized about a specific carbon atom. Tight orbitals are basically 2pπ atomic-like, but somewhat delocalized onto neighboring carbon atoms in a bonding manner. All states depicted in Figure 1 consist of entirely of tight 2p-like orbitals and thus are described as valence states. Each state depicted in Figure 2 has one diffuse orbital and is described as a Rydberg-like state.

## IV. Discussion

### A. The Fused Ethylene Model of Butadiene

Dunning[10] proposed a model for the pi-electron states of butadiene based upon constructing the states of butadiene by fusing two pi-electron states of ethylene.[11] Previously[1] we had associated the ground state ($^1A_g$) of butadiene as two ethylene ground (N) state, the lowest triplet ($^3B_u$) state as a fused ethylene N state with an ethylene lowest triplet (T) state, and the first excited singlet ($2^1A_g$) state as two fused ethylene T states. However, since the GVB orbitals for all other states were delocalized, it was not possible to identify other states with combinations of ethylene states. Since the GVB(SP) orbitals for the states of butadiene are localized, we should be able to identify the states of butadiene with combinations of ethylene states.

1. Valence-like states

There are only two valence states of ethylene[5] so all of the valence states of butadiene should be describable as combinations of these two states. The ground ($^1A_g$) state should be two fused ethylene N states. The spin coupling would be predominately G1 (18). Our results are fully consistant with this model, and the GVB description.[1]

The only other possible singlet state is obtained by coupling two ethylene T states to a singlet. In this case, the spin coupling is predominately GF (19). The excitation energy of the T state of ethylene is 4.20 eV.[5] The first excited ($2^1A_g$) state has predominately GF spin coupling and an excitation energy of 6.81 eV. Thus, the $2^1A_g$ state can be considered as two coupled ethylene T states, with the energy lowering resulting from delocalization of the orbitals.

The lowest triplet states should be the symmetric and antisymmetric combinations of an ethylene N state and ethylene T state. We expect the antisymmetric coupling to be lower in energy by analogy with allyl radical.[4] Applying the antisymmetric spatial projection operator to the G1 wavefunction (24) where we use localized orbitals since all the GVB(SP) orbitals for the $^3B_u$ state are localized, we obtain

$$P_{B_u}\left(\begin{array}{|cc|}\hline \varphi_{1r} & \varphi_{2r} \\ \hline \multicolumn{1}{|c|}{\varphi_{1\ell}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\varphi_{2\ell}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}\right) = \begin{array}{|cc|}\hline \varphi_{1r} & \varphi_{2r} \\ \hline \multicolumn{1}{|c|}{\varphi_{1\ell}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\varphi_{2\ell}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} - \begin{array}{|cc|}\hline \varphi_{1\ell} & \varphi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\varphi_{1r}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\varphi_{2r}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \tag{41}$$

This is identical to the anti-symmetric combination of an ethylene N state and an ethylene T state. Applying the symmetric spatial projection operator we obtain

$$P_{A_g}\left(\begin{array}{|cc|}\hline \varphi_{1r} & \varphi_{2r} \\ \hline \multicolumn{1}{|c|}{\varphi_{1\ell}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\varphi_{2\ell}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}\right) = \begin{array}{|cc|}\hline \varphi_{1r} & \varphi_{2r} \\ \hline \multicolumn{1}{|c|}{\varphi_{1\ell}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\varphi_{2\ell}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \begin{array}{|cc|}\hline \varphi_{1\ell} & \varphi_{2\ell} \\ \hline \multicolumn{1}{|c|}{\varphi_{1r}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{\varphi_{2r}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \tag{42}$$

which is the symmetric combination of an ethylene N state and an ethylene T state. From Table I the spin coupling for the $^3B_u$ and $^3A_g$ states is predominantly G1 as expected and the average excitation energy of these states is 4.215 eV in good agreement with excitation energy 4.20 eV of the ethylene T state.

The remaining possibility for forming a valence state of butadiene is coupling two ethylene triplet states to a triplet. The $3^3B_u$ state is identified as two triplet ethylenes coupled to a triplet with an excitation energy of 8.29 eV about twice that of the ethylene T state.

### 2. Rydberg-like states

The $1^1B_u$ state may be considered as the antisymmetric combination of an ethylene N state and a $2^1A_g$ (R) state ethylene. In accordance with this model the spin coupling should be predominately G1 (18) as was found and the diffuse orbital should be 3p$\pi$ like as it is (see Figure 2). The excitation of the R state is 8.55 eV[12] while the $1^1Bu$ state excitation found is 7.02 eV, the decrease resulting from delocalization of the tight orbitals.

The $2^1B_u$ state may be considered as the symmetric combination of an ethylene N state and an ethylene V state. The spin coupling is mainly G1 (18) as would be expected. The V state excitation energy is 8.91 eV[12] as compared to 8.19 eV for $2^1B_u$ state. From Figure 2 we see that the diffuse orbital has acquired some 4p$\pi$ character in addition to the 3d$\pi$ character associated with the ethylene V state diffuse orbital.[5] We find the quantum defect for this orbital (see Section D below) is between the values typically associated with P and D orbitals.

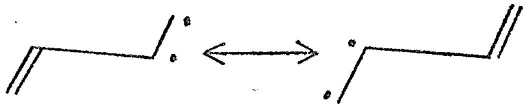
The $2^3B_u$ state may be considered as the antisymmetric combination of an N state ethylene and a $1^3A_g$ state ethylene. The spin coupling is G1 (18) and the diffuse orbital 3p$\pi$ like as expected. The excitation energy of the $1^3A_g$ state of ethylene is 8.38 eV[12] as compared to 7.11 for the $2^3B_u$ state of butadiene.

The $4^3B_u$ state may be considered as the symmetric combination of a state ethylene and a $2^3B_{1u}$ state ethylene. As can be seen from Figure 2, the diffuse orbital is for a 3d$\pi$ like. The excitation energy of the $2^3B_{1u}$ state of ethylene is 9.33 eV[12] as compared to 8.32 eV for the $4^3B_u$ state.

## B. Resonance

Since the two singlet VB canonical structures are not identical, the long bond form (16) being much less favored, resonance effects should be small for the singlet states of butadiene. The GVB and GVB(SP) resonance energies are 0.7[1] and 0.8 kcal respectively, in fair agreement with the thermochemical estimate of 3.6 kcal.[13]

From our discussion of the GVB(SP) wavefunction for triplet states, we expect there to be a significant mixing of states and thus a significant resonance energy. The lowest $1^3B_u$ state is described by (41) which is equivalent to



(43)

By comparing the energy of this state with the GVB wavefunction (using optimized orbitals in each case) for

$$\begin{array}{|c|c|}\hline \varphi_{1r} & \varphi_{2r} \\ \hline \varphi_{1\ell} & \multicolumn{1}{c}{} \\ \cline{1-1} \varphi_{2\ell} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \tag{44}$$

we obtain an estimate of the resonance energy of 11.9 kcal. The antiresonant state is the $1^3A_g$ state with a wavefunction given by (42). We obtain an estimate of antiresonance energy of 23.9 kcal. The $3^3B_u$ state is also a valence-like state with a wavefunction

$$P_A\left(\begin{array}{|c|c|}\hline \varphi_{1r} & \varphi_{2\ell} \\ \hline \varphi_{2r} & \multicolumn{1}{c}{} \\ \cline{1-1} \varphi_{1\ell} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}\right) = \begin{array}{|c|c|}\hline \varphi_{1r} & \varphi_{2\ell} \\ \hline \varphi_{2r} & \multicolumn{1}{c}{} \\ \cline{1-1} \varphi_{1\ell} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} - \begin{array}{|c|c|}\hline \varphi_{1\ell} & \varphi_{2r} \\ \hline \varphi_{2\ell} & \multicolumn{1}{c}{} \\ \cline{1-1} \varphi_{1r} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \tag{45}$$

## C. Comparison With Other Calculations and Experiments

In Table I, we have included for comparative purposes the GVB, and full (or complete within the basis set) CI total energies, all calculations having been performed with the same basis set. In general, there is good agreement among the three results. The GVB(SP) total energies are lower than GVB total energies and less than 0.003 h greater than the CI energies. The ground state GVB wavefunction (with localized orbitals) possessed the correct spatial symmetry so that the spatial projection operator has little effect for this state.

Table II compares the excitation energies obtained from the GVB(SP) calculations with other theoretical and experimental results. The GVB(SP), CI, and experimental values are in good agreement. The frozen sigma core approximation is suitable for describing valence-like excited states, but is not as appropriate for Rydberg-like states. For example, in ethylene SCF relaxation of the sigma core lowered the calculated excitation energies of Rydberg states by about 0.6 eV.[14] Thus the calculated vertical excitation energies for Rydberg-like states of butadiene, (e.g. $1^1Bu$), should be too high by 0.5 - 1.0 eV because the sigma core is not allowed to relax.

## D. Rydberg-Like States

From Figure 2, we see that of the states reported herein, four have one diffuse orbital and may be described as Rydberg-like states. The GVB(SP) orbitals for these states are localized, with even the diffuse orbital associated primarily with one center. To test the designation of these states as Rydberg-like, we have calculated the quantum defects, $\zeta$, for these states using

$$E_n = A - {}^{R}/(\eta - \zeta)^2$$

where $E_n$ is the energy of the state and A the GVB(SP) energy of the cation. We obtain

$1^1Bu$: $\zeta = 0.47$ (3p$\pi$)

$2^1Bu$: $\zeta = 0.23$ (4d$\pi$-4p$\pi$)

$2^3Bu$: $\zeta = +0.413$ (3p$\pi$)

$4^3Bu$: $\zeta = -0.06$ (4d$\pi$)

Since our basis set contains only p$\pi$ functions, a 4d$\pi$ orbital may not be well described, accounting for the negative quantum defect for the $4^3Bu$ state. Experimental values for quantum defects are 0.50 for p orbitals and 0.10 for d orbitals.[15]

## Table I. Butadiene Total Energies

| State | GVB(SP) Wavefunction Spin Coupling Coefficient[c] $c_1$ | $c_2$ | $c_3$ | Total Energy | GVB[a] Energy | Full[b] CI Energy |
|---|---|---|---|---|---|---|
| $1^1A_g$ | 0.991 | -0.132 | - | -154.93575 | -154.93555 | -154.94015 |
| $1^3B_u$ | 0.9998 | 0.0002 | 0.022 | -154.80946 | -154.80627 | -154.81327 |
| $1^3A_g$ | 0.9998 | -0.018 | -0.006 | -154.75223 | -154.74673 | -154.75489 |
| $2^1A_g$ | 0.123 | 0.992 | - | -154.68545 | -154.67881 | -154.69123 |
| $1^1B_u$ | 0.990 | -0.138 | - | -154.67778 | -154.66360 | -154.68093 |
| $2^3B_u$ | 0.999 | -0.050 | -0.010 | -154.67435 | -154.65961 | -154.67775 |
| $2^1B_u$ | 0.996 | -0.093 | - | -154.63486 | - | -154.64381 |
| $3^3B_u$ | 0.465 | 0.350 | 0.809 | -154.63113 | - | -154.643103 |
| $4^3B_u$ | 0.998 | -0.067 | 0.003 | -154.62991 | - | - |
| Cation ($^2B_u$) | 0.981 | -0.192 | - | -154.59964 | -154.59576 | - |

[a] Reference 1.

[b] Reference 14

[c] Refer to equations (35) and (36).

Table II. Butadiene Excitation Energies

| State | VB (Ref. 1) | GVB (Ref. 1) | GVB(SP) | CI | | Experimental |
|---|---|---|---|---|---|---|
| | | | | Dunning et al. (Ref. 14) | Shih et al.[a] (Ref. 15) | Mosher et al. (Ref. 16) |
| Valence States | | | | | | |
| $1^1A_g$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $1^3B_u$ | 3.13 | 3.52 | 3.44 | 3.45 | 3.24 | 3.22 |
| $1^3A_g$ | 4.66 | 5.14 | 4.99 | 5.04 | 4.95 | 4.92 |
| $2^1A_g$ | 6.77 | 6.99 | 6.81 | 6.77 | 6.67 | |
| $3^3B_u$ | 7.68 | - | 8.29 | 8.08 | 7.92 | |
| Rydberg-like States | | | | | | |
| $1^1B_u$ | | 7.40 | 7.02 | 7.05 | 6.60 | 5.96 |
| $2^3B_u$ | | 7.51 | 7.11 | | 7.04 | 7.25 |
| $2^1B_u$ | | - | 8.19 | 8.06 | 7.98 | |
| $4^3B_u$ | | - | 8.32 | | | |
| Cation | | 9.25 | 9.15 | | | 9.08 |

[a] Ground state energy is -154.9181 h.

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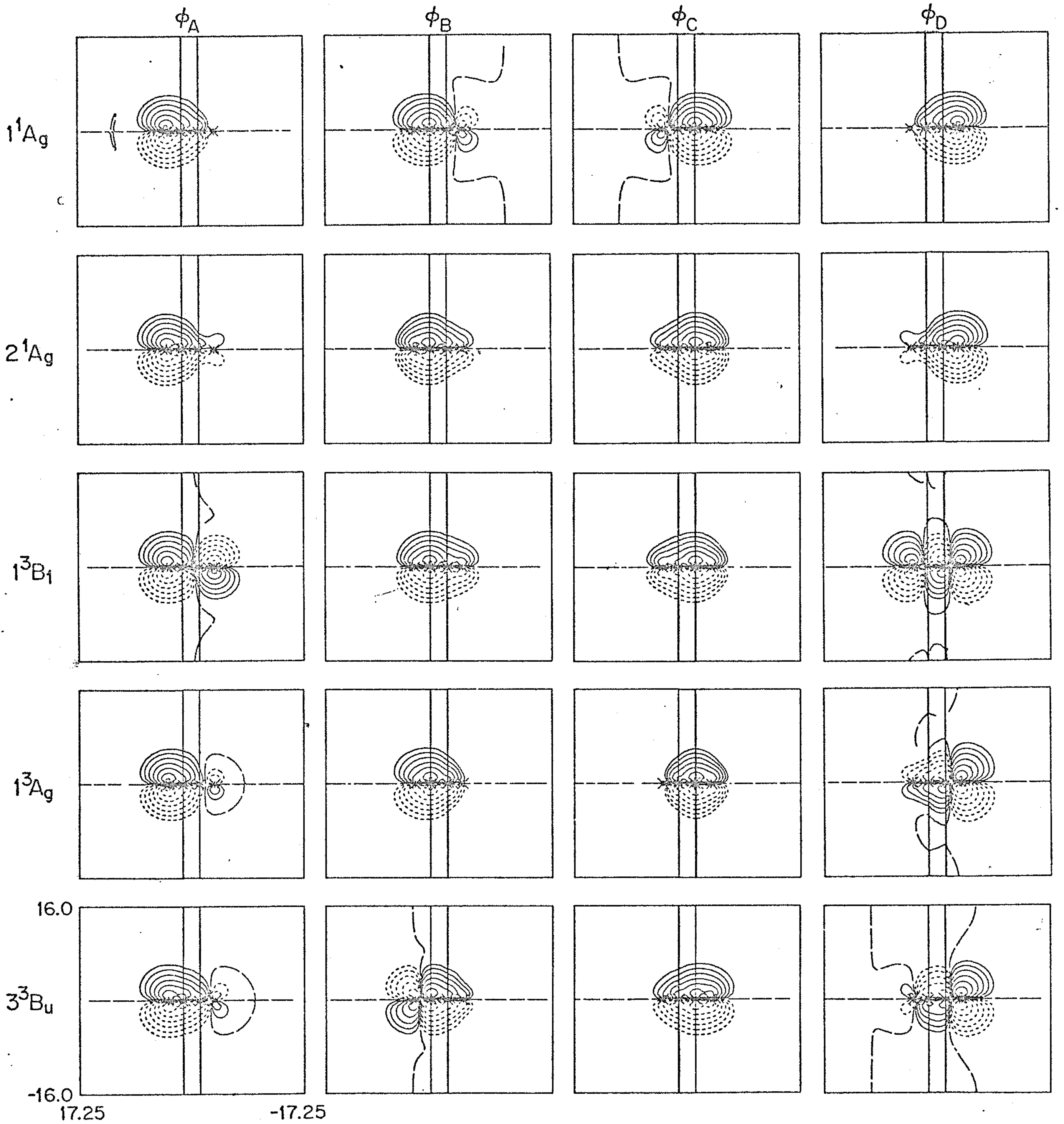
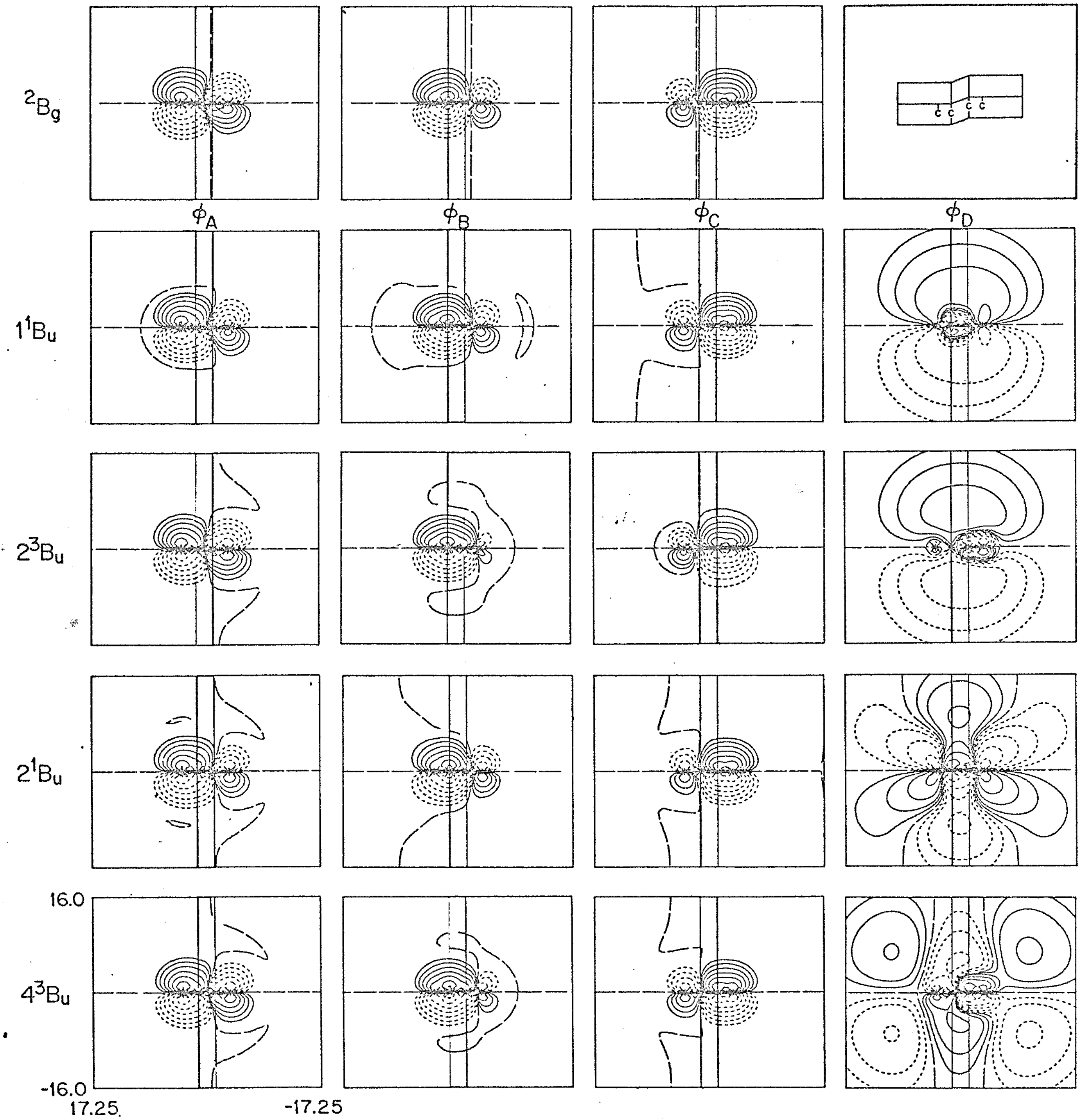
# LIST OF FIGURES

1. The Valence States of Butadiene. The ordering of orbitals in each state is such that the first two are uniquely coupled in the predominate spin coupling. 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.
2. The Rydberg-like States of Butadiene. The order of orbitals is as in Figure 1. The figure in the upper right corner indicates the planes in which the orbitals have been plotted. The amplitudes are identical to those in Figure 1.

VALENCE STATES OF BUTADIENE
GVB(SP) PI ORBITALS



# RYDBERG - LIKE STATES OF BUTADIENE
# GVB(SP) PI ORBITALS



# APPENDIX VI

# THE GENERALIZED VALENCE BOND DESCRIPTION OF THE ELECTRONIC STATES OF BENZENE

## I. Introduction

Previously, we reported the generalized valence bond (GVB) description of the pi-electron systems of ethylene,[1] allyl cation,[1] allyl radical,[2] and s-trans-1, 3-butadiene.[3] We found that the GVB method generated energies for ground and excited states in good agreement with full configuration interaction (CI) calculations and provided a chemically useful description of the pi-electron systems leading for example to a description of resonance in close correspondence to chemical intuition. In this paper we consider the classic case of benzene.

According to VB theory,[4] benzene has five valence-like singlet states usually represented as a linear combination of the two Kekule and the three Dewar structures. We find the GVB description of the valence singlet states of benzene to be qualitatively similar to the VB description and total energies and excitation in good agreement with full CI results. VB theory predicts that there are nine valence-like triplet states, and again the GVB results are consistent with this model.

In the VB description, the valence states are described in terms of a linear combination of canonical structures, wherein each structure involves electrons in orbitals on the various centers. The GVB description is quite similar. In place of the five canonical valence bond structures for the six electron singlet states, we use a set of five orthogonal spin couplings of six electrons. In lieu of the atomic orbitals of VB theory, the GVB method involves optimization of each orbital. This allows for important delocalization effects. However, the optimum orbitals are found to each be mainly concentrated on one center, much as for the atomic orbitals. The self-consistent orbitals found for the ground state are quite similar to the self-consistent orbitals for the valence excited states. Thus the resulting description of the electronic structure is quite close to that of the VB wavefunction.

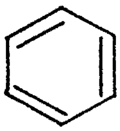
In Section II, we develop the GVB wavefunction for the benzene pi electron system. Section III presents our results. In Section IV, we present our interpretation of the results and compare the results with other results and experimental data.

## II. The Wavefunctions

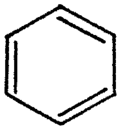
As a basis for the discussion of the GVB wavefunction, we will first review the VB description of benzene.

### A. The Valence Bond Wavefunction

The VB wavefunction for the pi electrons of singlet benzene is well known.[4] The wavefunction consists of a linear combination of the five canonical structures, specifically the two Kekule structures



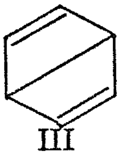
I

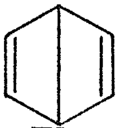


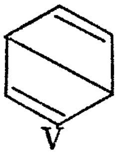
II

(1a)

and the three Dewar structures


III


IV


V

(1b)

For example the $\pi$ system of I is described as

$$\mathcal{A}[\chi_1\chi_2\chi_3\chi_4\chi_5\chi_6(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)] \qquad (2)$$

where the $\chi_r$ are p atomic orbitals on the various carbons and $\chi_1$ and $\chi_2$ are paired into a singlet pair, $\chi_3$ and $\chi_4$ into a singlet pair and $\chi_5$ and $\chi_6$ into a singlet pair. Each structure in (1a) and (1b) has a form like that in (2) with the same product of orbitals; the only differences are in the spin functions.

The optimum VB wavefunction is that combination of the VB canonical structures (1a) and (1b) giving the lowest energy. There are five VB canonical structures, and hence five valence-like states for singlet benzene. According to the theory of the symmetric group,[5] there are five linearly independent ways to combine six spin $\frac{1}{2}$ particles to achieve a spin zero state, and the VB canonical structures are one particular choice for the five basis states. The VB canonical structures are not orthogonal and as a result are not the most convenient choice for calculational purposes.

Let $\chi_1$, $\chi_2$, $\chi_3$, $\chi_4$, $\chi_5$, $\chi_6$ denote atomic pi orbitals centered on the six carbon atoms. The VB canonical structures

(1a) - (1b) may be represented as

$$\Phi_{I} \equiv \begin{array}{|cc|}\hline \chi_1 & \chi_6 \\ \hline \chi_2 & \chi_3 \\ \hline \chi_4 & \chi_5 \\ \hline \end{array} \qquad (3)$$

$$\Phi_{II} \equiv \begin{array}{|cc|}\hline \chi_1 & \chi_2 \\ \hline \chi_3 & \chi_4 \\ \hline \chi_5 & \chi_6 \\ \hline \end{array} \qquad (4)$$

$$\Phi_{III} \equiv \begin{array}{|cc|}\hline \chi_1 & \chi_6 \\ \hline \chi_2 & \chi_5 \\ \hline \chi_3 & \chi_4 \\ \hline \end{array} \qquad (5)$$

$$\Phi_{IV} \equiv \begin{array}{|cc|}\hline \chi_1 & \chi_4 \\ \hline \chi_2 & \chi_3 \\ \hline \chi_5 & \chi_6 \\ \hline \end{array} \qquad (6)$$

$$\Phi_{V} \equiv \begin{array}{|cc|}\hline \chi_1 & \chi_2 \\ \hline \chi_3 & \chi_6 \\ \hline \chi_4 & \chi_5 \\ \hline \end{array} \qquad (7)$$

where a horizontal box denotes that the two orbitals within are singlet coupled. The valence bond wavefunction for the singlet states of benzene is then

$$\psi_{\pi}^{VB} = C_{I}\Phi_{I} + C_{II}\Phi_{II} + C_{III}\Phi_{III} + C_{IV}\Phi_{IV} + C_{V}\Phi_{V} \qquad (8)$$

The wavefunctions associated with the five VB canonical structures are given in Table I. Then (8) can be written as

$$\Psi^{VB} = \mathcal{A}[\chi_1 \chi_2 \chi_3 \chi_4 \chi_5 \chi_6 \Theta] \tag{9}$$

where $\Theta$ is

$$\Theta = C_I \theta_I + C_{II} \theta_{II} + C_{III} \theta_{III} + C_{IV} \theta_{IV} + C_V \theta_V \tag{10}$$

Optimizing the mixing of the VB canonical structures is equivalent to optimizing the spin function (10) in (9).

Similarly for the triplet states of benzene, the VB wavefunctions are described in terms of nine nonorthogonal structures. Thus there should be nine valence-like triplet states for benzene. Just as for the singlet wavefunction, the VB triplet wavefunction for benzene may be written in the form (9) with the spin function (10) replaced by an appropriate spin function for a six electron triplet wavefunction.

## B. The Generalized Valence Bond Method

The GVB wavefunction[6, 7] has the same form as the VB wavefunction but the individual electron orbitals are found self-consistently rather than being taken as atomic orbitals. Although the GVB orbitals are allowed to be of any shape, we find that for the ground state of benzene they are each mainly concentrated near a single carbon atom. Thus we will denote the GVB orbitals as $\varphi_1$,

$\varphi_2$, $\varphi_3$, $\varphi_4$, $\varphi_5$, or $\varphi_6$, indicating the location of the maximum amplitude.

The GVB wavefunction is

$$\psi^{\mathrm{GVB}} = \mathcal{A}[\Phi_\sigma \varphi_a \varphi_b \varphi_c \varphi_d \varphi_e \varphi_f \Theta] \tag{11}$$

where $\Phi_\sigma$ is the frozen Hartree-Fock wavefunction describing the sigma core; $\varphi_a$, $\varphi_b$, $\varphi_c$, $\varphi_d$, $\varphi_e$, and $\varphi_f$ are general self consistent GVB orbitals and $\Theta$ is a linear combination of spin function analogous to (10). However, it is convenient to use orthogonal spin function rather than the VB canonical structures, (3) - (7). The five orthogonal spin functions used in the GVB wavefunction may be represented as

$$\theta_1 = \begin{array}{|cc|}\hline \varphi_a & \varphi_b \\ \hline \varphi_c & \varphi_d \\ \hline \varphi_e & \varphi_f \\ \hline \end{array} \tag{12}$$

$$\theta_2 = \begin{array}{|c|c|}\hline \varphi_a & \varphi_c \\ \varphi_b & \varphi_d \\ \hline \multicolumn{1}{|c}{\varphi_e} & \multicolumn{1}{c|}{\varphi_f} \\ \hline \end{array} \tag{13}$$

$$\theta_3 = \begin{array}{|c|c|}\hline \multicolumn{1}{|c}{\varphi_a} & \multicolumn{1}{c|}{\varphi_b} \\ \hline \varphi_c & \varphi_d \\ \varphi_e & \varphi_f \\ \hline \end{array} \tag{14}$$

$$\theta_4 = \begin{array}{|c|c|}\hline \varphi_a & \varphi_c \\ \cline{2-2} \varphi_b & \varphi_e \\ \cline{1-1} \varphi_d & \varphi_f \\ \hline \end{array} \tag{15}$$

$$\theta_5 = \begin{array}{|c|c|} \hline \varphi_a & \varphi_d \\ \varphi_b & \varphi_e \\ \varphi_c & \varphi_f \\ \hline \end{array} \tag{16}$$

where orbitals contained in vertical boxes are coupled in a triplet manner, i.e. antisymmetrically for spatial orbitals. Then

$$\Theta = c_1\theta_1 + c_2\theta_2 + c_3\theta_3 + c_4\theta_4 + c_5\theta_5 \tag{17}$$

subject to the requirement

$$c_1^2 + c_2^2 + c_3^2 + c_4^2 + c_5^2 = 1 \tag{18}$$

for normalization purposes.

The optimum GVB wavefunction is found by optimizing the orbital in (11) for a given spin function and then optimizing the spin function (17) for the spatial orbitals.

The triplet wavefunction also has the form (11) with an appropriate spin function replacing (17). There are nine orthogonal spin functions for a six electron triplet state.

## C. The Core Hamiltonian

As discussed in reference 1, the problem of finding a wavefunction of the form

$$\mathcal{A}[\Phi_{\text{core}}\Phi_{\text{val}}] \tag{19}$$

may be reduced to finding the wavefunction

$$\mathcal{A}[\Phi_{\text{val}}] \tag{20}$$

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 $\Phi_{core}$. The Hamiltonian for the valence orbitals will have the form

$$\mathcal{H} = \sum_{i=1}^{n_\pi} h^{core}(i) + \sum_{i>j}^{n_\pi} {}^{1}/_{r_{ij}} \tag{21}$$

where

$$h^{core}(i) = h(i) + \sum_{j=1}^{g} (2J_j - K_j) \tag{22}$$

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

$$h(i) = \tfrac{1}{2}\nabla_i^2 - \sum_a \frac{Z_a}{r_{ia}} \tag{23}$$

is the usual one-electron Hamiltonian, and $n_\pi$ is the number of electrons in pi orbitals. For benzene, the sigma-electron core was formed from an ab-initio Hartree-Fock (HF) calculation on the ground state.

## 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.[8] This was contracted to a double-zeta basis (4s, 2p) on each carbon and (2s) on each hydrogen as suggested by Dunning.[9]

All calculations used the same geometry as Steven, et al.[10]

## III. Results

Table II summarizes the result of VB and GVB calculations of singlet valence states. The wavefunction is expressed more in terms of the VB canonical basis. The GVB results in Table II were obtained by solving for the optimum spin couplings, $\Theta$, in (11) using the optimum GVB orbitals from the ground (${}^1A_g$) state of benzene. The results of self-consistent GVB calculations on the ${}^1A_{1g}$ and ${}^1B_{2u}$ states are summarized in Table III. One of the six identical GVB orbitals for each of these states is depicted in Figure 1.

The results of VB and GVB calculations on benzene triplet states are contained in Table IV. The GVB results were obtained in a similar manner as for the singlet states, but using the self-consistent GVB orbitals for the lowest (${}^3B_1$) triplet state. One of the six identical ${}^3B_1$ state GVB orbitals is depicted in Figure 1.

From Figure 1, we see that the orbitals for the three different states are very similar and all quite localized. Since each state involves similar orbitals the differing spatial symmetries obtained for the various states arise from the different spin couplings $\Theta$. Examining the orbitals for the ${}^1A_{1g}$, ${}^1B_{2u}$, and ${}^3B_{1u}$, states in Figure 1 we see that the slight differences in these orbitals are manifested mainly in the nodal structure.

In Table V we compare the energies of the lowest $^1A_g$, $^1B_{2u}$, and $^3B_{1u}$ states as obtained from various types of calculations. For the ground state wavefunction the energy drops 0.0698 h (1.90 eV) in going from HF to GVB, indicating the importance of allowing each electron to be described by a different orbital. The drop in energy is 0.1606 h (4.37 eV) in going from VB to GVB. This large energy lowering is primarily due to delocalization of the orbitals as can be seen in Table VI where the orbital coefficients of different wavefunctions are compared. Carrying out a full CI among the six GVB orbitals (denoted as GVB-CI), then leads to an additional drop of only 0.0169 h (0.46 eV). The GVB-CI wavefunction is essentially the best wavefunction that can be formed with just six orbitals (in any combination). In the usual VB terminology the GVB-CI includes all the ionic terms, i.e. wavefunctions in which the orbital product of (11) contains one or more orbitals twice. The small drop in energy from such terms indicates that the wavefunction can be accurately visualized in terms of a product of (GVB) orbitals.

In the double zeta basis there are 12 pi basis functions. Taking linear combinations to obtain the six GVB orbitals leaves a total of six additional orbitals that we will refer to as virtual orbitals. We carried out CI calculations within this larger set by adding to the GVB-CI all configurations obtained by triple excitation from the ground state but restricted so that only single excitations to the virtual space are allowed. From Table V we see that this leads to a drop of 0.0061 h (0.17 eV) in the energy from the GVB-CI, an energy that is only .0005 h (0.01 eV) above the energy of the extensive CI calculations of Hay and Shavitt using an extended basis set.

## IV. Discussion

### A. VB and GVB Models

For singlet benzene, the VB and GVB wavefunction spaces are each five dimensional, and as a result we expect there to be five valence-like singlet states. Since $\underset{\sim}{D}_{6h}$, the spatial symmetry group of benzene, is a subgroup of $S_6$, the symmetric group on six objects, we can determine the representations of $\underset{\sim}{D}_{6h}$ in the VB wavefunction by analyzing the behavior of the VB wavefunction under those operations of $S_6$ corresponding to elements of $\underset{\sim}{D}_{6h}$. Using the representation of $S_6$ corresponding to a singlet state, we find the symmetries of the states appearing in the VB wavefunction to be ${}^1A_{1g}$, ${}^1B_{2u}$, ${}^1E_{2g}$, and $2{}^1A_{1g}$. (The $E_{2g}$ state is doubly degenerate.) For triplet benzene, there are nine VB states and using the representation of $S_6$ corresponding to a triplet state, we find the symmetry of the states in the VB wavefunction to be ${}^3A_{2g}$, $1{}^3B_{1u}$, $2{}^3B_{1u}$, ${}^3E_{2g}$,

$1^3E_{1u}$, and $2^3E_{1u}$. (The $^3E_{1u}$ and $^3E_{2g}$ states are doubly degenerate.) Since the GVB wavefunction has the same form as the valence bond wavefunction and in fact our six GVB orbitals are identical, the GVB wavefunction contains the same symmetries as the VB wavefunction.

Analysis of the two Kekule structures (I and II) indicates that the wavefunction for these forms includes summetries $^1A_{1g}$ and $^1B_{2u}$. The wavefunction for the Dewar structures (III, IV, and V) includes symmetries $^1A_{1g}$ and $^1E_{2g}$. From symmetry considerations, we expect two $^1A_{1g}$ states involving all five VB canonical forms, one $^1B_{2u}$ state constructed out of the Kekule structures, and one $^1E_{2g}$ state constructed out of the Dewar structures.

From Table I, we see that the VB states are as anticipated and further that the VB and GVB descriptions of the $1^1A_{1g}$, $1^1B_{2u}$ and $2^1A_{1g}$ states are essentially identical. The two descriptions of the $E_{2g}$ state differ, but since these states are degenerate mixing of them can occur and the description is not unique. The components of all states are in accordance with our analysis of the symmetries above.

In Table V we compare the GVB results with some CI results.[11] The agreement between the two sets of results is quite good. The GVB wavefunction provides a good quantitative description of the pi-excited states of benzene. The agreement between the GVB results and the CI results indicates that the GVB wavefunction includes the important correlation effects.

The quantitative agreement between the GVB results and the CI results and the qualitative agreement between the VB description of benzene and the GVB description of benzene allows us to conclude that the VB resonance model for benzene provides an accurate and reasonable model for benzene. The similarity of the GVB pi orbitals of two singlet states and of a triplet state indicates further that the VB approach of using the same pi orbital for all valence states is basically correct. However, atomic orbitals are too localized and do not in any way reflect the fact that other centers are present. Localized orbitals which have overlap with both nearest neighbor centers in a bonding manner are required. For example, the ground (${}^1A_{1g}$) state GVB orbitals have an overlap of 0.524 with each nearest GVB orbital. In other pi electron systems, the overlap between neighboring GVB orbitals is typically greater, being 0.67 in ethylene, 0.642 in each pi-bond of the ${}^1A_g$ state of butadiene, and 0.58 in allyl radical. However only the center orbital of allyl radical has two equal nearest neighbors as does benzene.

## B. Resonance

One of the main features of the VB description of benzene is resonance. Experimentally, the resonance energy of benzene is found by comparing the heat of hydrogenation of cyclohexene with heat of hydrogenation of benzene using the assumption that three times the heat of hydrogenation of cyclohexene would be the heat of hydrogenation of the mythical cyclohexatriene (benzene with frozen bonds). The value typically cited is 36 kcal.[12] From VB calculations using $\Phi_{II}$ (4) as the wavefunction for cyclohexatriene, we obtain a value of 31.82 kcal for the resonance energy. Since the spatial orbitals for the VB wavefunctions for cyclohexene, cyclohexatriene, and benzene are the same, all being atomic orbitals, there is no ambiguity in this calculation.

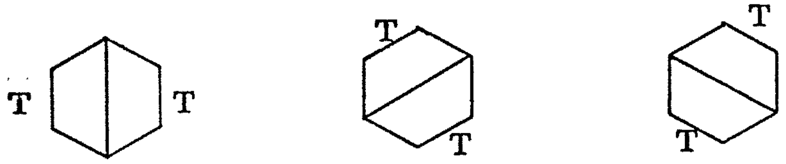
With the GVB method there is more than one choice for the wavefunction of the cyclohexatriene wavefunction. The form of the wavefunction to be used is the G1 (12) wavefunction since in this wavefunction the orbitals are coupled into three singlet pairs corresponding to three pi bonds. We will use the optimum ground ($^1A_{1g}$) state orbitals in (12) so that the resonance energy will correspond to the decrease in energy associated with changing the spin coupling from the G1 (12) spin coupling to the optimum spin coupling without changing the orbitals. This is directly analogous to the VB definition of resonance energy. In this manner, we obtain a value of 20.98 kcal for the resonance energy of benzene.

One of six identical GVB pi orbitals for the $^1A_{1g}$ state is depicted in Figure 1. We see that this orbital is rather delocalized, and in fact has amplitude on all six centers. However, the pi bond in cyclohexene, the basis for the experimental value of the resonance energy, should be more localized and be similar to the ethylene pi bond. Using the ethylene GVB orbitals[1] in the GVB G1 wavefunction (12), yields an energy 3.02 eV (69.7 kcal) above the optimum GVB energy. Allowing two orbitals to delocalize slightly by using the localized GVB orbitals for the ground state of allyl radical[2] and a spin coupling so that in the two allyl radicals two orbitals were singly coupled, lowered the energy 0.21 eV (4.8 kcal). Allowing two orbitals to be delocalized further by using four GVB butadiene orbitals[3] and two ethylene orbitals[1] in the G1 wavefunction (12) lowered the energy 0.47 eV (10.8 kcal) further. Thus allowing two of six orbitals to delocalize from GVB ethylene pi orbitals to GVB butadiene pi orbitals lowered the energy 0.68 eV (15.6 kcal). Allowing all six orbitals to delocalize over four centers then lowers the energy 2.04 eV (46.8 kcal). If allowing all six orbitals to delocalize over two additional centers reduces the energy by 0.18 eV or about 0.03 eV per orbital, the energy of the system would be reduced to the G1 energy.

From these calculations, we conclude that there is a large energy difference between pi electron orbitals of cyclohexene and cyclohexatriene. This energy difference results from additional delocalization of the orbitals in cyclohexatriene and the associated reduction in kinetic energy. The experimentally measured resonance energy can be attributed to two factors, delocalization of the orbitals from mainly two to six centers and the spin coupling optimization, which is directly analogous to the VB description of resonance.

## C. Fused Ethylene Model

Previously we have discussed [2, 3] a model for the pi-electron states proposed for butadiene by Dunning[13], in which the pi-electron states are formed by fusing ethylene molecules (in various states) together. Both allyl radical[2] and s-trans-1, 3-butadiene[3] were well described by this model. The ground ($1^1A_{1g}$) state of benzene would be described as the symmetric combination of three ethylene ground (N) states. The first excited or antiresonant ($1^1B_{2u}$) state may be considered as the anti-symmetric combination of three N state ethylenes, or equivalently as the anti-symmetric combination of three T state ethylenes, or equivalently as three lowest triplet (T) states ethylenes across the long bonds, that is orbitals $\varphi_1$ and $\varphi_4$ are triplet coupled as are orbitals $\varphi_2$ and $\varphi_5$ and $\varphi_3$ and $\varphi_6$ and the triplet entities coupled into a singlet. Since the triplet couplings are across the long bonds, there should be a small overlap between the triplet pairs, which is a favorable interaction. We find for the ground state orbitals, the 1-4 overlap is -0.17; the 1-4 overlap is reduced slightly to -0.15 for the self-consistent orbitals for the antiresonant ($^1B_{2u}$) state. The $^1E_{2g}$ state is a linear combination of two ethylene T states coupled to a singlet and an ethylene N state. There are unique three choices for the NTT states



(27)

The $2^1A_{1g}$ will be a symmetric combination of three T state ethylene plus a component of the symmetric sum of the three NTT states.

The benzene triplet state may also be analyzed in the same manner. For example the lowest triplet ($1^3B_{1u}$) state is the antisymmetric combination of two N state ethylenes and a T state ethylene. The $1^3E_{1u}$ and $1^3E_g$ are the antisymmetric and symmetric combinations of an N state ethylene and two T state ethylenes, coupled to a triplet with appropriate considerations with regard to spatial symmetry as in (27).

## D. Comparison with Other Results

Using orthogonal symmetry orbitals formed from the GVB orbitals for the $1^1A_{1g}$ state, we performed full minimum basis set CI calculations on the singlet and triplet manifolds of states. Table V summarizes these results. We see in Table V that there is very little decrease in the energy in the CI calculations, a further indication that the GVB wavefunction includes the important correlation effects. In Table V we compare the GVB, and GVB-CI total energies with full CI calculations using the same basis set.

We see in Table V that not all of the low energy singlet and triplet states correspond to the GVB states and are therefore valence like. Since our basis set does not include any diffuse basis functions, all of the states in Table V are described using tight or valence like orbitals. Those states which were present in CI calculations, but which do not correspond to states described in the GVB calculations must be ionic-like states or poorly described Rydberg states. The spatial extent of the pi-orbitals of these states should be slightly greater than for true valence states. From Table V and reference 11 we can identify the $1^3B_{2u}$ and $1^1B_{1u}$ as ionic like states.

In Table VI, we compare excitation energies from VB, GVB, GVB-CI, and other calculations and experimental values. For the low-lying valence states the agreement is good. The higher valence states are not reported by others.

Table I. Valence Bond Wavefunctions

$$\Phi_i^{VB} = [\Phi_i \alpha\beta\alpha\beta\alpha\beta] = [\chi_1\chi_2\chi_3\chi_4\chi_5\chi_6\theta_i]$$

| | $\Phi_r$ | $\theta_i$ |
|---|---|---|
| $\Phi_I$[a] | $(\chi_1\chi_6 + \chi_6\chi_1)(\chi_2\chi_3 + \chi_3\chi_2)(\chi_4\chi_5 + \chi_5\chi_4)$ | $\alpha\alpha\beta\alpha\beta\beta - \alpha\alpha\beta\beta\alpha\beta - \alpha\beta\alpha\alpha\beta\beta + \alpha\beta\alpha\beta\alpha\beta - \beta\alpha\beta\alpha\beta\alpha + \beta\alpha\beta\beta\alpha\alpha - \beta\beta\alpha\alpha\beta\alpha - \beta\beta\alpha\beta\alpha\alpha$ |
| $\Phi_{II}$ | $(\chi_1\chi_2 + \chi_2\chi_1)(\chi_3\chi_4 + \chi_4\chi_3)(\chi_5\chi_6 + \chi_6\chi_5)$ | $\alpha\beta\alpha\beta\alpha\beta - \beta\alpha\alpha\beta\alpha\beta - \alpha\beta\beta\alpha\alpha\beta + \beta\alpha\beta\alpha\alpha\beta - \alpha\beta\alpha\beta\beta\alpha + \beta\alpha\alpha\beta\beta\alpha + \alpha\beta\beta\alpha\beta\alpha - \beta\alpha\beta\alpha\beta\alpha$ |
| $\Phi_{III}$ | $(\chi_1\chi_6 + \chi_6\chi_1)(\chi_2\chi_5 + \chi_5\chi_2)(\chi_3\chi_4 + \chi_4\chi_3)$ | $-\alpha\alpha\alpha\beta\beta\beta + \alpha\alpha\beta\alpha\beta\beta + \alpha\beta\alpha\beta\alpha\beta - \alpha\beta\beta\alpha\alpha\beta + \beta\alpha\alpha\beta\beta\alpha - \beta\alpha\beta\alpha\beta\alpha - \beta\beta\alpha\beta\alpha\alpha + \beta\beta\beta\alpha\alpha\alpha$ |
| $\Phi_{IV}$ | $(\chi_1\chi_4 + \chi_4\chi_1)(\chi_2\chi_3 + \chi_3\chi_2)(\chi_5\chi_6 + \chi_6\chi_5)$ | $-\alpha\alpha\beta\beta\alpha\beta + \alpha\alpha\beta\beta\beta\alpha + \alpha\beta\alpha\beta\alpha\beta - \alpha\beta\alpha\beta\beta\alpha + \beta\alpha\beta\alpha\alpha\beta - \beta\alpha\beta\alpha\beta\alpha - \beta\alpha\alpha\beta\alpha\beta + \beta\alpha\alpha\beta\beta\alpha$ |
| $\Phi_V$ | $(\chi_1\chi_2 + \chi_2\chi_1)(\chi_3\chi_6 + \chi_6\chi_3)(\chi_4\chi_5 + \chi_5\chi_4)$ | $-\alpha\beta\alpha\alpha\beta\beta + \alpha\beta\alpha\beta\alpha\beta + \alpha\beta\beta\alpha\beta\alpha - \alpha\beta\beta\beta\alpha\alpha + \beta\alpha\alpha\alpha\beta\beta - \beta\alpha\alpha\beta\alpha\beta - \beta\alpha\beta\alpha\beta\alpha + \beta\alpha\beta\beta\alpha\alpha$ |

[a] The numbering of the wavefunction is consistent with numbering of Rumer diagrams in (1a) and (1b) and with the tableaux (3) through (7).

Table II. The Singlet Valence States of Benzene

| State | $\Delta E$ (eV)[b] | Spin Coupling I | II | III | IV | V |
|---|---|---|---|---|---|---|
| VB States | | | | | | |
| $^1A_{1g}$ | $0^a$ | 0.42 | 0.42 | -0.17 | -0.17 | -0.17 |
| $^1B_{2u}$ | 3.96 | -0.82 | 0.82 | 0.00 | 0.00 | 0.00 |
| $^1E_{2g}$ | 7.21 | 0.00 | 0.00 | 0.20 | 0.70 | -0.90 |
| $E_{2g}$ | 7.23 | -0.00 | 0.00 | 0.92 | -0.64 | -0.29 |
| $2^1A_{1g}$ | 11.46 | -1.35 | -1.35 | -1.04 | -1.04 | -1.04 |
| GVB States<br>(Using $1^1A_{1g}$ Orbitals) | | | | | | |
| $^1A_{1g}$ | $0^a$ | 0.50 | 0.50 | -0.11 | -0.11 | -0.11 |
| $^1B_{2u}$ | 5.32 | 0.82 | -0.82 | -0.00 | -0.00 | -0.00 |
| $^1E_{2g}$ | 8.90 | 0.00 | 0.00 | 0.94 | -0.44 | -0.50 |
| $^1E_{2g}$ | 8.91 | 0.00 | 0.00 | -0.03 | 0.83 | -0.80 |
| $2^1A_{1g}$ | 14.81 | -1.34 | -1.34 | -1.04 | -1.04 | -1.04 |

[a] Calculated total energies for the ground state are -230.54931 h and -230.70988 h for the VB and GVB ($1^1A_{1g}$ orbitals).

[b] 1 hartree = 27.2117 eV.

Table III. Self Consistent GVB Results

| State | Total Energy (h) | Excitation Energy (eV) |
|---|---|---|
| $1^1A_{1g}$ | -230.70992 | 0 |
| $1^3B_1$ | -230.57213 | 3.749 |
| $1^1B_{2u}$ | -230.52961 | 4.901 |

Table IV. Valence Triplet States of Benzene

| State | VB<br>Excitation Energy (eV)[a] | GVB ($^3B_{1u}$ Orbitals)<br>Excitation Energy (eV)[a] |
|---|---|---|
| $^3B_{1u}$ | 2.170[b] | 3.749[b] |
| $^3E_{1u}$ | 4.534<br>4.739 | 5.444<br>5.481 |
| $^3E_{2g}$ | 5.503<br>5.844 | 7.339<br>7.396 |
| $^3B_{1u}$ | 9.344 | 11.074 |
| $^3A_{2g}$ | 10.527 | 11.876 |
| $^3E_{1u}$ | 11.383<br>12.062 | 13.120<br>13.465 |

[a] With respect the ground state

[b] The total energy for the $^3B_{1u}$ state is -230.46958 for VB and -230.57213 for GVB.

Table V. Comparison of Energies for Different Types of Wavefunctions

| | $1^1A_g$ | $1^1B_{2u}$ | $1^3B_{1u}$ |
|---|---|---|---|
| HF[a] | -230.64001 | -230.37326 | -230.46506 |
| VB | -230.54931 | -230.40387 | -230.46958 |
| GVB($^1A_g$ orbitals) | -230.70992 | -230.51435 | - |
| GVB (opt. orbitals) | -230.70992 | -230.52961 | -230.57213 |
| GVB - CI [b,c] | -230.71677 | -230.51766 | -230.56373 |
| CI - Valence Basis[d] | -230.72287 | -230.54006 | -230.580508 |
| CI - Full Basis[e] | -230.72339 | -230.53950 | -230.58265 |

[a] The HF calculations used $a_{2u}$, $e_{1g}$, $e_{2u}$, and $b_{1g}$ orbitals from symmetrizing the GVB orbitals of the ground state. The excited states were then obtained by exciting one electron from $e_{1g}$ to $e_{2u}$ and combining pairs of configurations to obtain the proper symmetry. The exact HF energy for the $^1A_{1g}$ state is -230.6410 from reference 11.

[b] Using orbitals for the ground state.

[c] A full CI among the six GVB orbitals using the orbitals from the $1^1A_g$ state.

[d] In adding to the configurations of GVB-CI, we included all configurations obtained by up to triple excitations from the ground state but restricted to only one excitation outside the GVB space (to the six virtual functions).

[e] Hay and Shavitt (reference 11). In addition to the DZ valence basis, two diffuse functions per center were included.

Table VI. Comparison of Orbital Coefficients for GVB Calculations

| | Nuclear Center[a] | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 6 | 3 | 5 | 4 |
| VB | 0.7926 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | 0.3174 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| GVB ($1^1A_{1g}$) | 0.7025 | 0.1323 | 0.1323 | -0.0047 | -0.0051 | -0.0530 |
| | 0.2994 | 0.0345 | 0.0345 | -0.0279 | -0.0281 | -0.0462 |
| GVB ($1^3B_{1u}$) | 0.6863 | 0.1502 | 0.1393 | 0.0304 | 0.0289 | 0.0063 |
| | 0.3648 | -0.0240 | -0.0209 | -0.01488 | -0.0201 | 0.0247 |
| GVB ($1^1B_{2u}$) | 0.6775 | 0.1559 | 0.1553 | 0.0039 | 0.0035 | -0.0851 |
| | 0.3696 | -0.01988 | -0.0203 | -0.0231 | -0.0232 | -0.0166 |

[a] In each center there are two basis functions, the upper one refers to the tighter of the two.

Table VII. Comparison of Benzene Excitation Energies

|  | Current Work |  |  |  |  |  | Other CI Calculations |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| State | HF[a] | VB | GVB |  | GVB-CI |  | HS[a] | PB[b] | BWP[c] | EXP |
|  |  |  | Fixed Orbitals | Optimum Orbitals |  |  |  |  |  |  |
| $1^1A_g$ |  | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $1^3B_{1u}$ | 4.76 | 2.17 | 3.75 | 3.75 | 4.16 | 3.87 | 3.83 | 4.21 | 3.98 | 3.9[d] |
| $1^1B_{2u}$ | 7.26 | 3.96 | 5.32[e] | 4.90 | 5.42 | 4.97 | 5.00 | 5.27 | 5.26 | 4.80[d] |
| $1^3E_{1u}$ | 5.88 | 4.63 | 5.46 |  | 5.55 | 5.01 | 4.98 | 5.21 | 5.39 | 4.7[d] |
| $1^3E_{2g}$ | 10.30 | 5.62 | 7.37 |  | 7.72 | 7.24 | 7.28 | 7.65 | 7.48 | 6.55[f]<br>8.84[g] |
| $^3B_{2u}$ | 7.03 | - | - |  | 8.16 | 7.26 | 7.00 | 7.28 | 7.76 | 5.4[h] |
| $1^1E_{2g}$ | 12.85 | 7.22 | 8.90 |  | 8.91 | 8.23 | 8.33 | 8.60 | 8.62 | 7.24[i] |
| $1^1B_{1u}$ | 8.41 | - | - |  | 9.44 | 8.01 | 7.63 | 8.09 | 9.48 | 6.16[d] |
| $^1E_{1u}$ | 10.94 | - | - |  | 10.60 | 9.11 |  |  |  |  |
| $^3B_{1u}$ |  | 9.34 | 11.07 |  | 11.73 | 10.99 |  |  |  |  |
| $^3A_{2g}$ |  | 10.53 | 11.88 |  | 12.20 | 11.12 |  |  |  |  |
| $^1A_{1g}$ |  | 11.46 | 14.81 |  | 12.86 | 11.40 |  |  |  |  |
| $^3E_{2g}$ |  | - | - |  | 13.15 | 11.52 |  |  |  |  |
| $^3E_{1u}$ |  | 11.72 | 13.24 |  | 13.90 | 12.87 |  |  |  |  |

[a] Reference 11.

[b] Reference 14.

[c] Reference 15.

[d] Reference 16.

[e] Using self-consistent orbitals from $^1A_g$ for singlet states and from $^3B_{1u}$ for triplet states.

[f] References 17 and 18.

[g] References 17 and 19.

[h] Shoulder in band in reference 16.

[i] References 18 and 20.

[j] See footnote a of Table V.

[k] See footnote d of Table V.

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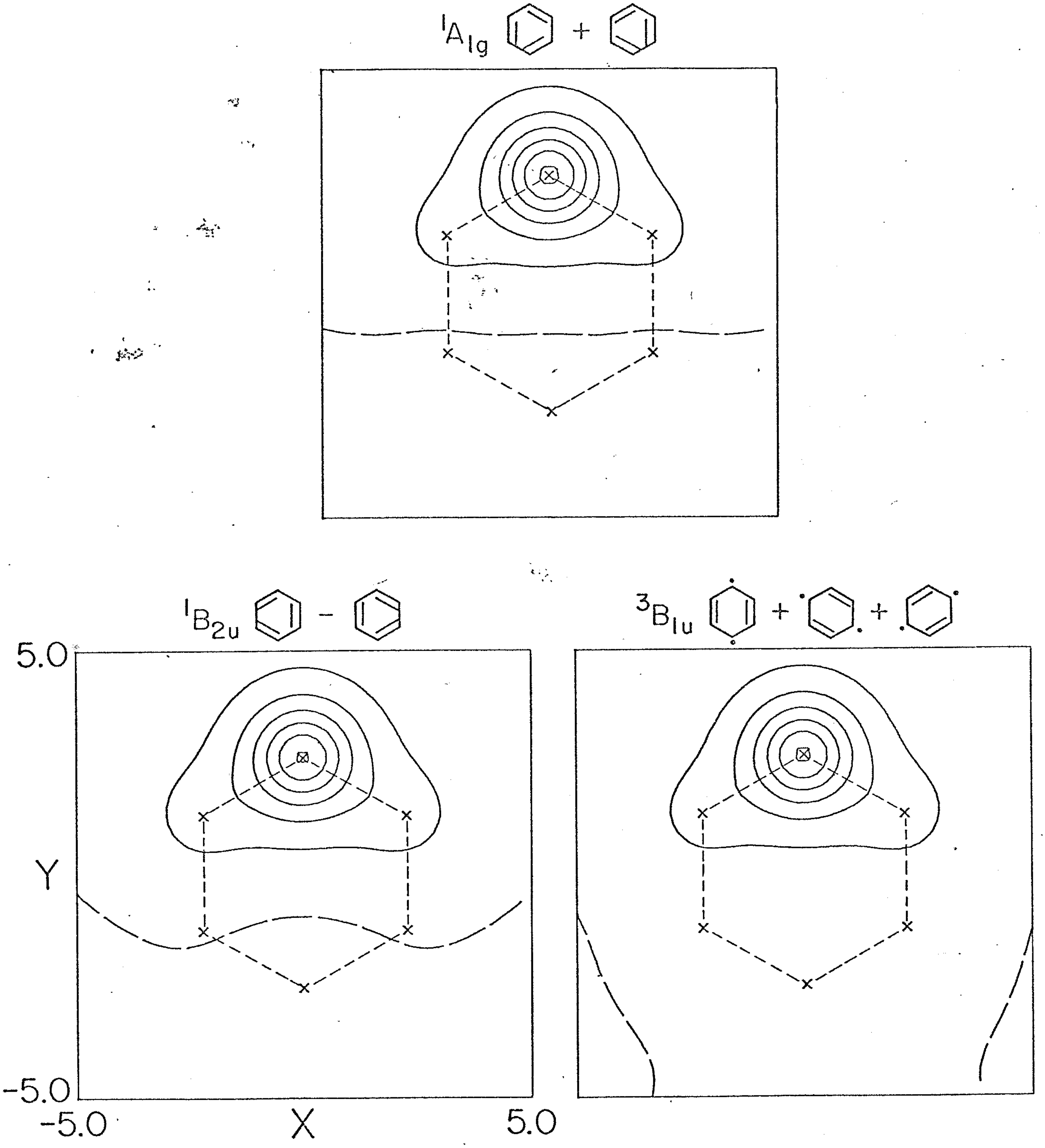
## Figure Captions

Figure 1 - One of the six equivalent GVB pi orbitals of benzene is shown for (a) the optimum GVB description of the $^1A_{1g}$ state, (b) the antiresonant $^1B_{2u}$ state, and (c) the lowest triplet ($^3B_{1u}$) state. In all plots, the most diffuse contour has an amplitude of 0.05 and each succeeding contour increases by 0.05. Nodal lines are represented by dashed lines.

# GVB PI ORBITALS FOR BENZENE



# APPENDIX VII

# THE SPATIALLY PROJECTED GENERALIZED VALENCE BOND METHOD AND CALCULATIONAL DETAILS

## I. GENERAL DISCUSSION

The goal of the spatially projected generalized valence bond (GVB(SP)) method is to generate a wave function that is an eigenfunction of spin and that also possesses the correct spatial symmetry without restricting the individual orbitals to be symmetry functions. The spin coupling is optimized among all possible spin couplings for the particular number of electrons and the multiplicity. The spatial orbitals are also optimized self-consistently.

The calculations are performed by optimizing the spatial orbitals with the spin coupling fixed. The spin coupling is then optimized using the initial spatial orbitals. The orbitals and the spin are then changed for the next iteration. Both spin coupling coefficients and the spatial orbitals are changed concurrently without permitting any direct interaction between the two. These operations are treated separately for reasons of convenience. It has been found that the spatial nature of the orbitals and the spin coupling can and do affect each other so one must be sure that the optimum description has been obtained, rather than a local minimum.

### A. Spatial Solution

The GVB(SP) wave function is based upon the GVB wave function of Ladner and Goddard[1,2]. The Ladner-Goddard version of the GVB wave function solves for an eigenfunction of the spin operator without any restrictions except that the form of the wave function is the independent particle type. This wave function has the general form

$$\Psi = \sum_{\alpha}^{f_\alpha} c_\alpha G_\alpha(\phi_1 \cdots \phi_n \alpha\beta \cdots) \qquad (1)$$

where $f_\alpha$ is the number of possible spin couplings for n electrons of spin s

denotes the particular spin coupling

$c_\alpha$ are the spin coupling coefficients

$G_\alpha$ is an operator which creates an eigenfunction of spin corresponding to the $\alpha$ th spin coupling and incorporates the Pauli principle directly into the wave function

Previous calculations have indicated that this method generates excellent independent particle wave functions.

Certain systems, typically excited states, are not correctly described by this wave function. One of the simplest systems for which this GVB description is not adequate is $He_2^+$ . This system may be described by either of two equivalent pictures

| $He - He^+$ | $He^+ - He$ |
|---|---|
| I | II |

as there is no *a priori* reason to choose either. The standard GVB or Hartree-Fock method will only describe such a system by using delocalized symmetry functions so that these wave functions will not properly describe such a system at all internuclear distances. In addition, localized orbital descriptions of systems should be lower in energy as more correlation effects are included.

In order to properly describe such a system and not restrict the individual orbitals to symmetry functions, a spatial projection operator, denoted as P , was added to the wave function of (1) giving

$$\Psi = \sum_{\alpha}^{f_\alpha} C_\alpha P G_\alpha (\phi_1 \cdots \phi_n \alpha \beta \cdots) \tag{2}$$

This wave function has the following characteristics:

(1) It is an eigenfunction of the spin operator and explicitly includes the Pauli principle.

(2) It has the correct spatial symmetry without restricting the individual orbitals to being symmetry functions.

(3) A localized orbital description is usually obtained.

Using this wave function, variational conditions for the minimization of the energy can be derived. Three different equations are derived resulting from the consideration of first and second order changes in the wave function and the resulting first and second order changes in the energy.

The first equation to be considered results from a consideration of the first order variations in the wave functions and examining the resulting first order change in the energy. The condition that first order change in the energy be zero, i.e., that the state be stable with respect to first order changes in the wave function, is

$$H - EA' = 0$$

$$\sum_{\mu}^{NBF} < \Psi_k^{\mu} / \hat{H} / \Psi > - E < \Psi_k^{\mu} / \Psi > = 0 \tag{3}$$

where $\hat{H}$ is the hamiltonian, $\Psi_k^{\mu}$ denotes that orbital k is varied, NBF is the number of basis functions, and $A^1$ is the appropriate metric[3] for the space under consideration. In (3) the definitions of H and $A^1$ have been inserted. (The metric will be discussed more fully later.) In the GVB(SP) method, there is one hamiltonian for each electron. All of the hamiltonians may be diagonalized simultaneously changing all of the orbitals at once. Alternatively, a single hamiltonian for orbital k may be formed, diagonalized, and a new orbital k found. This new orbital is substituted into the wave function and the next hamiltonian formed, etc. This process is repeated until a new orbital has been found for each electron.

The second method of solutions results from examination of the second order change in the energy resulting from a first order change in the wave function. This condition insures that the state found which is stable under first order changes in the energy is in fact a true minimum rather than a stationary point. The equation derived for this condition is

$$(B' - EA^2)\,\Delta = -X$$

$$\begin{aligned}\sum_{\nu,l}\Big(&\langle\Phi_k^\mu|\hat{H}|\Phi_l^\nu\rangle - 2(\langle\Phi_k^\mu|\hat{H}|\Phi\rangle\langle\Phi|\Phi_l^\nu\rangle \\ &- E\langle\Phi_k^\mu|\Phi\rangle\langle\Phi|\Phi_l^\nu\rangle) - E\langle\Phi_k^\mu|\Phi_l^\nu\rangle\Big)\Delta_{\nu l} \\ &= -\langle\Phi_k^\mu|\hat{H}-E|\Phi\rangle \qquad (4)\end{aligned}$$

where B' is the matrix of second order changes in the energy

$A^2$ is the correct metric for this space

X is the vector of the first order changes in the wave function

$\Delta$ is the change in the wave function

and the new wave function is found by:

$$\Psi^{(i+1)} = \Psi^{(i)} + \Delta \qquad (5)$$

where i denotes the iteration number.

The third condition is derived by considering the second order change in the energy resulting from a second order change in the wave function. The resulting equation is

$$(B^2 - EA')\Delta = -X$$

$$\begin{aligned} &\sum_{\nu,\ell} \Big( \langle \Psi_k^\mu | \hat{H} | \Psi_\ell^\nu \rangle + \langle \Psi_{k\ell}^{\mu\nu} | H | \Psi \rangle (1-\delta_{k\ell}) - \\ &\quad E \langle \Psi_{k\ell}^{\mu\nu} | \Psi \rangle (1-\delta_{k\ell}) - 2 \left( \langle \Psi_k^\mu | \hat{H} - E | \Psi \rangle \langle \Psi | \Psi_\ell^\nu \rangle \right) \\ &\quad - E \langle \Psi_k^\mu | \Psi_\ell^\nu \rangle \Big) \Delta_{\nu\ell} = - \langle \Psi_k^\mu | \hat{H} - E | \Psi \rangle \end{aligned} \qquad (6)$$

Again $\Delta$ is the change in the wave function for iteration i , and $\Psi_{k\ell}^{\mu\nu}$ indicates orbitals $k$ and $\ell$ are changed. The new wave function is found using (5).

The metrics in equations (3), (4), and (6) project out those changes in the wave function which do not change the energy for the particular variational condition. The first order change in the energy is considered in (3). In this case, a typical example of a trivial change in the wave function which does not change the energy is the addition of two triplet coupled orbitals. If the spin coupling is

$$\begin{array}{|c|c|} \hline a & b \\ \hline c \\ \cline{1-1} d \\ \cline{1-1} \end{array}$$

adding any part of orbital d to orbital c will not change the energy, since orbitals c and d are triplet coupled. Diagonalizing $A^1$ will yield all positive eigenvalues except for those changes in the wave function which do not change the energy. There will be a zero eigenvalue for each trivial change in the wave function. Transforming H to the space of nonzero eigenvalues of $A^1$ will project away the trivial changes in the wave function leaving only the real changes in the wave function.

Equation (4) is the condition for the second order change in the energy associated with a first order change in the wave function. An example of a trivial change to the wave function in this case is changing the norm of any orbital. The metric is used in an identical manner as $A^1$ discussed above.

The metric used for the second order change in the energy associated with a second order change in the wave function is the same as used in (4). This metric is used because the first order changes in the wave function are considered most important and the elimination of the trivial first order changes in the wave function is most important.

## B. Spin Variation

The spin coupling optimization is performed by a configuration interaction type procedure. Letting $\{\Phi_\alpha\}$ denote the set of spin eigenfunctions for the same set of fixed spatial orbitals, the optimal wave function is

$$\Psi = \sum_{\alpha}^{f_\alpha} c_\alpha \Psi_\alpha \tag{7}$$

where the $c_\alpha$ are such that (7) gives the minimum energy. This is found by solving

$$\sum_{\alpha,\beta=1}^{f_\alpha} \left[ \langle \Phi_\alpha | \hat{H} | \Phi_\beta \rangle - E \langle \Phi_\alpha | \Phi_\beta \rangle \right] = 0 \tag{8}$$

## C. Excited States

One-electron excited states may be found by the hamiltonian methods. Since there is a separate hamiltonian for each electron, a state that can be described as a single electron excitation may be found by selecting an excited solution for a particular hamiltonian. This method will converge toward a particular, one-electron excited state.

The matrix of second order changes in the energy will contain one negative eigenvalue for each possible path for lowering the energy. Thus, in solving for the ground state, this matrix should have no negative eigenvalues. The first excited state will have at least one (hopefully no more) negative eigenvalue. Using those methods based upon the second order change in the energy, one may converge to a double excitation state (in theory) if the trial guess is good enough and one selects the correct number of negative eigenvalues.

For spatially projected states, the lowest state of each symmetry type will have zero negative eigenvalues. Each symmetry type will behave as a separate spectrum of states.

Another possible type of excited state is obtained by choosing a higher solution from the spin optimization, configuration interaction matrix. This type of situation arises when two states can be described by the same spatial orbitals, but with different spin couplings. Such excited states may display the characteristics of double excitation states.

## II. DERIVATION OF EQUATIONS

A historical discussion and derivation of GVB equations is presented in Appendix I of Reference 1. Our derivations will parallel this presentation. It is recommended that the interested reader become familiar with Appendix I, Reference 1, as in many ways our derivations are identical with those, but are further complicated by the addition of spatial symmetry considerations. It is also instructive to see the additional complications introduced by the spatial symmetry operator.

The energy for the GVB(SP) wave function is

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{9}$$

where $\hat{H}$ is the hamiltonian of the system

$$H = \sum_{i=1}^{\mu\nu} \left( h(i) + \sum_{j>i}^{\mu\nu} g(i,j) \right) \tag{10}$$

k(i) is a one-electron operator and g(i,j) a two-electron operator. $\Psi$ is the final wave function. NX is the number of electrons.

Let $\Psi^{(i)}$ denote a specific order of the variation of the wave function. $\Psi^{(o)}$ represents the zero order wave function or the present best guess at the wave function. $\Psi^{(1)}$ represents the first order change in $\Psi^{(o)}$. Expanding $\Psi$ in (9), we get

$$E = \frac{\langle \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \cdots / \hat{H} / \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} \cdots \rangle}{\langle \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} \cdots / \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} \cdots \rangle} \tag{11}$$

By keeping terms through various orders in the variations in (11), we obtain different equations for finding the optimum GVB(SP) wave function.

## A. The Energy

If only $\Psi^{(o)}$ is retained, we get

$$E = \frac{\langle \Psi^{(0)} / \hat{H} / \Psi^{(0)} \rangle}{\langle \Psi^{(0)} / \Psi^{(0)} \rangle} \tag{12}$$

This is the energy of the system with the trial wave function.

## B. First Order Equation

Keeping terms which contain up to first order variation in the wave function and have a total first order variation, we obtain

$$E = \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | \hat{H} | \Psi^{(1)} \rangle + \langle \Psi^{(1)} | \hat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle + \langle \Psi^{(1)} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | \Psi^{(1)} \rangle} \tag{13}$$

Since we will only allow real wave functions, (13) is

$$E = \frac{\langle \Psi^{(0)} | \hat{H} | \Psi \rangle + 2 \langle \Psi^{(0)} | \hat{H} | \Psi^{(1)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle + 2 \langle \Psi^{(0)} | \Psi^{(1)} \rangle} \tag{14}$$

Examining the denominator of (14),

$$\left[ \langle \Psi^{(0)} | \Psi^{(0)} \rangle + 2 \langle \Psi^{(0)} | \Psi^{(1)} \rangle \right]^{-1} = \langle \Psi^{(0)} | \Psi^{(0)} \rangle^{-1} \left[ 1 + \frac{2 \langle \Psi^{(0)} | \Psi^{(1)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \right]^{-1} \tag{15}$$

We assume $\Psi^{(0)} >> \Psi^{(1)}$, i.e., that the first order changes in the wave function are small. Then we can approximate (15) by

$$\left[ \langle \Psi^{(0)} | \Psi^{(0)} \rangle + 2 \langle \Psi^{(0)} | \Psi^{(1)} \rangle \right]^{-1} \approx \langle \Psi^{(0)} | \Psi^{(0)} \rangle^{-1} \left[ 1 - \frac{2 \langle \Psi^{(0)} | \Psi^{(1)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \right] \tag{16}$$

where we have retained only first order terms. Substituting (16) in (14)

$$E = \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle + 2 \langle \Psi^{(0)} | \hat{H} | \Psi^{(1)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \left[ 1 - \frac{2 \langle \Psi^{(0)} | \Psi^{(1)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \right] \tag{17}$$

Expanding and keeping terms only first order and using (12) we obtain

$$E = E_0 + \frac{2\langle\Psi^{(0)}|\hat{H}|\Psi^{(1)}\rangle}{\langle\Psi^{(0)}|\Psi^{(0)}\rangle} - 2E_0\frac{\langle\Psi^{(0)}|\Psi^{(1)}\rangle}{\langle\Psi^{(0)}|\Psi^{(0)}\rangle} \tag{18}$$

Then, the first order change in the energy due to first order change in the wave function is

$$\Delta E = E - E_0 = 2\left[\frac{\langle\Psi^{(0)}|\hat{H}|\Psi^{(1)}\rangle}{\langle\Psi^{(0)}|\Psi^{(0)}\rangle} - E_0\frac{\langle\Psi^{(0)}|\Psi^{(1)}\rangle}{\langle\Psi^{(0)}|\Psi^{(0)}\rangle}\right] \tag{19}$$

The condition for convergence is $\Delta E = 0$ giving

$$\langle\Psi^{(0)}|\hat{H}|\Psi^{(1)}\rangle - E_0\langle\Psi^{(0)}|\Psi^{(1)}\rangle = 0 \tag{20}$$

Equation (20) is a homogeneous, first order equation for $\Psi^{(1)}$. The rate of convergence is proportional to the difference between the trial solution and the final solution so that as the solution is approached the rate of convergence decreases. Theoretically, (20) requires an infinite number of iterations to converge to the exact solution.

## C. Second Order Energy Variation

In order to improve the rate of convergence, higher order approximations are used. If we allow up to second order changes in the energy, but restrict the wave function to first order changes, we obtain from (11)

$$E = \frac{\langle \Phi^{(0)} + \Phi^{(1)} | \hat{H} | \Phi^{(0)} + \Phi^{(1)} \rangle}{\langle \Phi^{(0)} + \Phi^{(1)} | \Phi^{(0)} + \Phi^{(1)} \rangle} \tag{21}$$

$$E = \frac{\langle \Phi^{(0)} | \hat{H} | \Phi^{(0)} \rangle + 2 \langle \Phi^{(0)} | \hat{H} | \Phi^{(1)} \rangle + \langle \Phi^{(1)} | \hat{H} | \Phi^{(1)} \rangle}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle + 2 \langle \Phi^{(0)} | \Phi^{(1)} \rangle + \langle \Phi^{(1)} | \Phi^{(1)} \rangle} \tag{22}$$

where we have incorporated the real nature of one wave function in (22). The denominator of (22) may be written as

$$\langle \Phi^{(0)} | \Phi^{(0)} \rangle \left[ 1 + \frac{2 \langle \Phi^{(0)} | \Phi^{(1)} \rangle}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle} + \frac{\langle \Phi^{(1)} | \Phi^{(1)} \rangle}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle} \right] \tag{23}$$

and may be approximated in a similar manner to (16) by

$$\langle \Phi^{(0)} | \Phi^{(0)} \rangle \left[ 1 - \frac{2 \langle \Phi^{(0)} | \Phi^{(1)} \rangle}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle} - \frac{\langle \Phi^{(1)} | \Phi^{(1)} \rangle}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle} \right]^{-1} \tag{24}$$

Substituting (24) in (22) and keeping only second order terms gives

$$\begin{aligned} E = E_0 &+ \frac{2}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle} \langle \Phi^{(0)} | \hat{H} - E_0 | \Phi^{(1)} \rangle \\ &+ \frac{\langle \Phi^{(1)} | \hat{H} - E_0 | \Phi^{(1)} \rangle}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle} + \frac{(-4) \langle \Phi^{(0)} | \hat{H} - E | \Phi^{(1)} \rangle \langle \Phi^{(1)} | \Phi^{(0)} \rangle}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle \langle \Phi^{(0)} | \Phi^{(0)} \rangle} \end{aligned} \tag{25}$$

which may be written as

$$\Delta E = E - E_0 = \frac{1}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \left[ 2 \underset{\sim}{X} + (B' - E_0 A^2) \underset{\sim}{\Delta} \right] \tag{26}$$

where we have defined

$$\underset{\sim}{X} = \langle \Psi^{(0)} | \hat{H} - E | \Psi^{(1)} \rangle \tag{27}$$

$$B' = \langle \Psi^{(1)} | \hat{H} | \Psi^{(1)} \rangle - \frac{4 \langle \Psi^{(0)} | \hat{H} - E | \Psi^{(1)} \rangle \langle \Psi^{(1)} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \tag{28}$$

$$A^2 = \langle \Psi^{(1)} | \Psi^{(1)} \rangle \tag{29}$$

$\underset{\sim}{X}$ is the first order change in the energy as can be seen by comparing (27) with (19). $A^2$ is the metric, and $B^1$ is the matrix of second order changes in $E$ caused by first order changes in the wave function.

At convergence $\Delta E = 0$ giving

$$-2 \underset{\sim}{X} = (B' - E_0 A^2) \underset{\sim}{\Delta} \tag{30}$$

which is solved for $\underset{\sim}{\Delta}$ . The new wave function is found using (5).

## D. Second Order Variation in the Wave Function

We now consider second order variations in the wave function. Keeping terms through second order in (1) gives

$$E = \frac{\langle \Phi^{(0)} + \Phi^{(1)} + \Phi^{(2)} | \hat{H} | \Phi^{(0)} + \Phi^{(1)} + \Phi^{(2)} \rangle}{\langle \Phi^{(0)} + \Phi^{(1)} + \Phi^{(2)} | \Phi^{(0)} + \Phi^{(1)} + \Phi^{(2)} \rangle}$$

$$E = \frac{\langle \Phi^{(0)} | \hat{H} | \Phi^{(0)} \rangle + 2 \langle \Phi^{(1)} | \hat{H} | \Phi^{(0)} \rangle + \langle \Phi^{(1)} | \hat{H} | \Phi^{(1)} \rangle}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle + 2 \langle \Phi^{(1)} | \Phi^{(0)} \rangle + \langle \Phi^{(1)} | \Phi^{(1)} \rangle}$$

$$\frac{2 \langle \Phi^{(2)} | \hat{H} | \Phi^{(0)} \rangle}{2 \langle \Phi^{(2)} | \Phi^{(0)} \rangle} \tag{31}$$

where we have used the fact that only real wave functions are used in (31). Expanding the denominator and keeping terms through second order gives

$$\Delta E = \frac{1}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle} \left[ 2 \underset{\sim}{Y} + B^2 - E_0 A' \right] \underset{\sim}{\Delta} \tag{32}$$

where

$$\begin{aligned} B^2 = {} & \langle \Phi^{(1)} | \hat{H} | \Phi^{(1)} \rangle + 2(1 - \delta_{12}) \langle \Phi^{(2)} | \hat{H} | \Phi^{(0)} \rangle \\ & \frac{-4}{\langle \Phi^{(0)} | \Phi^{(0)} \rangle} \langle \Phi^{(0)} | \hat{H} - E_0 | \Phi^{(1)} \rangle \langle \Phi^{(1)} | \Phi^{(0)} \rangle \\ & - 2 E_0 (1 - \delta_{12}) \langle \Phi^{(0)} | \Phi^{(2)} \rangle \end{aligned} \tag{33}$$

As before, at convergence $\Delta E = 0$ and our equation becomes

$$-2 \underset{\sim}{Y} = (B^2 - E A') \underset{\sim}{\Delta} \tag{34}$$

which we solve for $\underset{\sim}{\Delta}$, the change in the wave function, and find the new wave function from (5).

## III. SOLUTION OF EQUATION

### A. Definitions and Notation

The GVB(SP) equations are solved using a basis set expansion. Letting $\{\chi_\mu\}$ be the set of basis functions (Greek letters will be used throughout to index basis functions), $\phi_k$ and $\delta\phi_k$ becomes

$$\phi_k = \sum_{\mu=1}^{NBF} \chi_\mu C_{\mu k} \tag{35}$$

$$\delta\phi_k = \sum_{\mu=1}^{NBF} \chi_\mu \Delta_{\mu k} \tag{36}$$

We will expand the GVB(SP) equations in terms of molecular integrals. To facilitate notation we define various quantities (being consistent with Reference 1). Define

$$V_{12} = \frac{1}{r_{12}} + \frac{h_1 + h_2}{(NX-1)} \tag{37}$$

where $h_i = \frac{1}{2}\nabla_i^2 + V_{\text{nuclear}}(i)$. Then the molecular integrals we need are

$$AMAM(\mu,i/\nu,j;NS) = \int \chi_\mu(1)_{LS}\, \phi_{i,NS}(2)\, V_{12}\, \chi_\nu(1)\, \phi_j(2)\, d\tau \tag{38}$$

$$AMMA(\mu,i/j,\nu;NS) = \int \chi_\mu(1)_{LS}\, \phi_i(2)_{NS}\, V_{12}\, \phi_j(1)\, \chi_\nu(2)\, d\tau \tag{39}$$

$$AAMM(\mu,\nu/i,j;NS) = \int \chi_\mu(1)_{LS}\, \chi_\nu(2)_{NS}\, V_{12}\, \phi_i(1)\, \phi_j(2)\, d\tau \tag{40}$$

$$AMMM(\mu,i/j,n;NS) = \int \chi_\mu(1)_{LS}\, \phi_i(2)_{NS}\, V_{12}\, \phi_j(1)\, \phi_n(2)\, d\tau \tag{41}$$

$$XMMM(i,j|m,n;NS) = \int \phi_i(1)_{LS}\, \phi_j(2)_{MS}\, V_{12}\, \phi_m(1)\, \phi_n(2)\, d\tau \qquad (42)$$

where LS = MS x NS and the symmetries not indicated on the right side of each integral indicate that a sum over all allowed symmetries on the right has been performed.

We define here the various density matrices. The basic definitions and indexing scheme are in Reference 1. The density matrices are as follows:

(i) DENOM $= \langle \Psi | \Psi \rangle$

There is one such term of each symmetry type.

(ii) DONE's are the coefficients of the one-electron terms. These will be denoted by $D1_{\ell}^{k}$, where k and $\ell$ are the electron numbers involved in the one-electron operator. Since there are NX choices for k and for $\ell$ and each orbital has NSYM symmetry types, there are (NX) x (NX) x (NSYM) different $D1_{\ell}^{k}$. The indexing is as described in Reference 1 for each block of a given symmetry.

(iii) DTWO's are the coefficients of two electron terms. These will be denoted as $D2_{\ell a}^{ks}$, $D2_{a\ell}^{ks}$ or $D2_{sa}^{k\ell}$, where k and $\ell$ will always denote excited orbitals and upper indices bra electrons. There are NX choices for the first upper (or lower) index, NX - 1 choices for the second upper (or lower) index, and NSYM choices for the symmetry of the D2's. Thus, there are $NX^2(NX-1)^2/2!$ NSYM D2's, since the order of electrons is immaterial.

(iv) DTHREE's are the coefficients of three electron terms. For three electrons there are 6 D3's and these are simply numbers. For four electrons there are $((4^2)(3^2)(2^2)/3!)$NSYM, or 96 D3's of each symmetry type.

(v) DFOUR's are the coefficients of four electron terms. There are 24 D4's for four electrons and they are simply numbers.

## B. Characteristics of Our Example Problem

In general we shall examine the various expressions which have been formally derived to display the full detail and complexity of these expressions. To avoid some unenlightening complexities, we shall use as an example the simplest possible choices, a three-electron system, G1 spin coupling, and two-symmetry types.

For three electrons there are two independent possible ways to couple the spins to a doublet state. We choose the orthogonal spin couplings[2]

$$\begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \equiv \frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)\alpha$$

$$\begin{array}{|c|c|}\hline \phi_1 & \phi_3 \\ \hline \phi_2 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \equiv \frac{1}{\sqrt{6}}(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)$$

The most general spin coupling for a three-electron doublet is some linear combination of G1 and GF. To simplify some expressions, only the G1 spin coupling will be used.

The GVB(SP) computer program may be used only for Abelian spatial groups. In general, non-Abelian spatial groups have multidimensional representations and the Kronecker product of two irreducible representations may be two or more irreducible representations and is therefore not precisely defined. For Abelian groups, the product of two irreducible representations is always a single irreducible representation. We will use in our example the simplest Abelian group consisting of two elements with a group representation multiplication table

|   | 1 | 2 |
|---|---|---|
| 1 | 1 | 2 |
| 2 | 2 | 1 |

1 will denote the totally symmetric representation.

Our final expressions will be fully general and be suitable for any spin coupling and any Abelian group.

## C. The Energy Expression

The zero order energy expression (12) after substituting (2) and cancelling spin functions is

$$E_0 = \frac{\langle P O_{11}^{\gamma}(\phi_1 \phi_2 \phi_3) | \hat{H} | P O_{11}^{\gamma}(\phi_1 \phi_2 \phi_3) \rangle}{\langle P O_{11}^{\gamma}(\phi_1 \phi_2 \phi_3) | P O_{11}^{\gamma}(\phi_1 \phi_2 \phi_3) \rangle} \qquad (43)$$

where $\gamma$ denotes a particular spin eigenfunction (G1 for our example) and $O_{11}$ is the Wigner projection operator which generates the appropriate spatial function[2]. P is the spatial projection operator.

Using the "turnover rule"[2a],

$$E_0 = \frac{\langle \phi_1 \phi_2 \phi_3 | \hat{H} | PO_{11}^{\gamma}(\phi_1 \phi_2 \phi_3)\rangle}{\langle \phi_1 \phi_2 \phi_3 | PO_{11}^{\gamma}(\phi_1 \phi_2 \phi_3)\rangle} \tag{44}$$

The denominator is DENOM and is equal to

$$D_{PS} = \sum_{\substack{\tau \in S_3 \\ l \neq k \\ n \neq l \neq k \\ LS, MS, NS}} \langle \phi_1 | \phi_k \rangle_{LS} \langle \phi_2 | \phi_l \rangle_{MS} \langle \phi_3 | \phi_n \rangle_{NS} \, U_{11}^{\gamma}(\tau) \tag{45}$$

$$PS = LS \times MS \times NS$$

The numerator is

$$\sum_{\substack{i \neq j \neq m \\ k \neq l \neq n \\ LS, MS}} \langle \phi_i \phi_j | V_{ij} | \phi_k \phi_l \rangle_{LS} \langle \phi_m | \phi_n \rangle_{MS} \, U_{11}^{\gamma}(\tau) \tag{46}$$

$$PS = LS \times MS$$

Generally

$$\begin{aligned} E_0 = \sum_{\mu=1}^{NBF} \Big\{ \sum_{b \neq k} \sum_{c} \sum_{d \neq c} \Big[ & AMMM(\mu, b | c, d; LS) \, D2(MS)_{cd}^{kb} \\ & + \sum_{a<b} \sum_{f \neq c} XMMM(a, b | f, d; LS) \, D3_{cfd}^{kab}(NS) \langle \mu | c \rangle_{MS} \Big] \\ & \times C_{\mu k} \Big\} \Big/ DENOM(PS) \end{aligned} \tag{47}$$

where the product of the symmetries in the numerator is restricted to be PS.

## D. First Order Variation in the Energy

Substituting (2) in (20), cancelling spin functions, and using the turnover rule, we get

$$\langle \phi_1 \phi_2 \phi_3 | \hat{H} | PO_{11}^{\gamma}(\delta\phi_k \, \phi_{k+1} \, \phi_{k+2}) \rangle - E_0 \langle \phi_1 \phi_2 \phi_3 | PO_{11}^{\gamma}(\delta\phi_k \, \phi_{k+1} \, \phi_{k+2}) \rangle$$
$$= 0 \qquad\qquad k=1,2,3 \tag{48}$$

and k+1 and k+2 are taken MOD 3 . Substituting (35) and (36), we generate a NBF x NBF matrix equation for each value of k (i.e., for each electron)

$$\sum_{\mu,\nu=1}^{NBF} C_{\mu k} \langle \chi_\mu \, \phi_{k+1} \, \phi_{k+2} | \hat{H} | PO_{11}^{\gamma}(\chi_\nu \, \phi_{k+1} \, \phi_{k+2}) \rangle$$
$$- E_0 \, C_{\mu k} \langle \chi_\mu \, \phi_{k+1} \, \phi_{k+2} | PO_{11}^{\gamma}(\chi_\nu \, \phi_{k+1} \, \phi_{k+2}) \rangle = 0$$
$$k=1,2,3 \tag{49}$$

These equations are solved by diagonalizing the coefficient of E , which is the metric for this space[3]. Any possible trivial changes in the wave function, i.e., changes which do not change the energy, will be manifest by zero eigenvalues of this matrix. These are removed by reducing the dimensionality of the space and then transformed to the space where the metric is the unit matrix. The transformed matrix is diagonalized, generating the spectrum of energies and eigenfunction. One-electron excited states may be generated by choosing a higher eigenvalue for a particular hamiltonian.

All hamiltonians may be diagonalized simultaneously, generating one new orbital for each electron. This process is reasonably efficient, but is not guaranteed to converge as the lower bound principle does not hold.

The first term in (49) is (ignoring $c_{\mu k}$)

$$\sum_{\substack{a \neq k \\ s \neq k \\ \gamma \in GI \\ b \neq a \neq k \\ c \neq s \neq k}} \Big\{ \langle \chi_\mu \phi_a | V_{ka} | \chi_\nu \phi_s \rangle_{LS} \langle \phi_b | \phi_c \rangle_{MS} U_{11}^{\gamma}(\tau) + \\ \langle \chi_\mu \phi_a | V_{ka} | \phi_s \chi_\nu \rangle_{LS} \langle \phi_b | \phi_c \rangle_{MS} U_{11}^{\gamma}(\tau) + \\ \langle \chi_\mu \phi_a | V_{ka} | \phi_s \phi_c \rangle_{LS} \langle \phi_b | \chi_\nu \rangle_{MS} U_{11}^{\gamma}(\tau) + \\ \langle \phi_a \phi_b | V_{ab} | \phi_s \chi_\nu \rangle_{LS} \langle \chi_\mu | \phi_c \rangle_{MS} U_{11}^{\gamma}(\tau) + \\ \langle \phi_a \phi_b | V_{ab} | \phi_s \phi_c \rangle_{LS} \langle \chi_\mu | \chi_\nu \rangle_{MS} U_{11}^{\gamma}(\tau) \Big\} \tag{50}$$

The coefficient of $E_0$ in (49) is

$$\sum_{\substack{a \neq k \\ b \neq k \\ c \neq a \neq k \\ d \neq b \neq k}} \Big\{ \langle \chi_\mu | \chi_\nu \rangle_{LS} \langle \phi_a | \phi_b \rangle_{MS} \langle \phi_c | \phi_d \rangle_{MS} U_{11}^{\gamma}(\tau) \\ + \langle \chi_\mu | \phi_b \rangle_{LS} \langle \phi_a | \chi_\nu \rangle_{MS} \langle \phi_c | \phi_d \rangle_{MS} U_{11}^{\gamma}(\tau) \Big\} \tag{51}$$

Generalizing, this equation becomes

$$\sum_{\substack{LS,MS\\NS}} \sum_{b\neq k} \sum_{c} \sum_{d\neq c} \Big\{ AMMM(\mu,b|c,d;LS)\, D2(MS)^{kb}_{cd} +$$

$$\sum_{a<b} \sum_{\substack{f\neq c\\ f\neq d}} XMMM(a,b|f,d;LS)\, S(\mu|c;MS)\, D3(NS)^{kab}_{cfd} \Big\}$$

$$- E_0 \sum_{c} S(\mu|c;LS)\, D1(MS)^{k}_{c} \quad = 0$$

(52)

where

$$S(\mu|c;LS) = \langle \chi_\mu | \phi_c \rangle_{LS} \qquad (53)$$

and the product of the symmetries is restricted to be PS, the symmetry of the state. It should be noted that for three electrons, D3 will be $U^{\gamma}_{11}(\tau)$, a number, and be totally symmetric necessarily.

## E. Second Order Energy Variation

Substituting (2) in (32), cancelling spin functions, and using the turnover rule, we get

$$-2 \Big[ \langle \phi_1 \phi_2 \phi_3 | \hat{H} | PO^{\gamma}_{11} (\delta\phi_k\, \phi_{k+1}\, \phi_{k+2}) \rangle \; -$$

$$E_0 \langle \phi_1 \phi_2 \phi_3 | PO^{\gamma}_{11} (\delta\phi_k\, \phi_{k+1}\, \phi_{k+2}) \rangle \Big] \; =$$

$$\langle \delta\phi_k\, \phi_{k+1} \phi_{k+2} | \hat{H} | PO^{\gamma}_{11} (\delta\phi_\ell\, \phi_{\ell+1}\, \phi_{\ell+2}) \rangle$$

$$- \frac{4}{\langle \phi_1 \phi_2 \phi_3 | PO_{11}^{\gamma} (\phi_1 \phi_2 \phi_3) \rangle} \Big[ \langle \phi_1 \phi_2 \phi_3 | \hat{H} - E_0 | PO_{11}^{\gamma} (\delta\phi_\ell \, \phi_{\ell+1} \, \phi_{\ell+2}) \rangle$$

$$\times \langle \delta\phi_k \, \phi_{k+1} \, \phi_{k+2} | PO_{11}^{\gamma} (\phi_1 \phi_2 \phi_3) \rangle \Big] -$$

$$E_0 \langle \delta\phi_k \, \phi_{k+1} \, \phi_{k+2} | PO_{11}^{\gamma} (\delta\phi_\ell \, \phi_{\ell+1} \, \phi_{\ell+2}) \rangle \qquad (54)$$

where k and $\ell$ are summed over all electrons and are taken MOD 3. Substituting (36) we generate a NB x NB matrix equation where NB = (NX) x (NBF). Letting $\Psi_k^{\mu}$ denote $\Psi^{(0)}$ with $\phi_k$ replaced by $\chi_\mu$

$$-\Delta_{\mu k} \langle \Psi^{(0)} | \hat{H} - E_0 | \Psi_k^{\mu} \rangle = \Delta_{\mu k} \Big[ \langle \Psi_k^{\mu} | \hat{H} | \Psi_\ell^{\nu} \rangle -$$

$$\frac{2}{DENOM} \langle \Psi^{(0)} | \hat{H} - E_0 | \Psi_k^{\mu} \rangle \langle \Psi_\ell^{\nu} | \Psi^{(0)} \rangle -$$

$$E_0 \langle \Psi_k^{\mu} | \Psi_\ell^{\nu} \rangle \Big] \Delta_{\nu \ell} \qquad (55)$$

or

$$-\sum_{\mu=1}^{NBF} \sum_{k}^{NX} \Delta_{\mu k} \Big[ \langle \phi_1 \phi_2 \phi_3 | \hat{H} - E_0 | PO_{11}^{\gamma} (\chi_\mu \, \phi_{k+1} \, \phi_{k+2}) \rangle \Big] =$$

$$\sum_{\mu,\nu=1}^{NBF} \sum_{k,\ell=1}^{NX} \Delta_{\mu k} \Big[ \langle \chi_\mu \, \phi_{k+1} \, \phi_{k+2} | \hat{H} | PO_{11}^{\gamma} (\chi_\nu \, \phi_{\ell+1} \, \phi_{\ell+2}) \rangle \Delta_{\nu \ell}$$

$$- \frac{2}{DENOM} \langle \chi_\mu \, \phi_{k+1} \, \phi_{k+2} | PO_{11}^{\gamma} (\phi_1 \phi_2 \phi_3 \rangle \quad X$$

$$\langle \phi_1 \phi_2 \phi_3 | \hat{H} - E_0 | PO_{11}^{\gamma} (\chi_\nu \, \phi_{\ell+1} \, \phi_{\ell+2}) \rangle \Delta_{\nu \ell}$$

$$-E_0 \langle \chi_\mu \, \phi_{k+1} \, \phi_{k+2} | PO_{11}^{\gamma} (\chi_\nu \, \phi_{\ell+1} \, \phi_{\ell+2}) \rangle \Delta_{\nu \ell} \Big]$$

(56)

Expanding $O_{11}$ and H will generate a series of terms similar to those developed in the previous section for the first order equation. The general form of (56) is

$$\sum_{\mu,k} \Delta_{\mu k} \sum_{\nu,l} \left( B'^{\mu k}_{\nu l} - E_0 A^{\mu k}_{\nu l} \right) \Delta_{\nu l} = -\sum \Delta_{\mu k} X_{\mu k} \tag{57}$$

where we define

$$\begin{aligned} X_{\mu k} = \sum_{\text{SYMMETRIES}} \sum_{c} \sum_{\substack{b \ne k \\ d \ne c}} \Big[ & AMMM(\mu,b|c,d;LS)\, D2(MS)^{k\,b}_{c\,d} \\ & + \sum_{a<b} \sum_{\substack{f \ne c \\ \ne d}} XMMM(a,b|f,d;LS)\, S(\mu|c;MS)\, D3(NS)^{k\,a\,b}_{c\,f\,d} \Big] \\ & - E_0 \sum_{c} S(\mu|c;LS)\, D1(MS)^{k}_{c} \end{aligned} \tag{58}$$

$$\begin{aligned} A^{\mu k}_{\nu l} = \sum_{\text{SYMMETRIES}} \Big[ & S(\mu,\nu;LS)\, D1(MS)^{k}_{l} + \\ & \sum_{\substack{a \ne k \\ s \ne l}} S(\mu|s;LS)\, S(\nu|a;MS)\, D2(NS)^{k\,a}_{s\,l} \Big] \end{aligned} \tag{59}$$

$$\begin{aligned} B'^{\mu k}_{\nu l} = \sum_{\text{SYMMETRIES}} \Big[ \sum_{\substack{a \ne k \\ s \ne l}} \Big[ & AMAM(\mu,a|\nu,s;LS)\, D2(MS)^{k\,a}_{l\,s} \\ & + AMMA(\mu,a|s,\nu;LS)\, D2(MS)^{k\,a}_{s\,l} \quad + \\ & \sum_{\substack{b \ne a \\ \ne k}} \sum_{\substack{t \ne s \\ \ne l}} \Big[ AMMM(\mu,b|s,t;LS)\, S(\nu|a;MS)\, D3(NS)^{k\,a\,b}_{s\,l\,t} \\ & + AMMM(\nu,t|a,b;LS)\, S(\mu|s;MS)\, D3(NS)^{k\,a\,b}_{s\,l\,t} \end{aligned}$$

$$+ XMMM(a,b|s,t;LS)\,S(\mu|\nu;MS)\,D3(NS)^{kab}_{lst} +$$

$$\sum_{\substack{c<b\\ \neq a\\ \neq k}} \sum_{\substack{u\neq t\\ \neq s\\ \neq l}} XMMM(b,c|t,u;LS)\,S(\mu|s;MS)\,S(\nu|a;NS)\,D4(NS)^{kabc}_{sltu} \Big]\Big]\Big]$$

$$-\frac{2}{DENOM} \sum_{b\neq k} \sum_{c} \sum_{d\neq c} \Big[ AMMM(\mu,b|c,d;LS)\,D2(MS)^{kb}_{cd}$$

$$+ \sum_{\substack{a<b\\ \neq k}} \sum_{\substack{f\neq c\\ \neq d}} XMMM(a,b|f,d;LS)\,S(\mu|c;MS)\,D3(NS)^{kba}_{cdf} \Big]$$

$$\times \Big[ \sum_{i} S(\mu|i;LS)\,D1(MS)^{l}_{i} \Big] \tag{60}$$

and the sum over symmetries is restricted so that the product of the symmetries is equal to PS, the symmetry of the state.

Equation (57) must hold for each independent value of $\Delta_{\mu k}$; by comparing coefficients of $\Delta_{\mu k}$ we obtain

$$\sum_{\nu,l} \left( B'^{\,\mu k}_{\nu l} - E_0 A^{2\,\mu k}_{\nu l} \right) \Delta_{\nu l} = - X_{\mu k} \tag{61}$$

Equation (61) is solved for $\Delta_{\nu l}$ and the new wave function is given by

$$\Psi^{(i+1)}_{\nu l} = \Psi^{(i)}_{\nu l} + \Delta_{\nu l} \tag{62}$$

Equation (61) is solved by first diagonalizing $A^2$ to yield the space of unique changes to the wave function as discussed in Section I. $B^1$ and $\underset{\sim}{X}$ are transformed to the space where $A^2$ is diagonal and has only positive, nonzero eigenvalues. $B^1$ is then inverted to find $\underset{\sim}{\Delta}$ .

## F. Second Order Orbital Variation

Equation (33) will be herein expanded into full detail. This equation is developed by examining the second order change in the energy resulting from second order changes in the wave function. Equation (33) is analogous to Newton's method for solving differential equations.

Substituting (2) in (33), cancelling spin functions and employing the rollover rule leads to

$$\begin{aligned}
&-2\langle\phi_1\phi_2\phi_3|\hat{H}|PO_{11}^{\gamma}(\delta\phi_k\,\phi_{k+1}\,\phi_{k+2})\rangle - \\
&\quad E_0\langle\phi_1\phi_2\phi_3|PO_{11}^{\gamma}(\delta\phi_k\,\phi_{k+1}\,\phi_{k+2})\rangle \quad = \\
&\langle\delta\phi_k\,\phi_{k+1}\,\phi_{k+2}|\hat{H}|PO_{11}^{\gamma}(\delta\phi_\ell\,\phi_{\ell+1}\,\phi_{\ell+2})\rangle \quad + \\
&(1-\delta_{k\ell})\langle\phi_1\phi_2\phi_3|\hat{H}-E_0|PO_{11}^{\gamma}(\delta\phi_k\,\delta\phi_\ell\,\phi_m)\rangle \\
&\frac{-\;4}{\langle\phi_1\phi_2\phi_3|PO_{11}^{\gamma}(\phi_1\phi_2\phi_3)\rangle}\langle\phi_1\phi_2\phi_3|\hat{H}-E_0|PO_{11}^{\gamma}(\delta\phi_k\,\phi_{k+1}\,\phi_{k+2})\rangle \\
&\times\langle\delta\phi_\ell\,\phi_{\ell+1}\,\phi_{\ell+2}|PO_{11}^{\gamma}(\phi_1\phi_2\phi_3)\rangle \quad - \\
&\quad E_0\langle\delta\phi_k\,\phi_{k+1}\,\phi_{k+2}|PO_{11}^{\gamma}(\delta\phi_\ell\,\phi_{\ell+1}\,\phi_{\ell+2})\rangle
\end{aligned} \qquad (63)$$

Substituting (36) and using the notation introduced prior to (55), (63) becomes

$$
\begin{aligned}
-\sum \Delta_{\mu k} \langle \Psi^{(0)} | \hat{H} - E_0 | \Psi_k^{\mu} \rangle = \sum_{\mu,k} \Delta_{\mu k} \Big[ & \sum_{\nu,l} \\
& \langle \Psi_k^{\mu} | \hat{H} | \Psi_l^{\nu} \rangle \Delta_{\nu l} + \sum_{\nu,l} (1-\delta_{kl}) \langle \Psi^{(0)} | \hat{H} - E_0 | \Psi_{kl}^{\mu\nu} \rangle \Delta_{\nu l} \\
& - \frac{2}{\text{DENOM}} \sum_{\nu,l} \langle \Psi^{(0)} | \hat{H} - E_0 | \Psi_k^{\mu} \rangle \langle \Psi_l^{\nu} | \Psi^{(0)} \rangle \Delta_{\nu l} \\
& - E_0 \sum_{\nu,l} \langle \Psi_k^{\mu} | \Psi_l^{\nu} \rangle \Delta_{\nu l} \Big]
\end{aligned}
\tag{64}
$$

where $\Psi_{kl}^{\mu\nu}$ denotes $\Psi^{(0)}$ with $\phi_k$ replaced by $\chi_\mu$ and $\phi_l$ replaced by $\chi_\nu$ . Since (64) is similar to (55), when expanded it will be similar to (56). For n electrons (64) becomes

$$
\sum_{\mu,k} \Delta_{\mu k} \sum_{\nu,l} \left( B_{\nu l}^{2\,\mu k} - E_0 A_{\nu l}^{2\,\mu k} \right) \Delta_{\nu l} = - \sum_{\mu,k} \Delta_{\mu k} X_{\mu k}
$$

where $A^2$ is given by (59), $X$ by (58), and $B^2$ is

$$
\begin{aligned}
B_{\nu l}^{2\,\mu k} = \sum_{\text{SYMMETRIES}} \Bigg\{ \sum_{\substack{a \neq k \\ s \neq l}} \Big[ & \text{AMAM}(\mu, a/\nu, s; LS)\, \text{D2}(MS)_{l\,s}^{k\,a} \\
& + \text{AMMA}(\mu, a/s, \nu; LS)\, \text{D2}(MS)_{s\,l}^{k\,a} + \\
(1-\delta_{kl})\, & \text{AAMM}(\mu, \nu/s, a; LS)\, \text{D2}(MS)_{s\,a}^{k\,l} - E_0\, S(\mu/s; LS)\, S(\nu/a; MS) \\
& \times \text{D2}(MS)_{s\,l}^{k\,a} + \sum_{\substack{b \neq a \\ b \neq k}} \sum_{\substack{t \neq s \\ t \neq l}} \Big[ \text{AMMM}(\mu, b/s, t; LS)
\end{aligned}
$$

$$\times\, S(\nu|a;MS)\,D3(NS)^{k\,a\,b}_{s\,l\,t} \quad +$$

$$AMMM(\nu,t|a,b;LS)\,S(\mu|s;MS)\,D3(NS)^{k\,a\,b}_{s\,l\,t} \quad +$$

$$XMMM(a,b|s,t;LS)\,S(\mu|\nu;MS)\,D^{k\,a\,b}_{l\,s\,t} \quad +$$

$$(1-\delta_{kl})\Big[AMMM(\mu,b|s,t;LS)\,S(\nu|a;MS)\,D3(NS)^{k\,l\,b}_{s\,a\,t}$$

$$AMMM(\nu,b|a,t;LS)\,S(\mu|s;MS)\,D3(NS)^{k\,l\,b}_{s\,a\,t}\Big] \quad +$$

$$\sum_{\substack{c<b \\ c\neq a \\ c\neq k}} \sum_{\substack{u\neq t \\ \neq s \\ \neq l}} \Big[XMMM(b,c|t,u;LS)\,S(\mu|s;MS)\,S(\nu|a;NS)\,D4(KS)^{k\,a\,b\,c}_{s\,l\,t\,u}$$

$$+(1-\delta_{kl})\,XMMM(b,c|t,u;LS)\,S(\mu|s;MS)\,S(\nu|a;NS)\,D4(KS)^{k\,l\,b\,c}_{s\,a\,t\,u}\Big]\Big]$$

$$-\frac{2}{DENOM}\Big[\sum_{b\neq k}\sum_{c}\sum_{d\neq c}\Big[AMMM(\mu,b|c,d;LS)\,D2(MS)^{k\,b}_{c\,d}$$

$$+\sum_{\substack{a<b \\ a\neq k}} \sum_{\substack{f\neq c \\ \neq d}} XMMM(a,b|f,d;LS)\,S(\mu|c;MS)\,D3(NS)^{k\,b\,a}_{c\,d\,f}\Big]\Big]$$

$$\times \sum_{i} S(\mu|i;LS)\,D1(MS)^{l}_{i}$$

(65)

Equation (65) must hold for all $\Delta_{\mu k}$ as these are linear independent. By comparing coefficients of $\Delta_{\mu k}$ we obtain

$$\sum_{\nu,\lambda} \left( B^{2\ \mu k}_{\nu\lambda} - E_0 A^{2\ \mu k}_{\nu\lambda} \right) \Delta_{\nu\lambda} = - Y_{\mu k}$$

This is solved identically to (61) for $\Delta_{\nu\ell}$ which are the changes in the wave function given by (62).

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3. George Levin, Candidacy Report, California Institute of Technology (1971), unpublished

# APPENDIX VIII

## THE GENERATION OF IRREDUCIBLE MATRIX REPRESENTATIONS OF THE SYMMETRIC GROUP ON N OBJECTS

## I. INTRODUCTION

The symmetric group on n objects (denoted throughout by $S_n$) is intimately involved in some calculation techniques of molecular quantum mechanics. GI and spin optimized GI (SOGI) methods incorporate all n! elements of $S_n$. The configuration interaction (CI) method using an orthogonal basis of spin eigenfunctions requires the matrices representing all transpositions, i.e., an interchange of two objects.

It is well known that an entire representation of $S_n$ is characterized by the n-1 generators, $P(1,2)$, $P(1,3) \cdots P(1,n)$. Further, these generators can be found by

$$P(1, L) = P(L, L-1)\, P(1, L-1)\, P(L, L-1) \tag{1}$$

so that it is sufficient to generate the matrices representing adjacent interchanges. If an entire representation is required, it may be calculated from the generators by not more than N matrix multiplications.[1]

Gabriel[2] has developed a method for calculating the matrices representing adjacent interchanges of $S_n$. This method is suitable to programming on a digital computer. In section II, Gabriel's method will be outlined. The computer program incorporating this method is listed in section III and an example reported in section IV.

## II. THEORETICAL DISCUSSION

Let M be the total number of electrons and k the number of beta (or down) spin electrons. S (M, k) will denote a particular Young's shape[3] and (M, k) a particular representation.

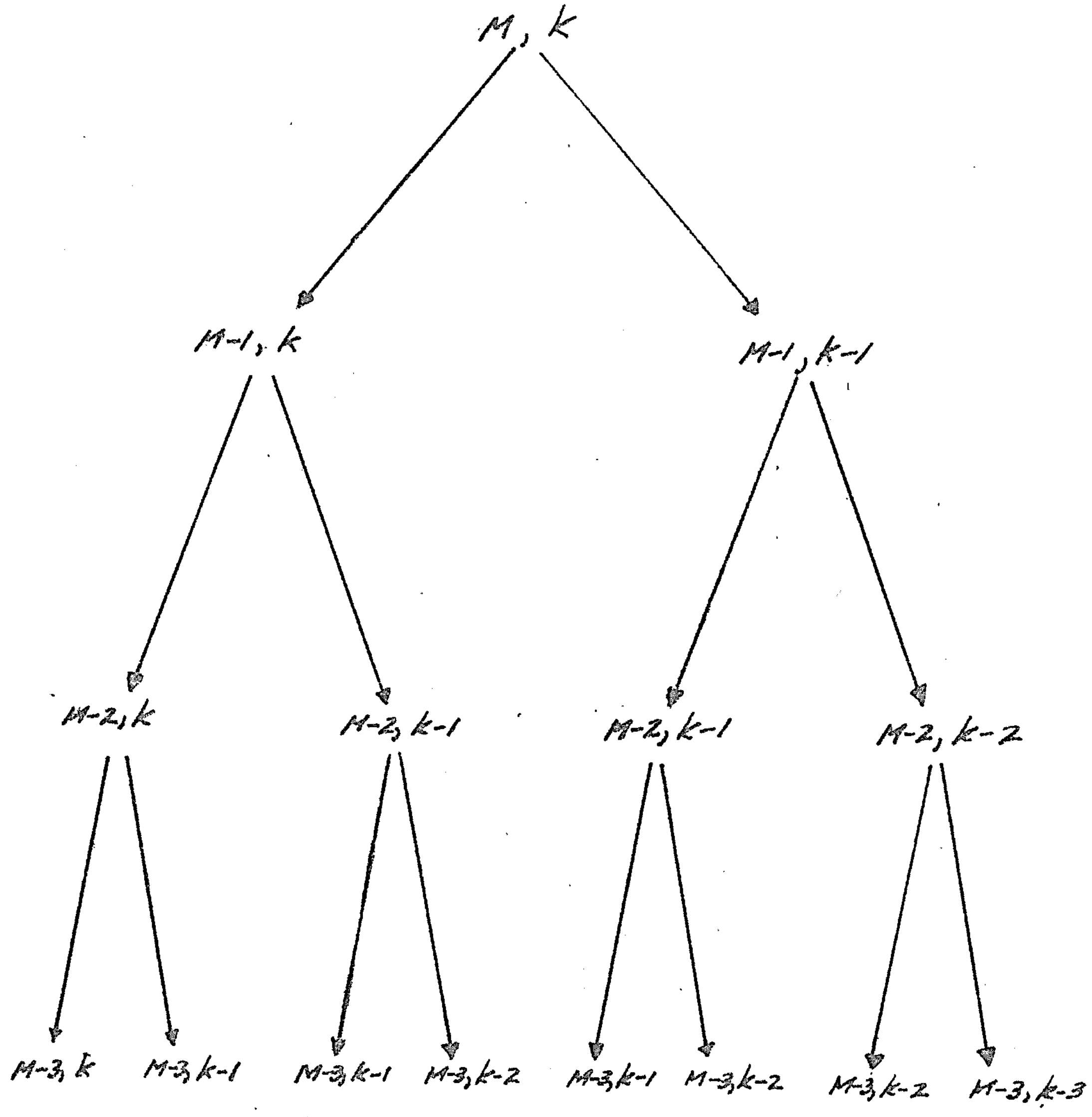
Let (N, k) be an irreducible, unitary representation of $S_N$. Because $S_N$ contains $S_{N-1}$ as a subgroup, the basis space S (N, k) affords a representation of $S_{N-1}$. This is either irreducible or completely reducible since the representation is unitary; S (N, k) is either reducible with respect to $S_{N-1}$ or it can be subdivided into mutually orthogonal irreducible subspaces with respect to $S_{N-1}$. Let us choose the particular subgroup of $S_N$ which leaves N untouched. Similarly, the subspaces which are irreducible with respect to $S_{N-1}$ are either irreducible with respect to $S_{N-2}$ or can be further subdivided into irreducible subspaces with respect to $S_{N-2}$. It follows, that there exists a basis for an irreducible, unitary representation of $S_N$ in which the matrix representations of the subgroups $S_N$, $S_{N-1}$, $S_{N-2}$, $\cdots$ $S_2$ appear fully reduced.

It has been proved[2] that S (M, k) is reducible into S (M-1, k-1) and S (M-1, k) with respect to $S_{M-1}$ unless (1) $k = 0$, when $S(M, 0) \equiv S(M-1, 0)$ or (2) M is even and $k = \frac{1}{2} M$ when $S(M, \frac{1}{2} M) \equiv S(M-1, \frac{1}{2} M-1)$.

The successive reduction of the representations $S_{N-1}$, $S_{N-2}$ $\cdots$ in (N, k) and the corresponding subdivision of S (N, k) can be displayed in a family tree. An example is shown in Figure 1. The order of the

FIGURE 1

A FAMILY TREE
TO LEVEL THREE



k-value in each generation is fixed by constructing the tree so that the two descendants of a general k-value at level M are written in order k-1, k at level M-1 and by requiring that descendants or pairs of descendants at level M-1 appear in the same order as their parents at level M. This ensures that blocks of terms at level 2 which are descendants of individual terms at level M appear consecutively in the same order as their ancestors and that blocks at level 2 descended from terms at level M having the same k-value are identical.

For example, for $M = 6$ and $k = 2$, the sequence of terms is in Table 1.[4]

TABLE 1

| Level | k-sequence |
|---|---|
| 6 | 2 |
| 5 | 2, 1 |
| 4 | 2, 1, 1, 0 |
| 3 | 1, 1, 0, 1, 0, 0 |
| 2 | 1, 0, 1, 0, 0, 1, 0, 0, 0 |

To calculate the representation of $P(M, M-1)$ in $S(N, k)$, we need to know the dimension of all the spaces $S(M, k_i)$ that appear in the family tree of k-sequences. Since the space $S(M, k)$ can be divided into two parts, it follows

$$D(M, k) = D(M-1, k-1) + D(M-1, k) \tag{2}$$

except for

$$k = 0; \quad D(M, 0) = D(M-1, 0) \tag{3}$$

$$k = \tfrac{1}{2} M (M_{\text{even}}); \; D(M, \tfrac{1}{2} M) = D(M-1, \; \tfrac{1}{2} M-1) \tag{4}$$

Since $D(1, 0) = 1$, all other cases can be calculated using (2)-(4). For example $S_2$ has two irreducible representations (2, 1) and (2, 0). (2, 1) has $k = \frac{1}{2} M$ and $M_{\text{even}}$, so $D(2, 1) = D(1, 0) = 1$. (2, 0) has $k = 0$ so $D(2, 0) = D(1, 0) = 1$. $S_3$ has two irreducible representations (3, 0) and (3, 1). $D(3, 0) = D(2, 0) = 1$. Using (2)

$$D(3, 1) = D(2, 0) + D(2, 1) = 2$$

Since all representations of $S_2$ are one-dimensional, we may take the base vectors $e_i$ of our representations to be the one-dimensional spaces $S(2, k_i)$ given as an ordered set by the k-sequence at level 2. Doing this ensures that the matrix representative of an element of $S_N$ in $S(N, k)$ has its representatives in the spaces $S(M, k_i)$ arranged down the diagonals of the matrices in the order given by the k-sequence at level M, where $M < N$ and $k \leqslant k$.

The details of the calculation of $P(M, M-1)$ are given in reference 2. Here only the results are given.

If $S(M, k_i)$ is subdivided according to its descendants at level M-2 and the matrix partitioned accordingly, the matrix appears in the form of Figure 2.[4] The corresponding k-tree is also shown to the right of the matrix. For certain k-values, some of the subspaces at level M-2 are excluded because of the special k-values discussed above. Table 2 summarizes these results.

# FIGURE 2

$$\begin{array}{r|c:c:c:c|}
S(M-2,K) & \begin{matrix}-1 & & & \\ & -1 & & \\ & & \ddots & \\ & & & -1 & \\ & & & & -1\end{matrix} & & & \\
\hdashline
S(M-2,K-1) & & \begin{matrix}-\lambda & & & \\ & -\lambda & & \\ & & \ddots & \\ & & & -\lambda & \\ & & & & -\lambda\end{matrix} & \begin{matrix}\mu & & & \\ & \mu & & \\ & & \ddots & \\ & & & \mu & \\ & & & & \mu\end{matrix} & \\
\hdashline
S(M-2,K-1) & & \begin{matrix}\mu & & & \\ & \mu & & \\ & & \ddots & \\ & & & \mu & \\ & & & & \mu\end{matrix} & \begin{matrix}\lambda & & & \\ & \lambda & & \\ & & \ddots & \\ & & & \lambda & \\ & & & & \lambda\end{matrix} & \\
\hdashline
S(M-2,K-2) & & & & \begin{matrix}-1 & & & \\ & -1 & & \\ & & \ddots & \\ & & & -1 & \\ & & & & -1\end{matrix}
\end{array}$$

A TYPICAL MATRIX

TABLE 2

| M | k | Excluded spaces |
|---|---|---|
| any | 0 | $S(M-2, k-2)$ |
| | | $S_1(M-2, k-1)$ |
| | | $S_2(M-2, k-2)$ |
| any | 1 | $S(M-2, k-2)$ |
| even | M/2 | $S_2(M-2, k-1)$ |
| | | $S(M-1, k)$ |
| odd | M/2 | $S(M-2, k)$ |

The values of $\mu$ and $\lambda$ in Figure 2 are given by

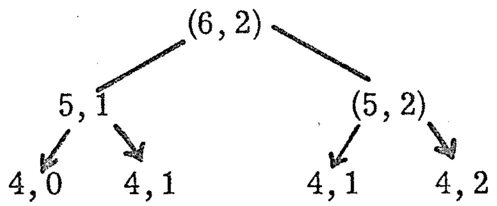
$$\lambda = \frac{1}{M - 2k_i + 1} \tag{5}$$

$$\mu = \sqrt{1 - \lambda^2} \tag{6}$$

For illustrative purpose, two examples will be worked, $P(5, 6)$ and $P(4, 5)$ in $S(6, 2)$.

1) P (5, 6) in S(6, 2)

Since the space S(6, 2) is the smallest space invariant under P(5, 6), the results in Figure 2 apply. The family tree is



There is only one term in the k-sequence M = 6, k = 2 and

$$\lambda = \frac{1}{M - 2k + 1} = \tfrac{1}{3}$$

$$\mu = \sqrt{1 - \lambda^2} = \sqrt{8/9}$$

The dimensions are

$$D(4,0) = 1$$
$$D(4,1) = 3$$
$$D(4,2) = 2$$

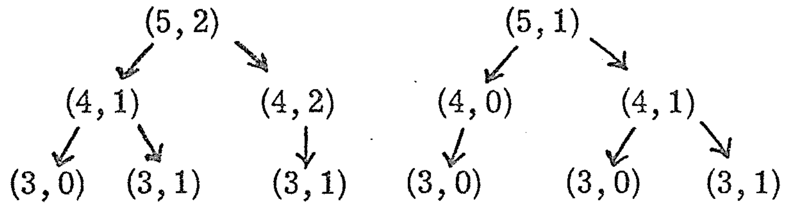
Thus

$$P(5,6) = \begin{array}{l} S(4,2) \\ \\ \\ S(4,1) \\ \\ S(4,1) \\ \\ \\ S(4,0) \end{array} \left[\begin{array}{cc|ccc|ccc|c} -1 & 0 & & & & & & & \\ 0 & -1 & & & & & & & \\ \hline & & -\frac{1}{3} & 0 & 0 & \sqrt{8/9} & 0 & 0 & \\ & & 0 & -\frac{1}{3} & 0 & 0 & \sqrt{8/9} & 0 & \\ & & 0 & 0 & -\frac{1}{3} & 0 & 0 & \sqrt{8/9} & \\ \hline & & \sqrt{8/9} & 0 & 0 & \frac{1}{3} & 0 & 0 & \\ & & 0 & \sqrt{8/9} & 0 & 0 & \frac{1}{3} & 0 & \\ & & 0 & 0 & \sqrt{8/9} & 0 & 0 & \frac{1}{3} & \\ \hline & & & & & & & & -1 \end{array}\right]$$

where the matrix has been written in block form and all not shown, elements are zero.

2) P(4,5) of S(6,2)

There are two terms in the k-sequence at level 5, S(5,1) and S(5,2). The family trees are



The representations of (4,5) in these subspaces are calculated as

$$\lambda(5,2) = \tfrac{1}{2}$$

$$\mu = \sqrt{3}/2$$

$$\begin{array}{c} P(4,5) \\ S(5,2) \end{array} = \begin{array}{r} S(3,1) \\ \\ S(3,1) \\ \\ S(3,0) \end{array} \left[ \begin{array}{cc|cc|c} -\frac{1}{2} & 0 & \sqrt{3}/2 & 0 & \\ 0 & -\frac{1}{2} & 0 & \sqrt{3}/2 & \\ \hline \sqrt{3}/2 & 0 & \frac{1}{2} & & \\ 0 & \sqrt{3}/2 & 0 & \frac{1}{2} & \\ \hline & & & & -1 \end{array} \right]$$

$$\lambda(5,1) = \tfrac{1}{4}$$

$$\mu = \tfrac{1}{4}\sqrt{5}$$

$$\begin{array}{c} P(4,5)= \\ S(5,1) \end{array} \begin{array}{r} S(3,1) \\ \\ S(3\mu) \\ \\ S(3P) \end{array} \left[ \begin{array}{cc|c|c} -\frac{1}{4} & \frac{1}{4}\sqrt{5} & & \\ \frac{1}{4}\sqrt{5} & \frac{1}{4} & & \\ \hline & & -1 & \\ \hline & & & -1 \\ & & & \end{array} \right] \begin{array}{c} \\ \\ \\ \\ -1 \end{array}$$

The final matrix is assembled in the order S(5,2) S(5,1).

# III. THE COMPUTER PROGRAM

## A. Outline:

The program essentially duplicates the theory. First the dimensions of all possible subspaces are calculated and stored in the array D. The dimension of S(M, K) is stored in location D(M, K + 1).

The family tree is calculated and the k values stored in K CASE linearly. The corresponding M values are stored in I CASE linearly. NTM holds the number of K CASE entries associated with each I CASE entry. MTM holds the (starting point-1) of the K CASE entries for each I CASE entry.

The matrices for M up to and including 4 are internally included and are entered as appropriate without calculations. The actual calculations are performed as outlined in section II.

## B. Input:

The input is simple, only 2 cards.

1) Title in format (10A8)
2) M, K, I STOP in format (3IS)
   M is the number of electrons
   K is the number of beta spin electrons
   I STOP = 0 final data
   ≠ 0 read another data set

## C. The program:

```
C     PROGRAM TO CALCULATE MATRIX REPRESENTATIONS FOR ADAJACENT
C      INTERCHANGES
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 LAMBDA,MU
      INTEGER*2 D(10,6),ICASE(10),KCASE(100),NTM(10),MTM(10)
      DIMENSION U(52)
      DIMENSION UT(2000)
      DIMENSION TITLE(10)
C     DIMENSIONS REQUIRED:
C        D(M,K+1)
C        ICASE(M-1)
C        UT((DM**2)*(M-1))
C        KCASE(1+2+2**2+...2**M-1)
C        WHERE M IS THE NUMBER OF ELECTRONS, K IS THE NUMBER OF BETA
C         SPIN ELECTRONS, AND DM IS THE DIMENSION OF THE REPRESENTATION
C         OF S(M)
      DATA U/2*-1.0D00,1.0D00,2*0.0D00,-1.0D00,-0.5D00,
     #2*0.866025403784439D00,
     &0.5D00,3*-1.0D00,1.0D00,3*0.0D00,-1.0D00,3*0.0D00,-1.0D00,-0.5D00,
     &0.866025403784439D00,0.0D00,0.866025403784439D00,0.5D00,3*0.0D00
     &,2*-1.0D00,3*0.0D00,-0.333333333333333D00,0.942809041582063D00,
     &0.0D00,0.942809041582063D00,0.333333333333333D00,1.0D00,2*0.0D00,
     #-1.0D00,-0.5D00,2*0.866025403784439D00,0.5D00,1.0D00,2*0.0D00,
     #-1.0D00/
    1 READ(5,1100) (TITLE(I),I=1,10)
      READ(5,1000) M,K,ISTOP
      KM2 = K -2
      N = M
      ITERM = 1
      DO 10 I=2,M
      ICASE(ITERM) = N
      N = N - 1
      ITERM = ITERM + 1
   10 CONTINUE
      ITERM = ITERM -1
      WRITE(6,1200) (TITLE(I),I=1,10)
      WRITE(6,1001) M,K,ITERM
       ITERM2 = ITERM*ITERM
      KP1 = K + 1
C     CALCULATE DIMENSIONS OF EACH S(M,K) BLOCK
      DO 17 I=1,M
      DO 18 J=1,KP1
      D(I,J) = 0
   18 CONTINUE
   17 CONTINUE
      D(2,1) = 1
      D(2,2) = 1
      DO 20 I=3,M
      D(I,1) = 1
      IM1 = I - 1
      IO2 = I/2
      DO 25 J=2,KP1
      JM1 = J-1
      IF (JM1 .GT. IO2) GO TO 25
      D(I,J) = D(IM1,JM1) + D(IM1,J)
   25 CONTINUE
```

```
   20 CONTINUE
C     DIMENSION OF S(M,K) STORED IN D(M,K+1)
C
C     CALCULATE THE BRANCHING TREE
      DO 22 I=1,10
      NTM(I) = 0
      MTM(I) = 0
   22 CONTINUE
      DO 23 I=1,100
   23 KCASE(I) = -1
      MTERM = 1
      NTERM=1
      I=1
       KCASE(1) = K
      L = M
      MTM(1) = 0
      NTM (1) = 1
   75 CONTINUE
      LM1 = L - 1
      LO2 = LM1/2
      I = I + 1
      MT = MTERM
      DO 35 J=1,NTERM
      JJ = J + MT
      JJO2 = JJ/2
      LL = KCASE(JJO2)
      IF (LL .LE. LO2) KCASE(JJ) = LL
      IF (LL .GT. 0) KCASE(JJ+1) = LL -1
      MT = MT +1
   35 CONTINUE
      MTM(I) = MTERM
      NTERM = 2*NTERM
      MTERM = MTERM + NTERM
      NTM(I) = NTERM
      L = L -1
      IF (L .GT. 2) GO TO 75
C     NOW CALCULATE THE U MATRICES IN ASCENDING ORDER
      ND = D(M,K+1)
      ND2 = ND*ND
      MM1 = M -1
      NUT = ND2*MM1
      DO 80 I=1,NUT
   80 UT(I) = 0.0D00
      LSTART = 1
      NN = ICASE(ITERM)
      MTERM = MTM(ITERM)
      NTERM = NTM(ITERM)
      DO 90 JJ=1,NTERM
      JM = JJ + MTERM
      IF (KCASE(JM) .LT. 0) GO TO 90
      LAMBDA = 1.0D00
      IF (KCASE(JM) .EQ. 0) LAMBDA = - LAMBDA
      UT(LSTART) = LAMBDA
      LSTART = LSTART + ND + 1
   90 CONTINUE
C     WE HAVE NOW CALCULATED U(1,2)
```

```
C
C     WE NOW PROCEDE TO THE OTHER PERMUTATIONS
      KK = ITERM - 1
   99 NN = ICASE(KK)
C     PERMUTATION IS (NN-1,NN)
      LSTART = (NN-2)*ND2
      NTERM = NTM(KK)
      MTERM = MTM(KK)
      IF (NN .LT. 5) GO TO 98
      NTK =NTM(KK+2)/NTERM
      MTK = MTM(KK+2)
      NNM2 = NN-2
C     MTERM IS THE LOCATION-1 IN KCASE WHERE THE K VALUES ARE STORED
C     NTERM IS THE NUMBER OF SUCH TERMS APPLICABLE TO NN
      ISTART = 1
      ISTOP = NTK
      LSTART = LSTART + 1
      DO 100 II=1,NTERM
      INDX = II + MTERM
      L = KCASE(INDX)
      IF (L .LT. 0) GO TO 103
      LM2 = L -2
      ISM1=ISTART-1
      DO 105 IJ=ISTART,ISTOP
      LL = KCASE(IJ+MTK)
      IF (LL .LT. 0) GO TO 105
      NDL = D(NNM2,LL+1)
C     NDL IS THE DIMENSION OF THIS BLOCK OF THE U MATRIX
      LAMBDA = - 1.0D00
      MU = 0.0D00
      IF (LL .EQ. L .OR. LL .EQ. LM2) GO TO 110
      TEMP = DFLOAT(NN-2*L + 1)
      LAMBDA = - 1.0D00/TEMP
      MU = DSQRT(1.0D00 - LAMBDA*LAMBDA)
      NSTEP = NDL
      LLL=KCASE(IJ-1+MTK)
      IF (LLL .EQ. LL) LAMBDA=-LAMBDA
      IF (LAMBDA .GT. 0.0D00) NSTEP = - NSTEP
      IF ( (IJ-ISM1) .GT. NTK/2 .AND. LLL .EQ. -1) LAMBDA=-LAMBDA
      DO 115 LN=1,NDL
      LNDX = LSTART
      LMU = LNDX + ND*NSTEP
      UT(LNDX) = LAMBDA
      UT(LMU) = MU
  115 LSTART = LSTART + ND + 1
      GO TO 105
  110 DO 120 LN=1,NDL
      LNDX = LSTART
      UT(LNDX) = LAMBDA
  120 LSTART = LSTART + ND + 1
  105 CONTINUE
  103 ISTART=ISTOP+1
      ISTOP = ISTOP + NTK
  100 CONTINUE
      GO TO 102
   98 CONTINUE
```

```
      DO 101 JK=1,NTERM
      JNDX = JK + MTERM
      L = KCASE(JNDX)
      IF (L .LT. 0) GO TO 101
      NDL = D(NN,L+1)
      NDL2 = NDL*NDL
      NSTART = (NN-3)*10
      IF (L .EQ. 0) GO TO 133
      DO 132 LS=1,L
      NND = D(NN,LS)**2
      NSTART = NSTART + (NN-1)*NND
  132 CONTINUE
  133 CONTINUE
      NSTART = NSTART + (NN-2)*NDL2
       ML = 0
      DO 134 MK=1,NDL
      DO 131 MM=1,NDL
      ML = ML + 1
      UT(MM+LSTART) = U(NSTART+ML)
  131 CONTINUE
      LSTART = LSTART + ND
  134 CONTINUE
      LSTART = LSTART + NDL
  101 CONTINUE
  102 CONTINUE
      KK = KK -1
      IF (KK .GT. 0) GO TO 99
C
C     FINISHED-NOW WRITE OUT RESULTS
 5000 FORMAT(1H1)
      WRITE(6,5000)
      WRITE(6,1200) (TITLE(I),I=1,10)
      MSTART = 0
      MM1 = M-1
      DO 150 I=1,MM1
      IP1 = I + 1
      WRITE(6,1150) I,IP1
      DO 160 J=1,ND
      JSTART = J + MSTART
      JSTOP = ND2 - ND + JSTART
      WRITE(6,1160) (UT(K),K=JSTART,JSTOP,ND)
  160 CONTINUE
      MSTART = MSTART + ND2
      CHI = 0.0000
      NST = (I-1)*ND2
      DO 151 LG=1,ND
      LLG = LG+ NST
      CHI = CHI + UT(LLG)
      NST = NST + ND
  151 CONTINUE
C     WRITE(6,1300) CHI
      IF (ND .GT. 10) GO TO 170
      IF (I .EQ. 1 .OR. I .EQ. 3 .OR. I .EQ. 5) GO TO  150
  170 WRITE(6,5000)
      WRITE(6,5001)
 5001 FORMAT(/////)
```

```
  150 CONTINUE
      IF (ISTOP .NE. 0) GO TO 1
 1001 FORMAT('0',10X,'CASE REQUESTED HAS',I5,' ELECTRONS WITH',I5,' BETA
     & SPINS'/11X,I5,' TOTAL CASES ARE INVOLVED')
 1000 FORMAT(3I5)
 1100 FORMAT(10A8)
 1150 FORMAT('0',30X,'PERMUTATION IS(',I2,',',I2,')')
 1160 FORMAT(10X,7F15.10/15X,7F15.10)
 1200 FORMAT('0',5X,10A8)
 1300 FORMAT('0',10X,'TRACE OF THIS MATRIX IS ',1PD18.9)
      STOP
      END
```

# IV.

```
SEVEN ELECTRON HEXTET
                          PERMUTATION IS( 1, 2)
  1.0000000000    0.0             0.0             0.0             0.0             0.0
  0.0            -1.0000000000    0.0             0.0             0.0             0.0
  0.0             0.0            -1.0000000000    0.0             0.0             0.0
  0.0             0.0             0.0            -1.0000000000    0.0             0.0
  0.0             0.0             0.0             0.0            -1.0000000000    0.0
  0.0             0.0             0.0             0.0             0.0            -1.0000000000
                          PERMUTATION IS( 2, 3)
 -0.5000000000    0.8660254038    0.0             0.0             0.0             0.0
  0.8660254038    0.5000000000    0.0             0.0             0.0             0.0
  0.0             0.0            -1.0000000000    0.0             0.0             0.0
  0.0             0.0             0.0            -1.0000000000    0.0             0.0
  0.0             0.0             0.0             0.0            -1.0000000000    0.0
  0.0             0.0             0.0             0.0             0.0            -1.0000000000



                          PERMUTATION IS( 3, 4)
 -1.0000000000    0.0             0.0             0.0             0.0             0.0
  0.0            -0.3333333333    0.9428090416    0.0             0.0             0.0
  0.0             0.9428090416    0.3333333333    0.0             0.0             0.0
  0.0             0.0             0.0            -1.0000000000    0.0             0.0
  0.0             0.0             0.0             0.0            -1.0000000000    0.0
  0.0             0.0             0.0             0.0             0.0            -1.0000000000
                          PERMUTATION IS( 4, 5)
 -1.0000000000    0.0             0.0             0.0             0.0             0.0
  0.0            -1.0000000000    0.0             0.0             0.0             0.0
  0.0             0.0            -0.2500000000    0.9682458366    0.0             0.0
  0.0             0.0             0.9682458366    0.2500000000    0.0             0.0
  0.0             0.0             0.0             0.0            -1.0000000000    0.0
  0.0             0.0             0.0             0.0             0.0            -1.0000000000



                          PERMUTATION IS( 5, 6)
 -1.0000000000    0.0             0.0             0.0             0.0             0.0
  0.0            -1.0000000000    0.0             0.0             0.0             0.0
  0.0             0.0            -1.0000000000    0.0             0.0             0.0
  0.0             0.0             0.0            -0.2000000000    0.9797958971    0.0
  0.0             0.0             0.0             0.9797958971    0.2000000000    0.0
  0.0             0.0             0.0             0.0             0.0            -1.0000000000
                          PERMUTATION IS( 6, 7)
 -1.0000000000    0.0             0.0             0.0             0.0             0.0
  0.0            -1.0000000000    0.0             0.0             0.0             0.0
  0.0             0.0            -1.0000000000    0.0             0.0             0.0
  0.0             0.0             0.0            -1.0000000000    0.0             0.0
  0.0             0.0             0.0             0.0            -0.1666666667    0.9860132972
  0.0             0.0             0.0             0.0             0.9860132972    0.1666666667
```

```
SEVEN ELECTRON QUARTET

                       PERMUTATION IS( 1, 2)
 1.0000000000   0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0           -1.0000000000   0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            1.0000000000   0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0           -1.0000000000   0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0           -1.0000000000   0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            1.0000000000   0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0           -1.0000000000
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
    -1.0000000000   0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0           -1.0000000000   0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            1.0000000000   0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0           -1.0000000000   0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0           -1.0000000000   0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0           -1.0000000000   0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0           -1.0000000000



                       PERMUTATION IS( 2, 3)
-0.5000000000   0.8660254038   0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.8660254038   0.5000000000   0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0           -0.5000000000   0.8660254038   0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.8660254038   0.5000000000   0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0           -1.0000000000   0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0           -0.5000000000   0.8660254038
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.8660254038   0.5000000000
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
    -1.0000000000   0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0           -1.0000000000   0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0           -0.5000000000   0.8660254038   0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.8660254038   0.5000000000   0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0           -1.0000000000   0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0           -1.0000000000   0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0           -1.0000000000
```

```
                  PERMUTATION IS( 3, 4)
 1.0000000000   0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0           -1.0000000000   0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0           -1.0000000000   0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0           -0.3333333333   0.9428090416   0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.9428090416   0.3333333333   0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0           -1.0000000000   0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0           -0.3333333333
      0.9428090416   0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.9428090416
      0.3333333333   0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0           -1.0000000000   0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0           -1.0000000000   0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0           -0.3333333333   0.9428090416   0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.9428090416   0.3333333333   0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0           -1.0000000000   0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0           -1.0000000000
```

```
                  PERMUTATION IS( 4, 5)
-0.5000000000   0.0            0.8660254038   0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0           -0.5000000000   0.0            0.8660254038   0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.8660254038   0.0            0.5000000000   0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.8660254038   0.0            0.5000000000   0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0           -1.0000000000   0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0           -1.0000000000   0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0           -1.0000000000
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     -0.2500000000   0.9682458366   0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.9682458366   0.2500000000   0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0           -1.0000000000   0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0           -1.0000000000   0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0           -0.2500000000   0.9682458366   0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.9682458366   0.2500000000   0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0           -1.0000000000
```

```
                   PERMUTATION IS( 5, 6)
-1.0000000000   0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0           -1.0000000000   0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0           -0.3333333333   0.0            0.0            0.9428090416   0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0           -0.3333333333   0.0            0.0            0.9428090416
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0           -0.3333333333   0.0            0.0
      0.9428090416   0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.9428090416   0.0            0.0            0.3333333333   0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.9428090416   0.0            0.0            0.3333333333
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.9428090416   0.0            0.0
      0.3333333333   0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0           -1.0000000000   0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0           -1.0000000000   0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0           -1.0000000000   0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0           -1.0000000000   0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0           -0.2000000000   0.9797958971
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.9797958971   0.2000000000
```

```
                   PERMUTATION IS( 6, 7)
-1.0000000000   0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0           -1.0000000000   0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0           -1.0000000000   0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0           -1.0000000000   0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0           -1.0000000000   0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0           -0.2500000000   0.0
      0.0            0.0            0.9682458366   0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0           -0.2500000000
      0.0            0.0            0.0            0.9682458366   0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
     -0.2500000000   0.0            0.0            0.0            0.9682458366   0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0           -0.2500000000   0.0            0.0            0.0            0.9682458366   0.0
 0.0            0.0            0.0            0.0            0.0            0.9682458366   0.0
      0.0            0.0            0.2500000000   0.0            0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.9682458366
      0.0            0.0            0.0            0.2500000000   0.0            0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.9682458366   0.0            0.0            0.0            0.2500000000   0.0            0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.9682458366   0.0            0.0            0.0            0.2500000000   0.0
 0.0            0.0            0.0            0.0            0.0            0.0            0.0
      0.0            0.0            0.0            0.0            0.0            0.0           -1.0000000000
```

```
SEVEN ELECTRON DOUBLET
                      PERMUTATION IS( 1, 2)
1.0000000000  0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0          -1.0000000000  0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0           0.0           1.0000000000  0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0           0.0           0.0          -1.0000000000  0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0           0.0           0.0           0.0          -1.0000000000  0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0           0.0           0.0           0.0           0.0           1.0000000000  0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0           0.0           0.0           0.0           0.0           0.0          -1.0000000000
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0           0.0           0.0           0.0           0.0           0.0           0.0
     1.0000000000  0.0           0.0           0.0           0.0           0.0           0.0
0.0           0.0           0.0           0.0           0.0           0.0           0.0
     0.0          -1.0000000000  0.0           0.0           0.0           0.0           0.0
0.0           0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0          -1.0000000000  0.0           0.0           0.0           0.0
0.0           0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           1.0000000000  0.0           0.0           0.0
0.0           0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0          -1.0000000000  0.0           0.0
0.0           0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0          -1.0000000000  0.0
0.0           0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0          -1.0000000000
```

```
                      PERMUTATION IS( 2, 3)
-0.5000000000  0.8660254038  0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.8660254038   0.5000000000  0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0            0.0          -0.5000000000  0.8660254038  0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0            0.0           0.8660254038  0.5000000000  0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0            0.0           0.0           0.0          -1.0000000000  0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0            0.0           0.0           0.0           0.0          -0.5000000000  0.8660254038
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0            0.0           0.0           0.0           0.0           0.8660254038  0.5000000000
     0.0           0.0           0.0           0.0           0.0           0.0           0.0
0.0            0.0           0.0           0.0           0.0           0.0           0.0
    -0.5000000000  0.8660254038  0.0           0.0           0.0           0.0           0.0
0.0            0.0           0.0           0.0           0.0           0.0           0.0
     0.8660254038  0.5000000000  0.0           0.0           0.0           0.0           0.0
0.0            0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0          -1.0000000000  0.0           0.0           0.0           0.0
0.0            0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0          -0.5000000000  0.8660254038  0.0           0.0
0.0            0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.8660254038  0.5000000000  0.0           0.0
0.0            0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0          -1.0000000000  0.0
0.0            0.0           0.0           0.0           0.0           0.0           0.0
     0.0           0.0           0.0           0.0           0.0           0.0          -1.000000000
```

```
                 PERMUTATION IS( 3, 4)
1.0000000000   0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0           -1.0000000000   0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0           -1.0000000000   0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0           -0.3333333333   0.9428090416   0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.9428090416   0.3333333333   0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            1.0000000000   0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0           -1.0000000000
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
    -1.0000000000   0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0           -0.3333333333   0.9428090416   0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.9428090416   0.3333333333   0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0           -1.0000000000   0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0           -0.3333333333   0.9428090416   0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.9428090416   0.3333333333   0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0           -1.0000000000
```

```
                 PERMUTATION IS( 4, 5)
-0.5000000000  0.0            0.8660254038   0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0           -0.5000000000   0.0            0.8660254038   0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.8660254038   0.0            0.5000000000   0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.8660254038   0.0            0.5000000000   0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0           -1.0000000000   0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0           -0.5000000000   0.0
     0.8660254038   0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0           -0.5000000000
     0.0            0.8660254038   0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.8660254038   0.0
     0.5000000000   0.0            0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.8660254038
     0.0            0.5000000000   0.0            0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0           -1.0000000000   0.0            0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0           -1.0000000000   0.0            0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0           -1.0000000000   0.0            0.0
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0           -0.2500000000   0.9682458366
0.0            0.0            0.0            0.0            0.0            0.0            0.0
     0.0            0.0            0.0            0.0            0.0            0.9682458366   0.2500000000
```

```
                    PERMUTATION IS( 5, 6)
1.0000000000      0.0               0.0               0.0               0.0               0.0               0.0
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               1.0000000000      0.0               0.0               0.0               0.0               0.0
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0              -1.0000000000      0.0               0.0               0.0               0.0
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.0              -1.0000000000      0.0               0.0               0.0
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.0               0.0              -1.0000000000      0.0               0.0
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.0               0.0               0.0              -1.0000000000      0.0
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.0               0.0               0.0               0.0              -1.0000000000
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
        -0.3333333333      0.0               0.0               0.9428090416      0.0               0.0               0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.0              -0.3333333333      0.0               0.0               0.9428090416      0.0               0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.0               0.0              -0.3333333333      0.0               0.0               0.9428090416      0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.9428090416      0.0               0.0               0.3333333333      0.0               0.0               0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.0               0.9428090416      0.0               0.0               0.3333333333      0.0               0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.0               0.0               0.9428090416      0.0               0.0               0.3333333333      0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.0               0.0               0.0               0.0               0.0               0.0              -1.0000000000
```

```
                    PERMUTATION IS( 6, 7)
-0.5000000000     0.0               0.0               0.0               0.0               0.8660254038      0.0
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0              -0.5000000000      0.0               0.0               0.0               0.0               0.8660254038
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0              -0.5000000000      0.0               0.0               0.0               0.0
         0.8660254038      0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.0              -0.5000000000      0.0               0.0               0.0
         0.0               0.8660254038      0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.0               0.0              -0.5000000000      0.0               0.0
         0.0               0.0               0.8660254038      0.0               0.0               0.0               0.0
0.8660254038      0.0               0.0               0.0               0.0               0.5000000000      0.0
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.8660254038      0.0               0.0               0.0               0.0               0.5000C00000
         0.0               0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.8660254038      0.0               0.0               0.0               0.0
         0.5000000000      0.0               0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.0               0.8660254038      0.0               0.0               0.0
         0.0               0.5000000000      0.0               0.0               0.0               0.0               0.0
0.0               0.0               0.0               0.0               0.8660254038      0.0               0.0
         0.0               0.0               0.5000000000      0.0               0.0               0.0               0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.0               0.0               0.0              -1.0000000000      0.0               0.0               0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.0               0.0               0.0               0.0              -1.0000000000      0.0               0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.0               0.0               0.0               0.0               0.0              -1.0000000000      0.0
0.0               0.0               0.0               0.0               0.0               0.0               0.0
         0.0               0.0               0.0               0.0               0.0               0.0              -1.0000000000
```

## References

1. W. Ledermanm, Introduction to the Theory of Finite Groups (Edinburgh and London 1953)

2. J.R. Gabriel, Proc. Cambridge Phil. Soc. **57**, 330 (1961).

3. For a particularly lucid and cogent discussion of the symmetric group and Young's shapes see Rutherford, Substitutional Analysis. For application in theoretical chemistry see Goddard Phys. Rev. **157**, 73 (1967).

4. The conjugate representation is generated by reversing the order of the k-sequence at each level and multiplying the diagonal matrix elements by -1. It should be noted that our development is for the representation conjugate to Gabriel's.[2]