INVESTIGATIONS OF SPIN-EIGENFUNCTION CORRELATED WAVEFUNCTIONS

Thesis by

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In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1974

(Submitted February 25, 1974)

Acknowledgment

I would like to thank my research advisor, Dr. W. A. Goddard III, for his advice and guidance during my graduate studies. In addition, I would like to thank the members of our research group, particularly R. J. Blint, G. Levin and W. R. Wadt, for many helpful and stimulating discussions.

I gratefully acknowledge the generous financial support received from the National Science Foundation, the Achievement Rewards for College Scientists Foundation, and the California Institute of Technology.

Finally, I would like to thank my wife and children for their patience and understanding throughout my years of graduate work.

Abstract

Part I

Generalized Valence-Bond descriptions for the low-lying ${}^2\pi$, ${}^2\Delta$, and ${}^4\Sigma^-$ states of CH are presented. These wavefunctions are found to behave properly at all internuclear distances, giving a clear and consistent physical picture of formation of these molecules from their constituent atoms.

Part II

A procedure for calculating Spin-Eigenfunction Configuration Interaction matrices utilizing the U matrices which form the irreducible representations of $\mathscr{S}_N$ is presented. In addition, an improved determinant method is summarized. By combining both of these U-matrix and Determinant methods, it has been possible to formulate a practical and yet highly efficient procedure for generating such CI matrices.

Part III

Even for relatively simple Hartree-Fock (HF) or Perfect-Pairing Generalized Valence-Bond (PPGVB) many-electron wavefunctions, self-consistent calculations can be prohibitively expensive for many chemically interesting systems. Considerable effort has

been devoted toward developing highly efficient computational techniques for solving for such wavefunctions. The results of this research, as embodied in the GVBTWO program, have made such calculations on relatively large systems a practical reality.

Part IV

The Generalized Valence-Bond (GVB) wavefunction has had considerable success in describing chemical reactions and molecular structure. Unfortunately, this method can only be applied to systems involving a few electrons. The Perfect-Pairing approximation to GVB (PPGVB) greatly simplifies the situation and is found to adequately describe the low-lying states of many molecules. However, in describing chemical reactions the restrictions of PPGVB are quite serious. The Strongly Orthogonal approximation (SOGVB) described here overcomes this problem by allowing the orbitals to recouple while still retaining the simplifying orbital restrictions of PPGVB. This intermediate method correctly describes many chemical reactions and is practical for treating relatively large systems.

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PART ONE

Generalized Valence-Bond Descriptions For Formation of the Low-Lying States of CH

Abstract

Generalized Valence-Bond descriptions for the low-lying $^2\pi$, $^2\Delta$, and $^4\Sigma^-$ states of CH are presented. These wavefunctions are found to behave properly at all internuclear distances, giving a clear and consistent physical picture of formation of these molecules from their constituent atoms.

I. INTRODUCTION

One of the major goals of theoretical chemistry is to develop a coherent physical model for explaining molecular structure and chemical reactivity. We attempt to do this through ab-initio calculations of wavefunctions and energies for relatively simple chemical systems. By interpreting the results obtained for these prototypes, general physical concepts can be developed which apply to whole classes of molecules and reactions.

In order to do this, the wavefunctions used must not only give good descriptions of the energetics involved, but must also be physically interpretable. The simplest approximation to the exact many-electron wavefunction is the well-known Hartree-Fock wavefunction. Hartree-Fock has had considerable success in qualitatively describing the electronic structures of atoms and many simple molecules. However, since Hartree-Fock describes a chemical bond by a single doubly-occupied orbital, it is incapable of even qualitatively describing the simplest reactions involving bond formation and/or dissociation. This deficiency is removed while still retaining a simple orbital description by the Generalized Valence-Bond (GVB) method.[1]

In the GVB wavefunction, each orbital is allowed its own orbital while still preserving the proper spin symmetry:

$$\Psi = \mathcal{A}\,\Phi\,\chi$$

$$\Phi = \prod_{i}^{N} \phi_i(i)$$

$$\hat{S}^2 \chi = S(S+1)\,\chi$$

where $\mathcal{A}$ is the antisymmetrizer (determinant operator), Φ is a product of singly-occupied orbitals, and χ is the associated spin function which we require to be a spin-eigenstate. The spin function χ is usually multidimensional. That is, it can be composed of several linearly independent spin-eigenfunctions $\{\chi\}$, all of which correspond to the same spin multiplicity (S). Therefore, we can rewrite (1) as:

$$\begin{aligned}\Psi &= \mathcal{A}\Phi\sum_i \varepsilon_i\chi_i \\ &= \sum_i \varepsilon_i\left[\mathcal{A}\Phi\chi_i\right] \\ &= \sum_i \varepsilon_i \psi_i\end{aligned}$$

where each of the linearly independent spin-eigenfunction configurations $\{\psi\}$ corresponds to coupling the orbitals in a different way.[2] Hence, solution of a GVB wavefunction involves unrestricted optimization of both the orbitals $\{\phi\}$ and the coupling between them $\{\varepsilon\}$.

We will now present the GVB descriptions for formation of the low-lying $^2\pi$, $^2\Delta$ and $^4\Sigma^-$ states of the CH molecule. As will be shown, the observed orbital and orbital-coupling changes involved in these wavefunctions form a clear and consistent physical picture for formation of these molecules from their constituent atoms.

II. PROCEDURE

Since the carbon 1s electrons are known to be very tightly bound, it can be safely assumed that this core will be virtually unaffected by molecule formation. Therefore, the problem was effectively reduced to one involving only five electrons by fixing this core as the doubly-occupied 1s orbital obtained from a symmetry-restricted Hartree-Fock calculation on the ^3P state of carbon using a (4S, 3P) contracted gaussian basis set (the $1s^2$ orbital for the ^1D state is essentially the same). As 5-electron GVB calculations are quite expensive even for modestly sized basis sets, SCF orbitals were first obtained using the computationally simpler Perfect-Pairing GVB (PPGVB)[3] approximation with a (3S, 2P, 1D/2S, 2Z) contracted gaussian basis set. In this approximation the 5-electron doublet and quartet wavefunctions are simply:

$$\psi_D = \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \phi_4 \\ \hline \phi_5 & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} = \mathcal{A}\,\phi_1\phi_2\phi_3\phi_4\phi_5(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)\alpha$$

$$\psi_Q = \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \multicolumn{1}{c}{} \\ \phi_4 & \multicolumn{1}{c}{} \\ \phi_5 & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} = \mathcal{A}\,\phi_1\phi_2\phi_3\phi_4\phi_5(\alpha\beta-\beta\alpha)\alpha\alpha\alpha$$

where all orbitals other than the two within a given singlet pair (i.e. those two orbitals associated with the same $\alpha\beta-\beta\alpha$ spin term) are taken to be orthogonal. GVB solutions were then obtained through inexpensive minimum basis set calculations using the PPGVB orbitals. For each state of CH investigated, the validity of this procedure was verified through complete (3S, 2P, 1D/2S, 2Z) GVB calculations at two or three points of interest.

III. THE ^{3}P AND ^{1}D STATES OF CARBON

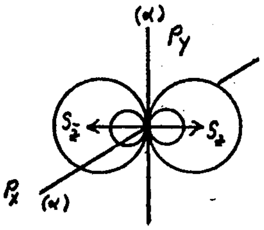
Before discussing the CH molecule, the GVB wavefunctions for the ground ^{3}P and low-lying ^{1}D states of carbon must be considered since they differ from the usual Hartree-Fock descriptions. The valence orbitals obtained from GVB calculations using a fixed $1s^2$ core (obtained from Hartree-Fock calculations) are essentially the same for both states. They consist of two singly-occupied p-orbitals along two axes and two highly overlapping singlet paired orbitals hybridized in opposite directions along the remaining axis (Fig. 1). In the ^{3}P state the p-orbitals are triplet coupled, whereas in the ^{1}D state they are singlet coupled. This orbital description differs from Hartree-Fock in that Hartree-Fock cannot allow for hybridization but, rather, replaces this singlet pair by a doubly-occupied 2s orbital.

The energies obtained for the ^{3}P and ^{1}D states are -37.7035 a.u. and -37.6462 a.u. as compared to experimental values of -37.8558 a.u. and -37.8093 a.u. respectively.[4] These energies are 0.015 a.u. lower than Hartree-Fock results using comparable basis sets.[5] The energy difference between these states is 0.0573 a.u., while the experimental value is 0.0456 a.u. This error of 0.0108 a.u. is about the same as obtained with Hartree-Fock.

The GVB wavefunction for the ^{3}P state is:

$$\Psi_{^3P} = \begin{array}{|c|}\hline s_z \; s_{\bar{z}} \\ \hline \end{array} \atop \begin{array}{|c|}\hline p_x \\ \hline p_y \\ \hline \end{array} = \mathcal{A}\, s_z s_{\bar{z}} p_x p_y (\alpha\beta - \beta\alpha)\alpha\alpha$$

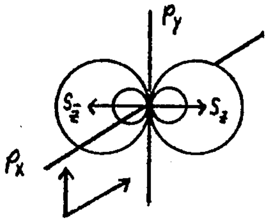
(In this and all subsequent wavefunctions the doubly-occupied Carbon 1s orbital is omitted). In discussing the C-H molecule we will find it convenient to pictorially represent this state as:



where the double arrow connecting orbitals s_z and $s_{\bar{z}}$ (represented as lobes) indicates that these two orbitals are singlet paired [i.e. are associated with an ($\alpha\beta-\beta\alpha$) spin term]. The (α) designations assigned to orbitals p_x and p_y (represented simply by their cartesian axes) serve only to indicate that these two orbitals are triplet coupled and do not necessarily imply that these orbitals are associated with α spins. The usefulness of such designations will become more apparent when discussing molecule formation. The GVB wavefunction for the ^1D state can be taken to be:

$$\psi_{^1D} = \begin{array}{|cc|}\hline s_z & s_{\bar{z}} \\ \hline p_x & p_y \\ \hline \end{array} = \mathcal{A}\, s_z s_{\bar{z}} p_x p_y (\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)$$

which we will represent as:



where the double arrow connecting orbitals p_x and p_y indicates that these two orbitals are singlet paired as are orbitals s_z and $s_{\bar{z}}$.

At first, it might appear that the presence of these hybrid orbitals might seriously contaminate the spatial symmetry of these wavefunctions. However, since we can rewrite these orbitals as:

$$s_z \propto s + \lambda p_z' \qquad s_{\bar{z}} \propto s - \lambda p_z'$$

where $\lambda = 0.38$ (i.e. these orbitals are dominantly 2s-like, having an overlap of about 0.75). Hence, these wavefunctions can be rewritten as:

$$\Psi = \mathcal{A}\, s^2 p_x p_y \alpha\beta\chi - \lambda^2 \mathcal{A}\, p_z'^2 p_x p_y \alpha\beta\chi$$

where $x = \alpha\alpha$ for the ^3P state and $x = \alpha\beta - \beta\alpha$ for the ^1D state. The first term is the dominant one and is obviously of the proper symmetry. The second term will also have the proper spatial symmetry if $p_z' \alpha p_z$ (i.e. is radially the same as p_x and p_y). Although this is not strictly the case, the differences are so small that for all practical purposes this minor defect can be ignored. Hence, these GVB wavefunctions can be taken to be of proper spatial symmetry.

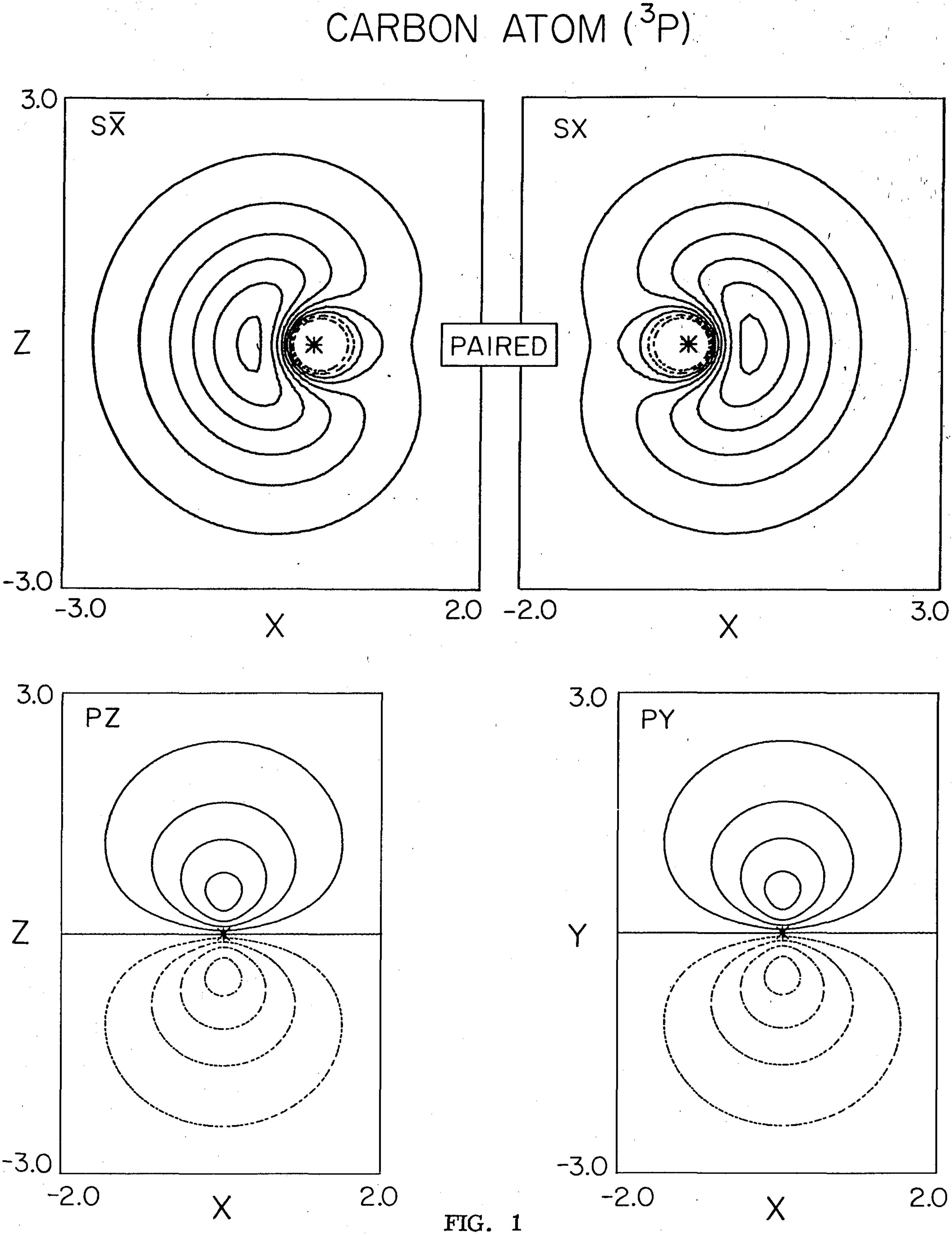


FIG. 1

IV. PRELIMINARY DISCUSSION

Since molecular binding energies are usually smaller than or comparable with the excitation energies of the constituent atoms, a reasonable starting point in examining molecular binding is to assume that the wavefunctions for the low-lying states of molecules will resemble the atomic configuration near each atom. This being the case, we can expect that the low lying-states of CH can be qualitatively described using a simple Valence-Bond model based on the GVB descriptions of the ^3P and ^1D states of carbon. Within such a model, each state can be envisioned to result from simply bonding a ^2S hydrogen atom to either a ^3P or ^1D carbon atom through a specific carbon orbital, with all orbitals remaining atomiclike (i.e. distorted owing to their molecular environment, but with their atomic identities easily discernible). Thus, bonding through one of the p-orbitals of a ^3P carbon atom results in the $X^2\pi$ state (Fig. 2). On the other hand, bonding through one of the hybrid orbitals of a C^3P atom can lead to the $\underline{a}^4\Sigma^-$ state or the $B^2\Sigma^-$ state (Fig.12). The $A^2\Delta$ state also results from bonding through a hybrid orbital, but with the carbon atom being in its ^1D state (Fig. 8).

Above, we used the term 'bonding' rather loosely, as if to imply that high overlap between an orbital of each atom is all that is required. Actually, the interaction between two highly overlapping orbitals is favorable only when they are singlet paired and is quite unfavorable when they are triplet coupled. As a consequence, it is safe to assume that formation of C-H bond in these molecules involves singlet pairing of these two orbitals as well. As we shall see, however, singlet pairing between the bonding orbitals is incompatible with the coupling which must prevail between the carbon orbitals prior to formation of the bond. Thus, there is little hope that a simple Valence-Bond model which preserves this atomic coupling can be used to describe molecule formation. On the other hand, a model preserving the expected molecular coupling at equilibrium cannot possibly describe the correct separated-atom limit. Therefore, in order to even qualitatively describe formation of these molecules we must use a model which not only allows for changes in the orbitals themselves, but also allows these orbitals to recouple as the internuclear separation is varied.

In the following sections we will attempt to develop such a model based upon GVB calculations on the $^2\pi$, $^2\Delta$ and $^4\Sigma^-$ states. In doing so, we will rely heavily upon the fact that significant overlap between two orbitals is favorable only when these orbitals are symmetrically coupled (more singlet than triplet coupled) and that small overlap between two proximate orbitals is favorable when these orbitals are antisymmetrically coupled (more triplet than singlet coupled). In an effort to demonstrate the general applicability of the concepts being developed, we will consider one state at a time, with initial qualitative considerations being based upon those ideas developed from results obtained for preceding states.

V. THE $^2\pi$ STATE

Qualitative Considerations

The ground state of CH($^2\pi$) can be envisioned to result when a hydrogen ^2S atom approaches a carbon ^3P atom along a p-orbital axis (Fig. 2). At infinite C-H separation, the carbon orbitals must be coupled as in C^{3}P. That is, orbitals s_x and $s_{\bar{x}}$ must be singlet paired and orbitals p_y and p_z must be triplet coupled:

$$\psi_\infty = \begin{array}{|c|c|}\hline \multicolumn{2}{|c|}{s_x \; s_{\bar{x}}} \\ \hline p_z & s_H \\ p_y & \\ \cline{1-1}\end{array} = \mathcal{A}\, s_x s_{\bar{x}} p_z p_y s_H (\alpha\beta - \beta\alpha)(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$$

This atomic coupling at infinite separation is pictorially represented in Fig. 2a by assignment of a (β) coupling label to orbital s_H in contrast to the (α) designations of the triplet coupled carbon p-orbitals. Again we emphasize that these symbols are not orbital spin labels. What these designations signify is that orbitals p_y, p_z and s_H are coupled into a doublet such that the (β) labeled s_H orbital is symmetrically coupled to both of the (α) labeled p_z and p_y (triplet coupled) orbitals. (This implies that ψ_∞ can be written in terms of the two configurations in which s_H is singlet paired to either p_y or p_z such that the wavefunction changes sign upon interchange of p_z and p_y).

At the equilibrium distance however, we expect the C-H bond to be described by singlet pairing of the bonding orbitals p_z and s_H:

$$\psi_e = \begin{array}{|c|c|}\hline s_x & s_{\bar{x}} \\ \hline p_z & s_H \\ \hline p_y & \\ \cline{1-1}\end{array} = \mathcal{A}\, s_x s_{\bar{x}} p_z s_H p_y (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\alpha$$

This molecular coupling is indicated in Fig. 2c by the double arrow connecting the singlet paired p_z and s_H orbitals. Since the original (α) and (β) coupling designations assigned to these two orbitals implied that the wavefunction could only be partially written in terms of $\boxed{p_z s_H}$ singlet pairing, these labels are dropped.

Hence, the simplest wavefunction capable of describing formation of this molecule from its constituent atoms is a linear combination of the atomic and molecular couplings:

$$\psi_{^2\pi} = \mathcal{E}_\infty \begin{array}{|c|c|}\hline s_x & s_{\bar{x}} \\ \hline p_z & s_H \\ \hline p_y & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \mathcal{E}_e \begin{array}{|c|c|}\hline s_x & s_{\bar{x}} \\ \hline p_z & s_H \\ \hline p_y & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

where, as the C-H distance decreases from infinity, $\mathcal{E}_\infty$ is expected to decrease from unity to zero as $\mathcal{E}_e$ gradually increases in magnitude from zero to approach unity at equilibrium. The coupling in intermediate regions is represented in Fig. 2b by the broken double arrow connecting orbitals p_z and s_H which we use to indicate singlet pair formation or dissolution. The (α) and (β) orbital coupling labels are retained to indicate how orbitals p_y, p_z and s_H tend to be coupled prior to complete formation of the $\boxed{p_z s_H}$ singlet pair.

GVB Results

GVB solutions obtained at several internuclear distances ranging from 6.0 $a_\circ$ to 1.9 $a_\circ$ are summarized in Table 1. The resulting potential energy curve (Fig 3a) behaves properly at all internuclear distances, giving a binding energy of 0.110 a.u. at 2.150 $a_\circ$. This is in good agreement with the experimental value of 0.134 a.u. at 2.124 a_0. As shown in Figs. 4 and 5, the orbitals change in a straightforward manner as the internuclear distance is decreased. The carbon p_z orbital (ϕ_3) gradually hybridizes into the internuclear region. The hydrogen 1s orbital (ϕ_4) polarizes slightly toward carbon, but remains essentially atomiclike throughout (the spike forming about the carbon nucleus is due to orthogonalization to the carbon 1s core). In order to minimize unfavorable interactions between the $\boxed{s_x s_{\bar{x}}}$ pair and the developing bonding pair, orbitals ϕ_1 and ϕ_2 (only one of which is shown) gradually bend back away from the internuclear region so as to remain essentially orthogonal to the bonding orbitals. At equilibrium these orbitals are at an angle of 128° to the C-H bond. The non-bonding p_y orbital (not shown) remains virtually unchanged throughout. The final set of orbitals at the equilibrium distance is shown in Fig. 6.

Orbital recoupling is also straightforward. Of the five linearly independent couplings possible for this 5-electron doublet system, only the atomic and molecular couplings have nonzero coefficients. This is because all other possibilities involve unfavorable triplet coupling between the highly overlapping s_x and $s_{\bar{x}}$ orbitals. As shown in Fig. 7, the orbitals recouple as expected, with molecular coupling being of increasing importance relative to atomic coupling as the C-H distance was decreased.

Discussion

With regard to changes in the orbitals themselves, the bending back of the original $\boxed{s_x s_{\bar{x}}}$ orbital pair is the most interesting feature. Due to the antisymmetric form of the total wavefunction (i.e. Pauli's Principle) there are repulsive interactions between orbitals in different singlet pairs. Since these orbitals are antisymmetrically coupled, these repulsive interactions decrease if the overlap between these orbitals decreases. Therefore, as the C-H bond forms, the $\boxed{s_x s_{\bar{x}}}$ pair bends back away from this bonding pair. The 128° angle achieved at equilibrium serves to explain the presumed $^{-}\text{C-H}^{+}$ dipole of this molecule.[6] Focusing attention solely on the bonding orbitals would, of course, lead to a $^{+}\text{C-H}^{-}$ prediction. In addition, envisioning the $^3B_1$ state of CH_2 to result by simply bonding another hydrogen atom to carbon through one of these orbitals leads directly to a H-C-H bond angle prediction of 128°. This is in good agreement with the observed value of 136°.[7]

Referring to Table 1, we see that coupling coefficients always differ in sign. The wavefunction is, of course, capable of going from atomic to molecular coupling regardless of whether or not these coefficients differ in sign. However, in GVB wavefunctions the relative signs of the coupling coefficients are nonetheless of great importance in that they tell us how the orbitals recouple in going from one coupling to another. This being the case, we would expect that such signs should be consistent with that path which avoids passing through (or tending toward) highly unfavorable and unlikely intermediate couplings. That this is presently the case can be clearly seen by reexpressing ψ_∞ in terms of the $\boxed{p_z s_H}$ and $\boxed{p_y s_H}$ singlet pairs:

$$\psi_\infty = \begin{array}{|c|c|}\hline s_x & s_{\bar{x}} \\ \hline p_z & s_H \\ \hline \multicolumn{1}{|c|}{p_y} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = \begin{array}{|c|c|}\hline s_x & s_{\bar{x}} \\ \hline p_y & s_H \\ \hline \multicolumn{1}{|c|}{p_z} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} - \begin{array}{|c|c|}\hline s_x & s_{\bar{x}} \\ \hline p_z & s_H \\ \hline \multicolumn{1}{|c|}{p_y} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

Hence, we can rewrite our wavefunction as

$$\psi_{2T} = \varepsilon_\infty \begin{array}{|c|c|}\hline s_x & s_{\bar{x}} \\ \hline p_y & s_H \\ \hline \multicolumn{1}{|c|}{p_z} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + (\varepsilon_e - \varepsilon_\infty)\, \psi_e$$

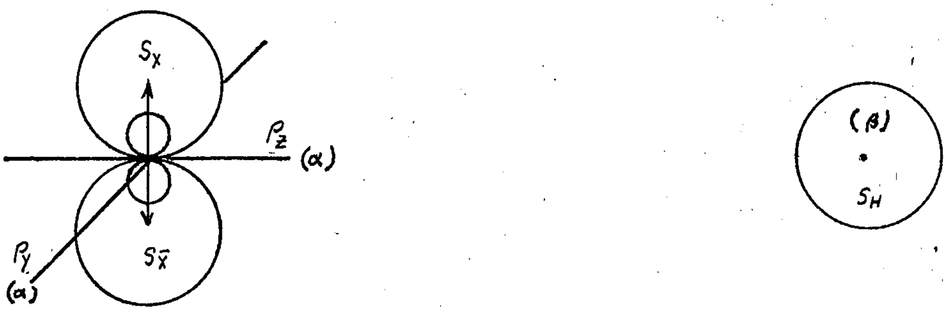
Therefore, in order for the wavefunction to monotonically change from atomic to molecular coupling as the internuclear separation decreases from infinity and yet avoid passing through the highly unfavorable coupling in which orbitals p_y and s_H are singlet paired, ε_∞ and ε_e should be opposite in sign. Moreover, this result is compatible with the physically intuitive notion that symmetric (singlet) coupling between ϕ_3 and ϕ_4 should continually be of greater importance with decreasing internuclear separation owing to the increasing overlap between these two orbitals. The coupling designations in Fig. 2 are meant to imply this continuity of the recoupling process by never picturing formation of any other singlet pair other than the one between orbitals p_z and s_H.

TABLE 1: $^2\pi$ RESULTS

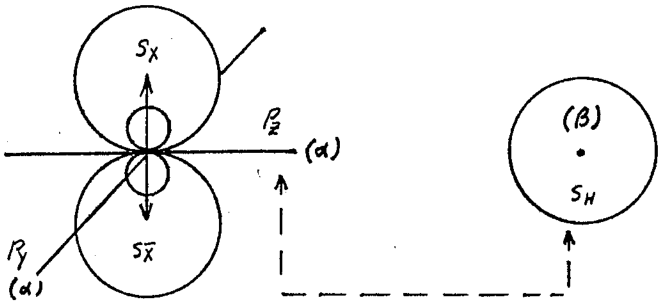
Distance R(bohr)	Energy -E(a.u.)	Binding Energy B.E. (a.u.)	Coupling Coefficients ε_2	ε_1
6.00	38.20432	0.00072	-.0511	.9489
5.00	38.20753	0.00393	-.2040	.7960
4.00	38.22338	0.01979	-.5216	.4787
3.50	38.24252	0.03892	-.6645	.3355
3.00	38.27064	0.06704	-.7588	.2412
2.40	38.30716	0.10357	-.8270	.1730
2.124	38.31376	0.11017	-.8488	.1512
1.90	38.30281	0.09921	-.8630	.1370
Complete GVB:				
6.00	38.20442	0.0008	-.0489	.9511
2.124	38.31402	0.1104	-.8372	.1628
HF:[8]				
2.124	38.27935	0.0907		
CI:[9]				
2.124	38.43990			
EXP[10]				
2.124	38.4898	0.134		

$$\Psi_{^2\pi} = \varepsilon_1 \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \phi_5 \\ \phi_4 & \\ \hline \end{array} + \varepsilon_2 \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \phi_5 \\ \hline \phi_4 & \\ \hline \end{array}$$

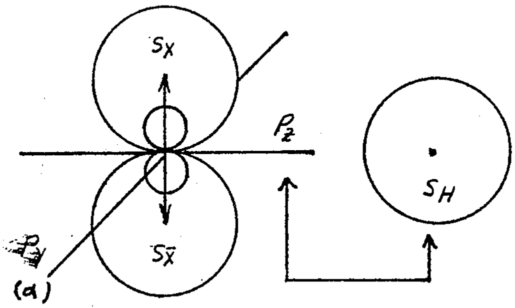
CH $^2\Pi$ FORMATION



a. Infinite Separation

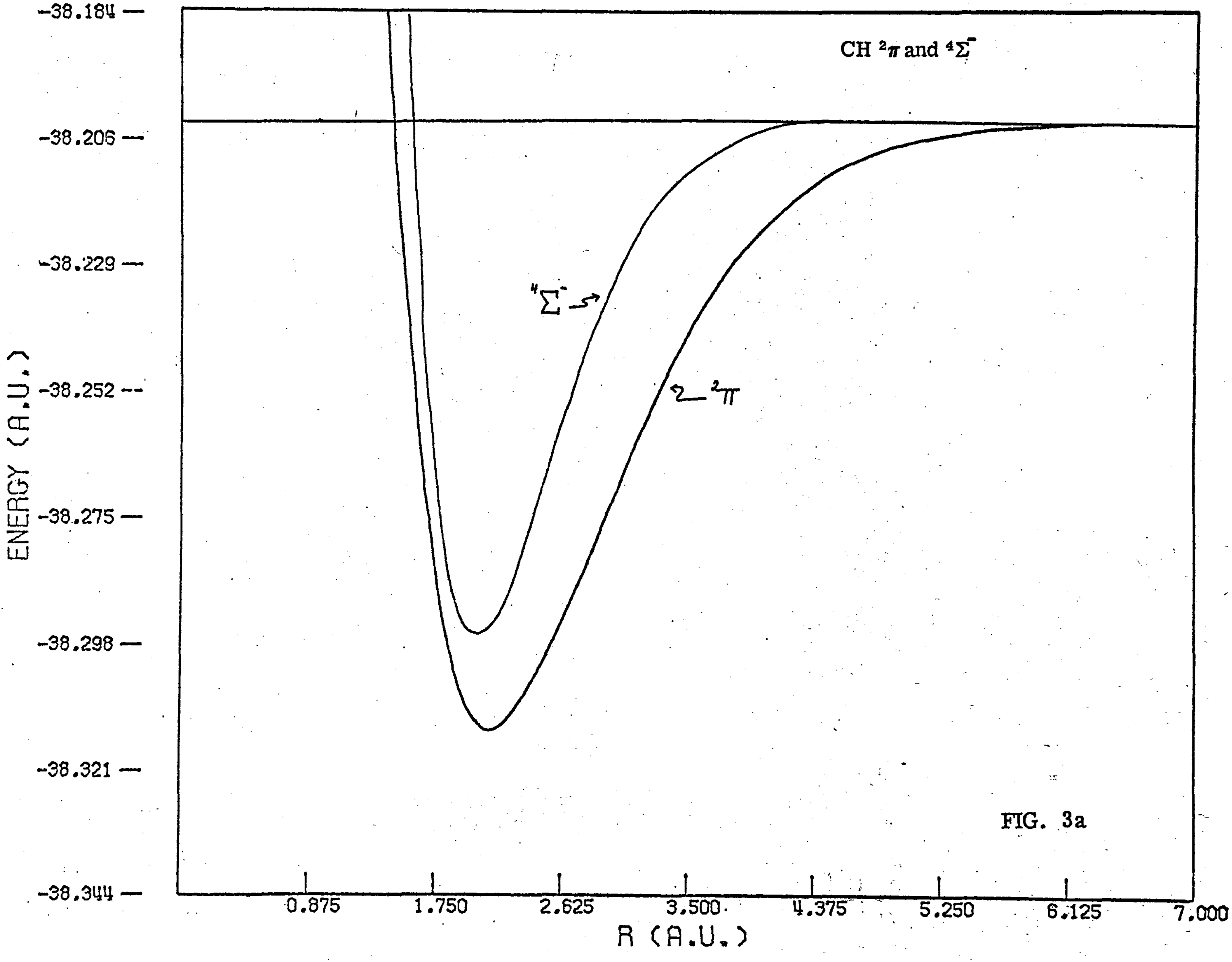


b. Intermediate Separation



c. Equilibrium

FIG. 2



CH $^2\pi$ and $^4\Sigma^-$

FIG. 3a

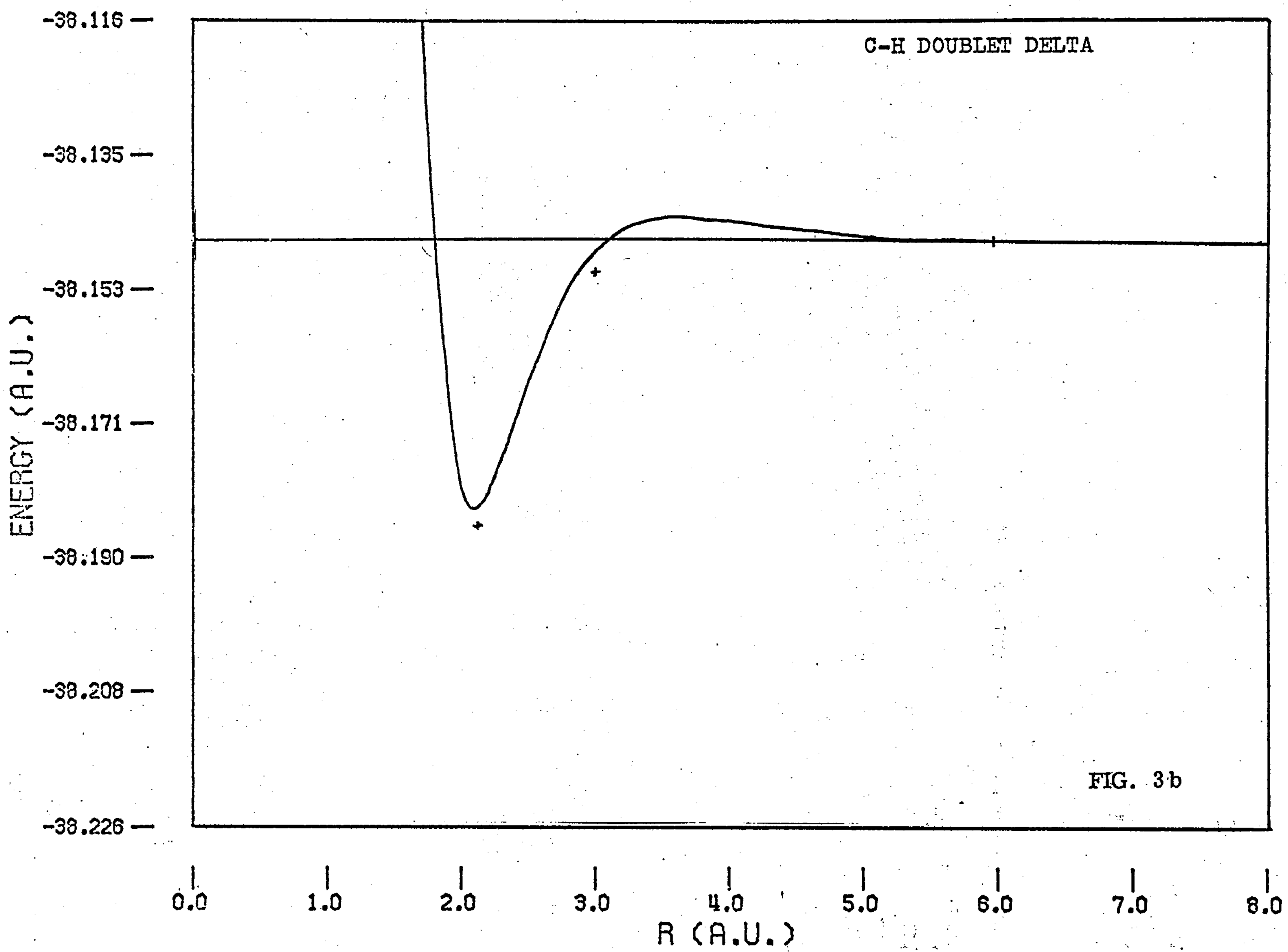

C-H DOUBLET DELTA
ENERGY (A.U.)
-38.116
-38.135
-38.153
-38.171
-38.190
-38.208
-38.226
R (A.U.)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

FIG. 3b

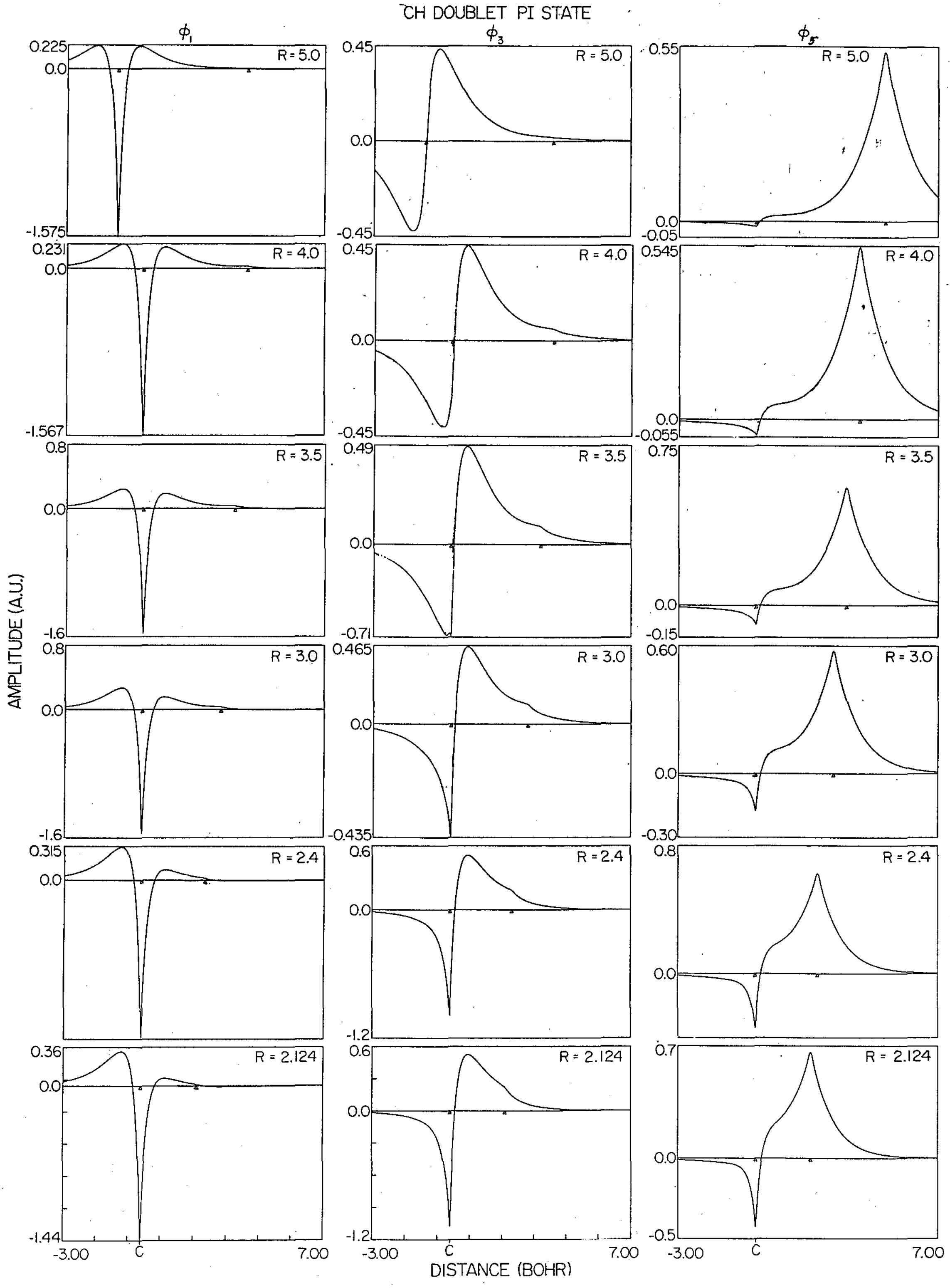

CH DOUBLET PI STATE
ϕ_1
ϕ_3
ϕ_5
AMPLITUDE (A.U.)
R = 5.0
R = 4.0
R = 3.5
R = 3.0
R = 2.4
R = 2.124
0.225
0.0
-1.575
0.231
-1.567
0.8
-1.6
0.315
0.36
-1.44
0.45
-0.45
0.49
-0.71
0.465
-0.435
0.6
-1.2
0.55
-0.05
0.545
-0.055
0.75
-0.15
0.60
-0.30
0.7
-0.5
-3.00
C
7.00
DISTANCE (BOHR)

FIG. 4

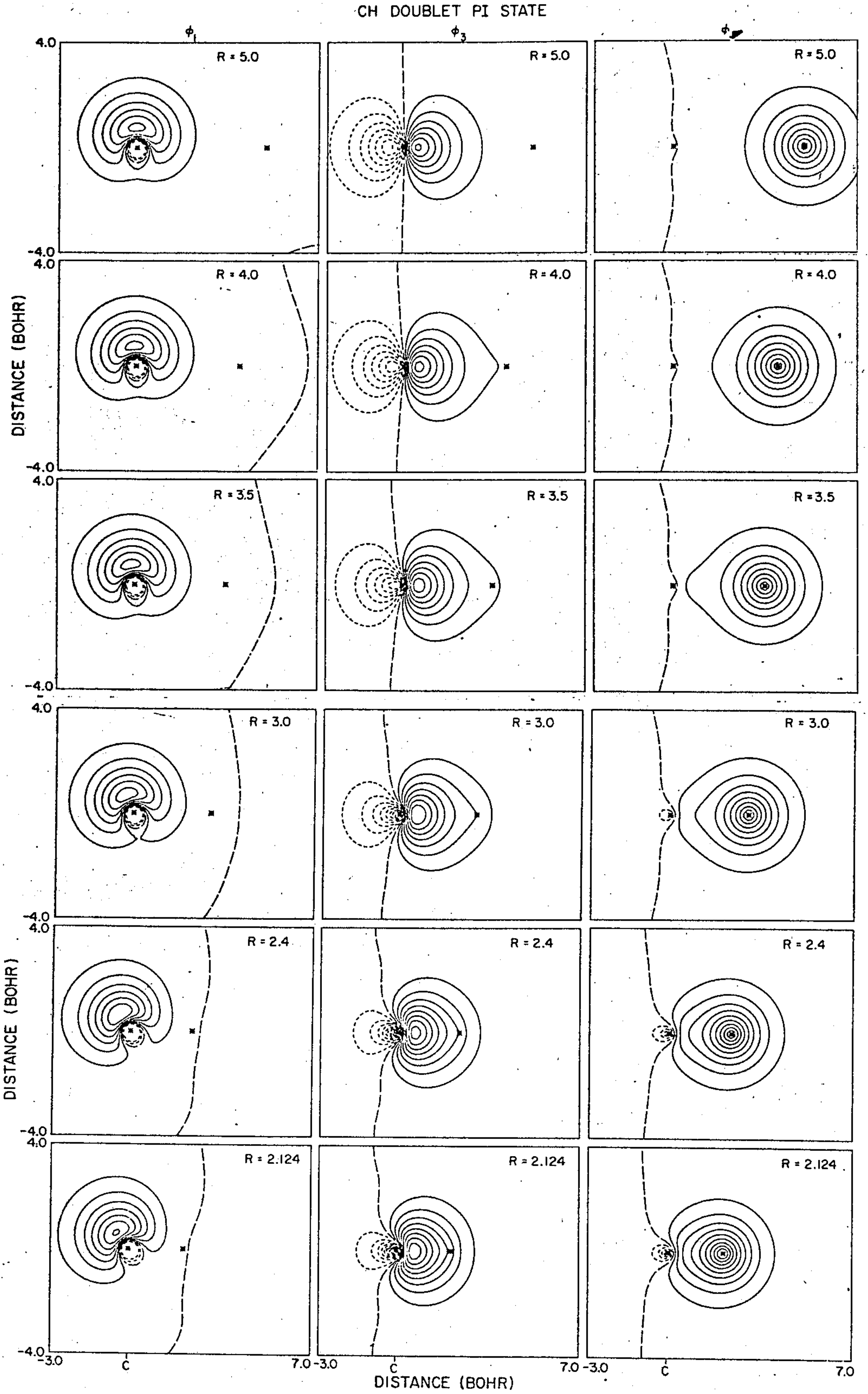

CH DOUBLET PI STATE
ϕ_1
ϕ_3
ϕ
R = 5.0
R = 5.0
R = 5.0
R = 4.0
R = 4.0
R = 4.0
R = 3.5
R = 3.5
R = 3.5
R = 3.0
R = 3.0
R = 3.0
R = 2.4
R = 2.4
R = 2.4
R = 2.124
R = 2.124
R = 2.124
4.0
-4.0
DISTANCE (BOHR)
DISTANCE (BOHR)
-3.0
C
7.0
DISTANCE (BOHR)

FIG. 5

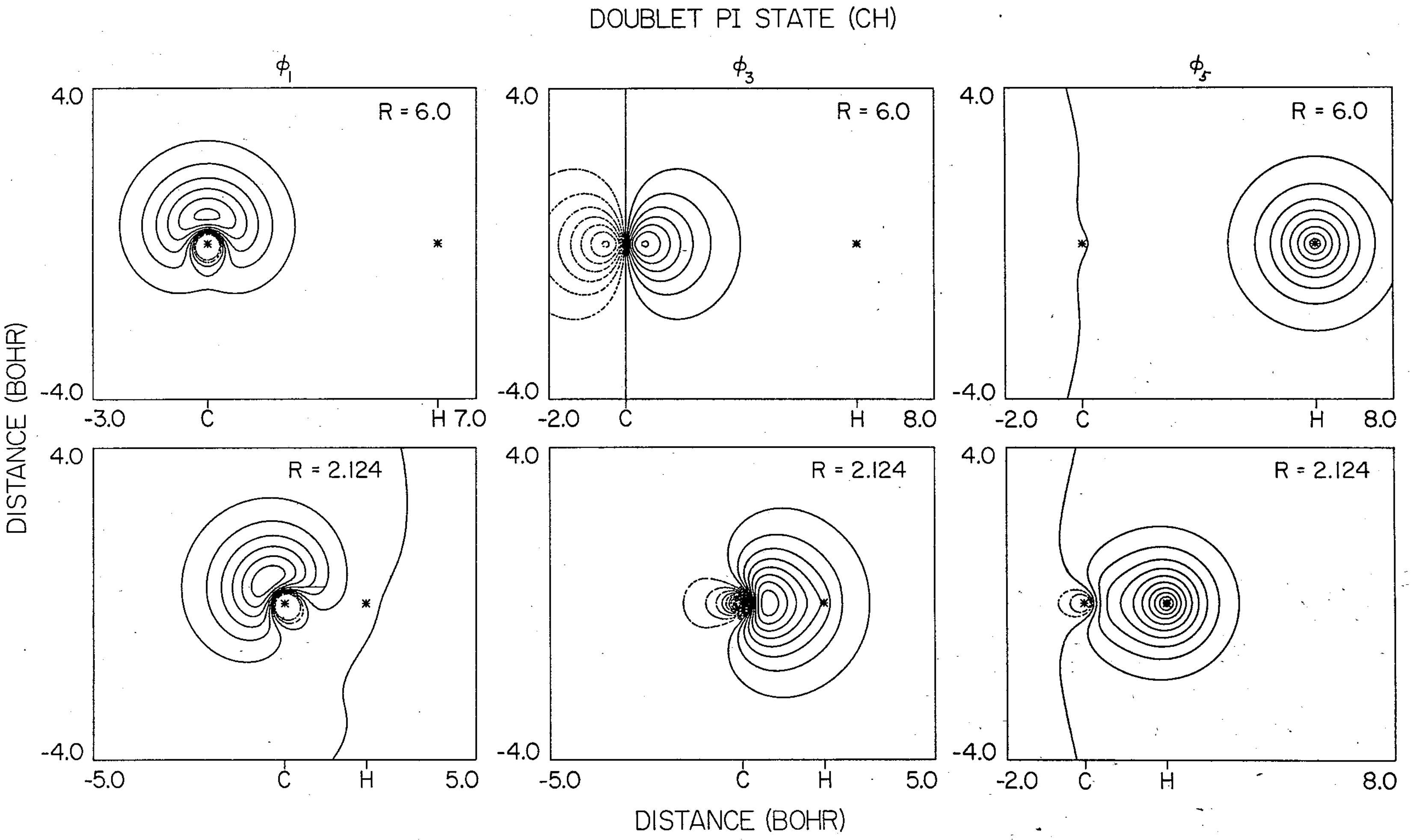

DOUBLET PI STATE (CH)
ϕ_1
ϕ_3
ϕ_5
R = 6.0
R = 6.0
R = 6.0
R = 2.124
R = 2.124
R = 2.124
4.0
-4.0
-3.0
C
H 7.0
-2.0
H
8.0
-5.0
5.0
DISTANCE (BOHR)
DISTANCE (BOHR)

FIG. 6

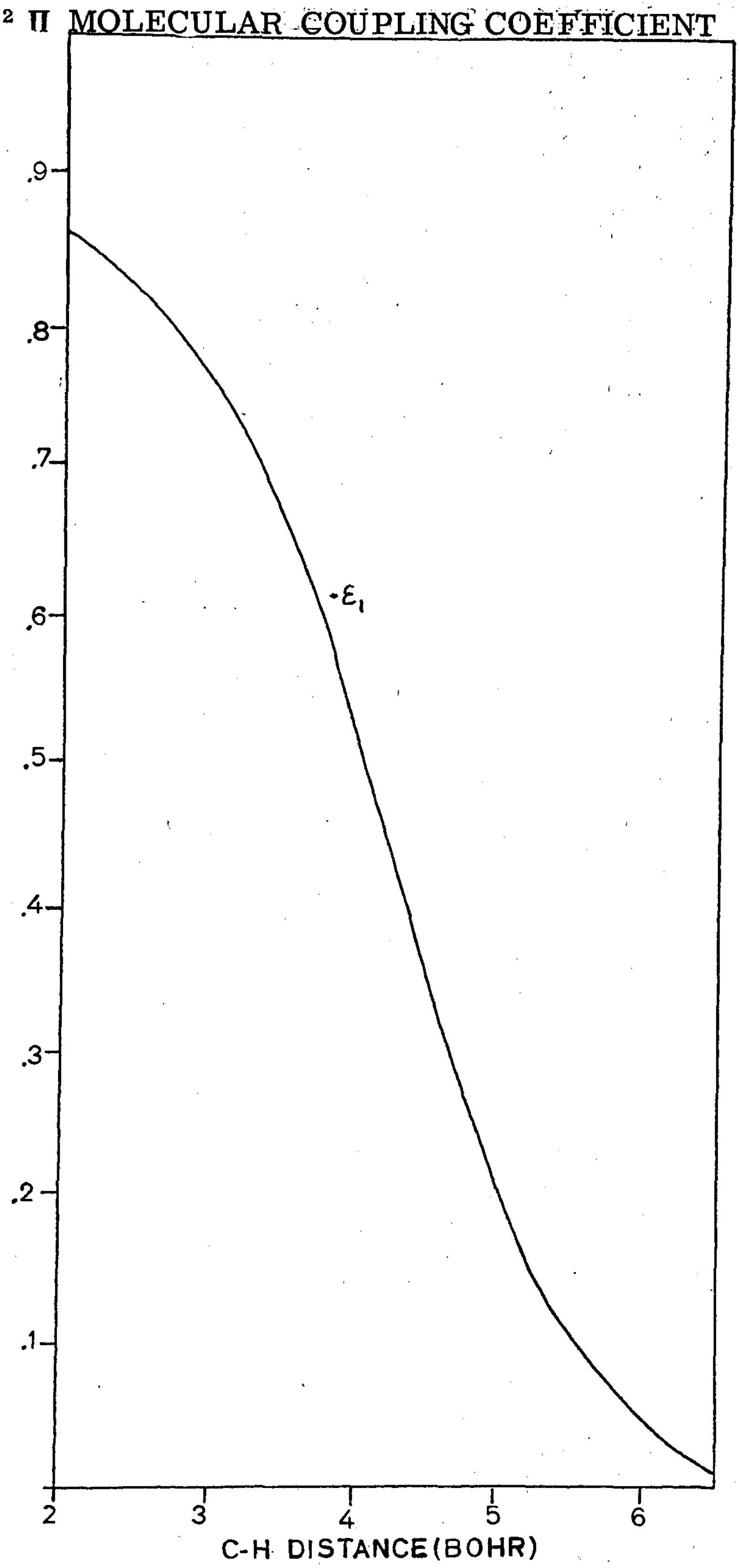

²Π MOLECULAR COUPLING COEFFICIENT
.9
.8
.7
.6
.5
.4
.3
.2
.1
-ε₁
2
3
4
5
6
C-H DISTANCE(BOHR)

FIG. 7

VI. THE $^2\Delta$ STATE

Qualitative Considerations

The $^2\Delta$ state of CH can be envisioned to form when a hydrogen ^2S atom approaches a carbon ^1D atom along the axis of hybridization (Fig. 8). At infinite separation (Fig. 8a), the carbon orbitals must be coupled as in C^1D. That is, orbitals p_x and p_y must be singlet paired as must be orbitals s_z and $s_{\bar{z}}$:

$$\psi_\infty = \begin{array}{|c|c|}\hline p_x & p_y \\ \hline s_z & s_{\bar{z}} \\ \hline s_H \\ \cline{1-1}\end{array} = \mathcal{A}\, p_x p_y s_z s_{\bar{z}} s_H (\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)\alpha$$

However, in terms of atomiclike orbitals, molecular coupling should correspond to having orbitals s_z and s_H singlet paired in order to describe the C-H bond (Fig. 8c). Therefore, at equilibrium the wavefunction is expected to be:

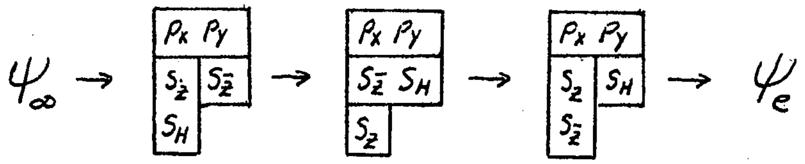
$$\psi_e = \begin{array}{|c|c|}\hline p_x & p_y \\ \hline s_z & s_H \\ \hline s_{\bar{z}} \\ \cline{1-1}\end{array} = \mathcal{A}\, p_x p_y s_z s_H s_{\bar{z}} (\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)\alpha$$

Hence, the simplest localized orbital wavefunction capable of describing formation of this molecule should be a linear combination of the atomic and molecular couplings:

$$\psi_{^2\Delta} = \mathcal{E}_1 \begin{array}{|c|c|}\hline p_x & p_y \\ \hline s_z & s_{\bar{z}} \\ \hline s_H \\ \cline{1-1}\end{array} + \mathcal{E}_2 \begin{array}{|c|c|}\hline p_x & p_y \\ \hline s_z & s_H \\ \hline s_{\bar{z}} \\ \cline{1-1}\end{array}$$

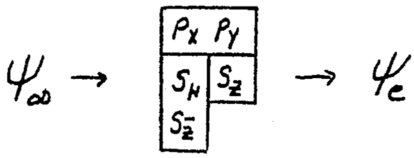
where, as the C-H separation decreases from infinity, $\mathcal{E}_1$ is expected to decrease from unity as $\mathcal{E}_2$ gradually increases in magnitude from zero to approach unity at equilibrium. That none of the remaining linearly independent couplings between these orbitals can contribute to the wavefunction even in intermediate regions is expected since they all involve triplet coupling between orbitals p_x and p_y, and are therefore all incorrect Σ symmetry. Thus, the localized orbital description of formation of this molecule simply involves dissolution of the original $\overline{s_z s_{\bar{z}}}$ singlet pair with simultaneous formation of the bonding $\overline{s_z s_H}$ singlet pair (as is indicated by the broken double arrows in Fig. 8b).

Of course, this wavefunction can monotonically go from atomic to molecular coupling in one of two ways depending on the sign of $\mathcal{E}_2$ relative to $\mathcal{E}_1$. Since the orbitals can be expected to recouple via the path which avoids the most unfavorable intermediate couplings, it should be possible to predict this sign a priori. If $\mathcal{E}_1$ and $\mathcal{E}_2$ have the same sign, the path from atomic to molecular coupling is:



(A)

whereas the negative sign path is:



(B)

At intermediate internuclear separations, orbital s_z should overlap substantially with both s_H and $s_{\bar{z}}$. However, these two orbitals should still have small overlap with each other. Therefore, the intermediate of the pathway B (in which orbital s_z is symmetrically coupled to the triplet coupled $s_{\bar{z}}$ and s_H orbitals) is preferable to the intermediates of pathway A (in which orbital s_z is at best antisymmetrically coupled to orbitals $s_{\bar{z}}$ and s_H).

Recoupling via pathway B is also consistent with the notion that symmetric (singlet) coupling between orbitals s_z and s_H should steadily increase in going from atomic to molecular coupling. The intermediates of the positive sign path, especially the first one in which orbitals s_z and s_H are actually triplet coupled, are obviously incompatable with this idea. This continuity of the recoupling process can be quite effectively represented pictorially using the (α) and (β) coupling designations introduced previously by requiring that the two orbitals between which a singlet pair is either forming or dissolving (i.e. are connected by a broken double arrow) have different coupling designations. As in the core of the $^2\pi$ state, this notation is meant to imply continually increasing symmetric coupling between those two orbitals which are to become unpaired. In doing so (Fig. 8b), we find that this implies that the wavefunction represented tends to triplet couple orbitals $s_{\bar{z}}$ and s_H since these two orbitals must be assigned the same designation.

GVB Results

GVB results obtained at several internuclear distances ranging from $6.0a_\circ$ to $1.9a_\circ$ are summarized in Table 2. The resulting potential energy curve (Fig.3b) behaves properly at all internuclear distances, giving a binding energy of 0.040 a.u. at $2.09a_\circ$ as compared to the experimental value of 0.076 a.u. at 2.08 $a_\circ$. The vertical $^2\pi \rightarrow {}^2\Delta$ excitation energy is 0.128 a.u. compared to the observed value of 0.105 a.u. This error of 0.023 a.u. not only reflects the added 0.013 a.u. correlation error of the $^2\Delta$ state over the $^2\pi$ state, but also the carbon $3P \rightarrow {}^1D$ correlation error of 0.011 a.u. An interesting feature of this curve is the potential barrier of 0.002 a.u. found at 3.5 $a_\circ$. This result is consistent with previous studies which have indicated that the required singlet-pair transfer is in itself an endothermic process.[11, 12]

As might have been expected, the singlet paired p_x and p_y orbitals remain essentially unchanged during molecule formation. However, of the sigma orbitals shown in Figs. 9 and 10, only the carbon s_z bonding orbital (ϕ_1) remains localized throughout. Beginning at around 3.5 $a_\circ$, the initial carbon $s_{\bar{z}}$ orbital (ϕ_2) gradually delocalizes over both centers and finally relocalizes to become the hydrogen centered bonding orbital. Simultaneously, orbital ϕ_3, which is initially the hydrogen 1s orbital, also delocalizes and finally relocalizes as the CH nonbonding sigma orbital. Comparing the initial and final sets of orbitals, the only indication that this spatial migration had taken place is that the nonbonding orbital differs in phase from the original carbon $s_{\bar{z}}$ orbital.

Looking at these orbitals it is tempting to believe that orbital recoupling is of no importance and that the required singlet-pair transfer is accomplished solely by spatial migration of a fixed $\boxed{\phi_1\phi_2}$ singlet pair. That this is not the case is clear from the coupling coefficients plotted in Fig. 11. At large internuclear distances, when the orbitals are still atomiclike, recoupling proceeds as expected; with $\mathcal{E}_1$ decreasing as $-\mathcal{E}_2$ steadily increases (negative sign path). This trend continues even as the orbitals delocalize, reaching a point of maximal change at about 2.9 a_0. With subsequent relocalization of ϕ_2 and ϕ_3 (which effectively interchanges their original identities), $\mathcal{E}_1$ steadily increases back toward unity as this coefficient now measures molecular coupling.

Discussion

Because of the observed orbital delocalization-relocalization, our initial concept of formation of this molecule must be modified somewhat. We will now show that there is no contradiction involved, but rather, that the orbital coupling changes predicted on the basis of localized orbitals actually favor the observed orbital spatial migration. At large internuclear distances, recoupling of the atomiclike orbitals proceeds as expected. In response to increasing overlap between $\phi_1(s_Z)$ and $\phi_3(s_H)$, these two orbitals become increasingly symmetrically (singlet) coupled. As we have seen, this recoupling also implies decreasing singlet coupling between ϕ_1 and $\phi_2(s_{\bar{Z}})$ and increasing antisymmetric (triplet) coupling between ϕ_2 and ϕ_3. That this process is initially endothermic is not too surprising since there is no way for recoupling to fully compensate for increasing overlap between ϕ_1 and ϕ_3 while still maintaining favorably high singlet coupling between ϕ_1 and ϕ_2. For atomiclike orbitals, this situation would become increasingly worse at smaller internuclear distances. However, these mounting repulsive interactions can be relieved while still utilizing the space of these orbitals through delocalization of ϕ_2 and ϕ_3. This is accomplished by allowing $\phi_2\,(s_{\bar{z}})$ to develop positive s_H character as $\phi_3(s_H)$ develops negative $s_{\bar{z}}$ character. In this way, ϕ_2 can move into the internuclear region while maintaining high overlap with ϕ_1 (to which it is still largely singlet coupled) as ϕ_3 moves in the opposite direction, achieving favorable small overlap with both ϕ_1 and ϕ_2. However, while initial delocalization does serve to minimize increasingly repulsive interactions, it cannot continue to any significant extent and still lead to an attractive potential until ϕ_2 and ϕ_3 have become largely triplet coupled; with this coupling becoming even more pronounced during delocalization. The reason for this is that increasing delocalization of ϕ_2 and ϕ_3 into each other's space would otherwise cause the wavefunction to develop significant ionic character ($^{+}$C-H^{-} and $^{-}$C-H^{+}). Qualitatively, this can be clearly seen by rewriting the wavefunction in terms of singlet and triplet coupling between ϕ_2 and ϕ_3:

$$\Psi = \lambda_1 \begin{array}{|c|c|}\hline \phi_2 & \phi_3 \\ \hline \phi_1 & \\ \cline{1-1}\end{array} + \lambda_2 \begin{array}{|c|c|}\hline \phi_2 & \phi_1 \\ \hline \phi_3 & \\ \cline{1-1}\end{array}$$

where $\lambda_1 = \varepsilon_1 + \varepsilon_2$ and $\lambda_2 = \varepsilon_2 - \varepsilon_1$ (for simplicity we have omitted the $p_x p_y$ singlet pair). Expressing ϕ_2 and ϕ_3 in terms of localized orbital $s_{\bar{z}}$ and s_H and expanding we obtain:

$$\phi_2 \propto s_{\bar{z}} + |\gamma_2|\, s_H \quad ; \quad \phi_3 \propto s_H - |\gamma_3|\, s_{\bar{z}}$$

$$\Psi = \underbrace{\lambda_1 (1 - |\gamma_2\gamma_3|) \begin{array}{|c|c|}\hline s_{\bar{z}} & s_H \\ \hline \phi_1 & \\ \cline{1-1}\end{array} + \lambda_2 (1 + |\gamma_2\gamma_3|) \begin{array}{|c|c|}\hline s_{\bar{z}} & \phi_1 \\ \hline s_H & \\ \cline{1-1}\end{array}}_{\text{covalent}} + 2\lambda_1 \underbrace{\left[|\gamma_2|\, \mathcal{A}\, s_H^2 \phi_1 \alpha\beta\alpha - |\gamma_3|\, \mathcal{A}\, s_{\bar{z}}^2 \phi_1 \alpha\beta\alpha \right]}_{\text{ionic}}$$

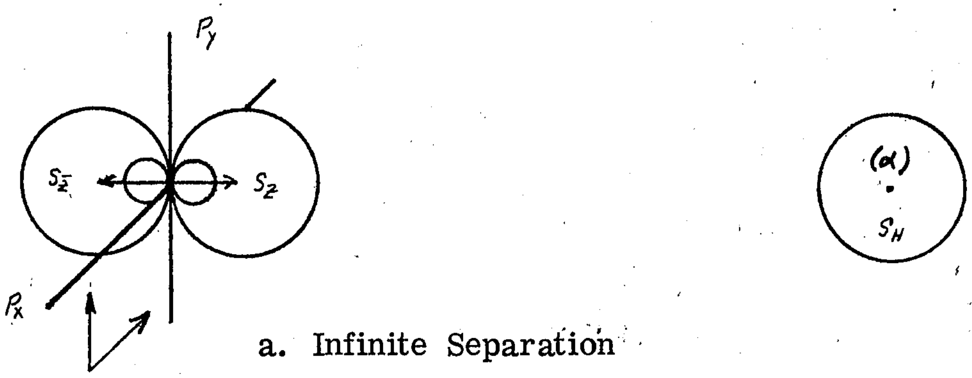
Hence, ionic character can only develop to the extent to which ϕ_2 and ϕ_3 are singlet coupled. Therefore, through increased triplet coupling between ϕ_2 and ϕ_3 delocalization can continue to be favorable since this coupling prevents what would otherwise be an excessive amount of ionic character from developing. Thus we see that the observed delocalization occurring in this singlet-pair transfer process is quite compatible with the recoupling path predicted for localized orbitals in that the expected increasing triplet coupling between ϕ_2 and ϕ_3 actually aids in their delocalization. Of course, once full delocalization has been achieved and ϕ_2 relocalizes to become the hydrogen centered bonding orbital as ϕ_3 becomes the nonbonding sigma orbital, this recoupling trend reverses itself since it is now singlet pairing between ϕ_1 and ϕ_2 which describes molecular coupling.

TABLE 2: $^2\Delta$ RESULTS

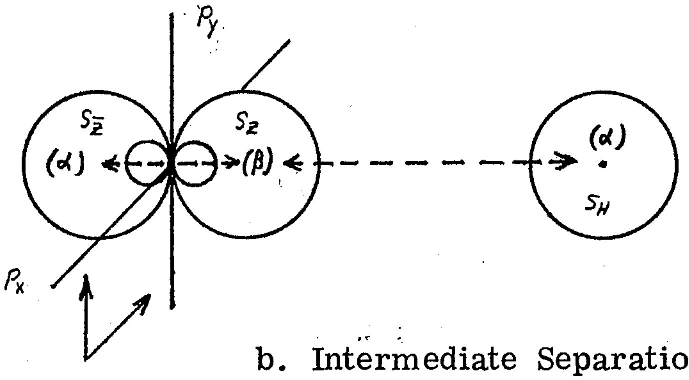
Distance R(bohr)	Energy -E(a.u.)	Binding Energy B.E. (a.u.)	Coupling Coefficients ε_1	ε_2
6.00	38.14619	-0.00010	.9966	-.0034
5.00	38.14547	-0.00081	.9812	-.0188
4.00	38.14359	-0.00270	.9055	-.0944
3.50	38.14322	-0.00308	.8042	-.1958
3.00	38.14772	0.00142	.6559	-.3441
2.40	38.17094	0.02464	.7894	-.2106
2.124	38.18294	0.03664	.8620	-.1380
1.90	38.17059	0.02426	.8959	-.1041
Complete GVB:				
3.50	38.14388	-0.00242	.7892	-.2107
3.00	38.1510	0.00473	.6212	-.3788
2.124	38.1854	0.03911	.8095	-.1905
HF:[13]				
2.05	38.17957	0.0484		
CI:[14]				
2.07	38.28973	0.06948		
EXP:[10]				
2.08	38.3093	0.076		

$$\Psi_{2\Delta} = \varepsilon_1 \begin{array}{|c|c|}\hline p_x & p_y \\ \hline \phi_1 & \phi_2 \\ \hline \phi_3 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \varepsilon_2 \begin{array}{|c|c|}\hline p_x & p_y \\ \hline \phi_1 & \phi_3 \\ \hline \phi_2 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

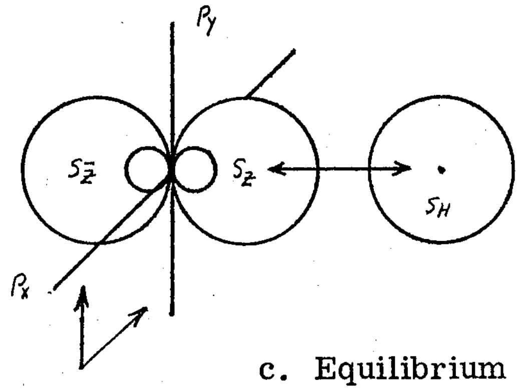
CH $^2\Delta$ FORMATION



a. Infinite Separation



b. Intermediate Separation



c. Equilibrium

FIG. 8

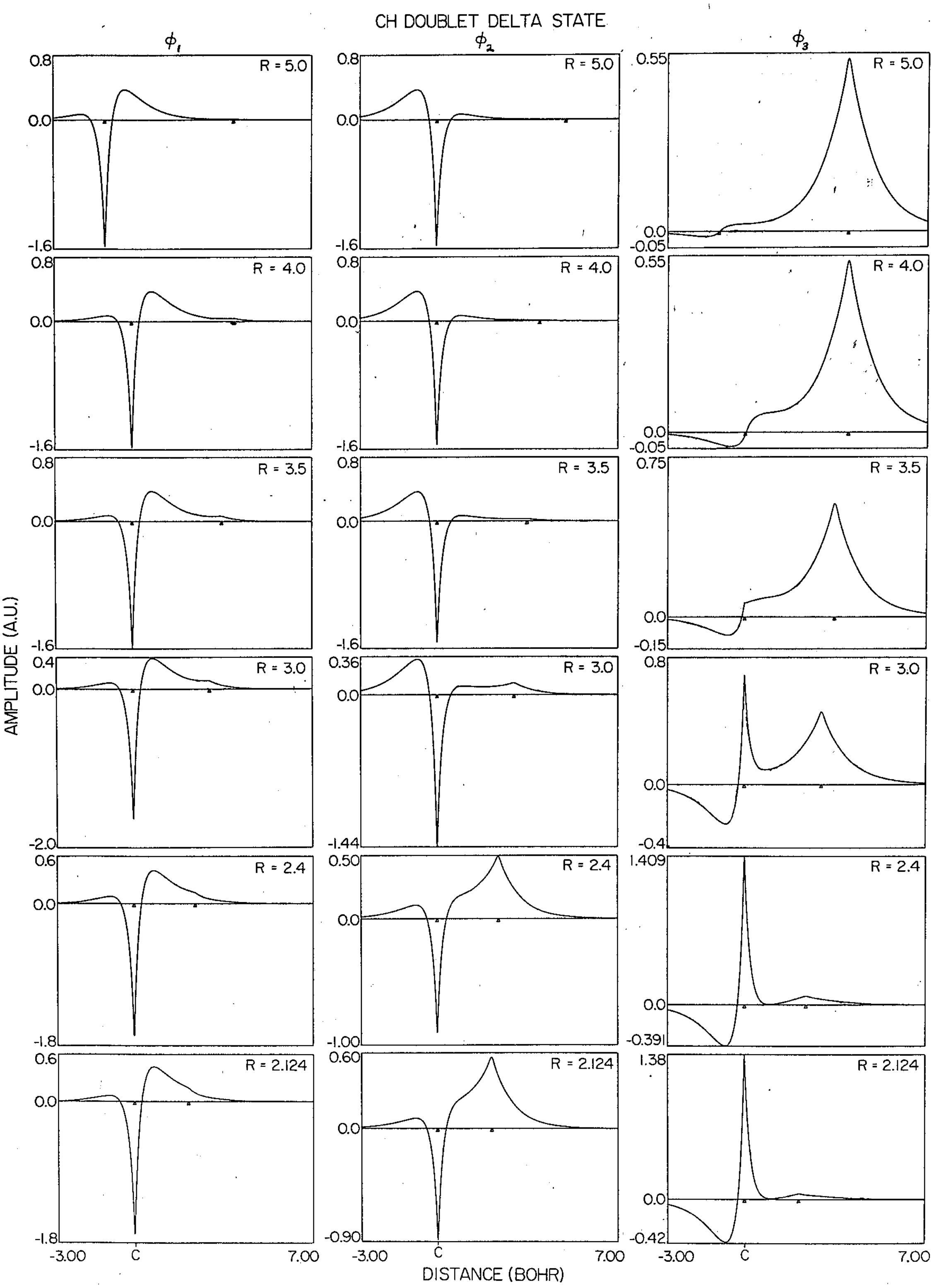

CH DOUBLET DELTA STATE
ϕ_1
ϕ_2
ϕ_3
R = 5.0
R = 4.0
R = 3.5
R = 3.0
R = 2.4
R = 2.124
0.8
0.0
-1.6
0.4
-2.0
0.6
-1.8
0.36
-1.44
0.50
-1.00
0.60
-0.90
0.55
-0.05
0.75
-0.15
-0.4
1.409
-0.391
1.38
-0.42
AMPLITUDE (A.U.)
-3.00
C
7.00
DISTANCE (BOHR)

FIG. 9

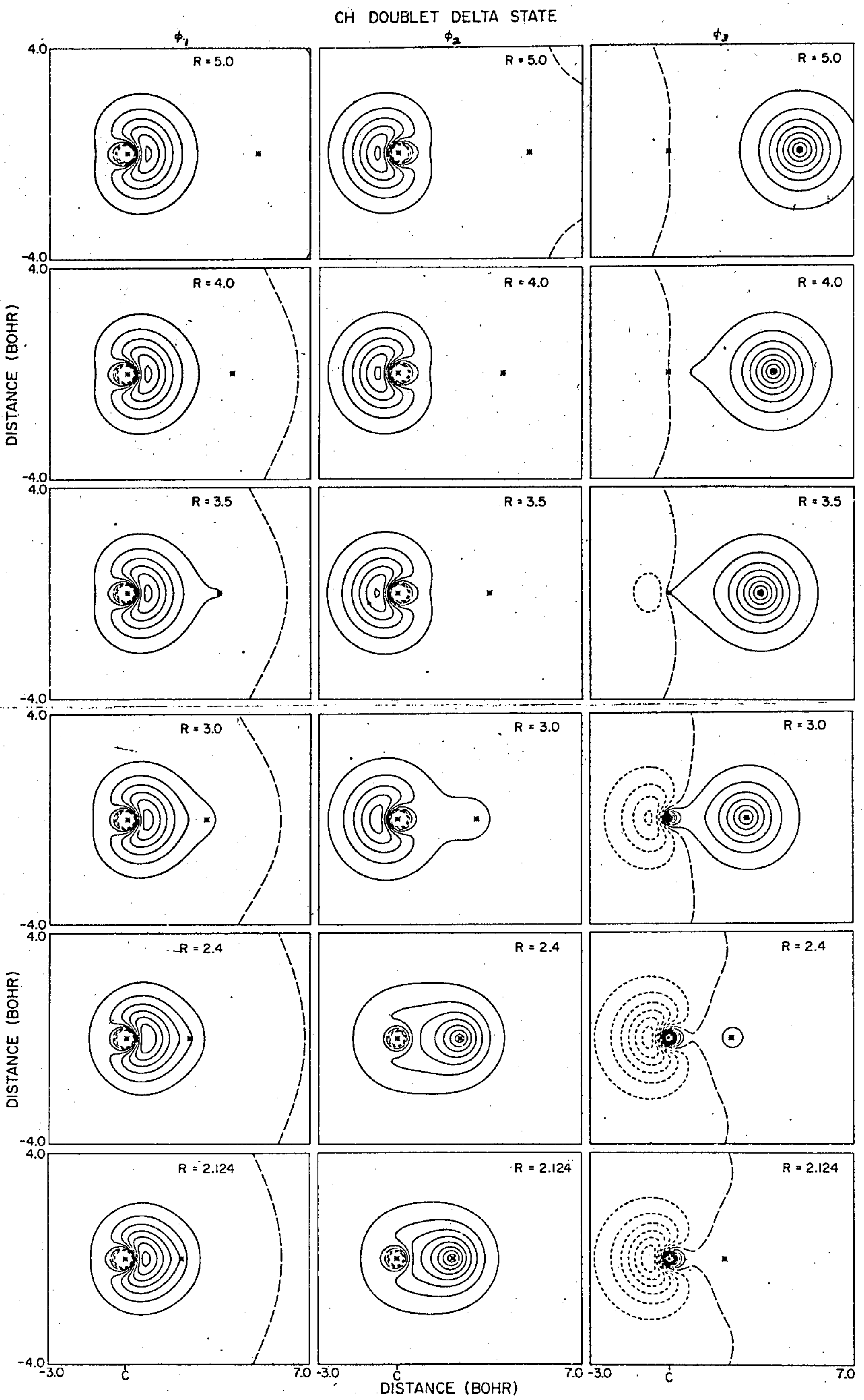

CH DOUBLET DELTA STATE
ϕ_1
ϕ_2
ϕ_3
R = 5.0
R = 4.0
R = 3.5
R = 3.0
R = 2.4
R = 2.124
DISTANCE (BOHR)
4.0
-4.0
-3.0
C
7.0
DISTANCE (BOHR)

FIG. 10

$^2\Delta$ COUPLING COEFFICIENTS

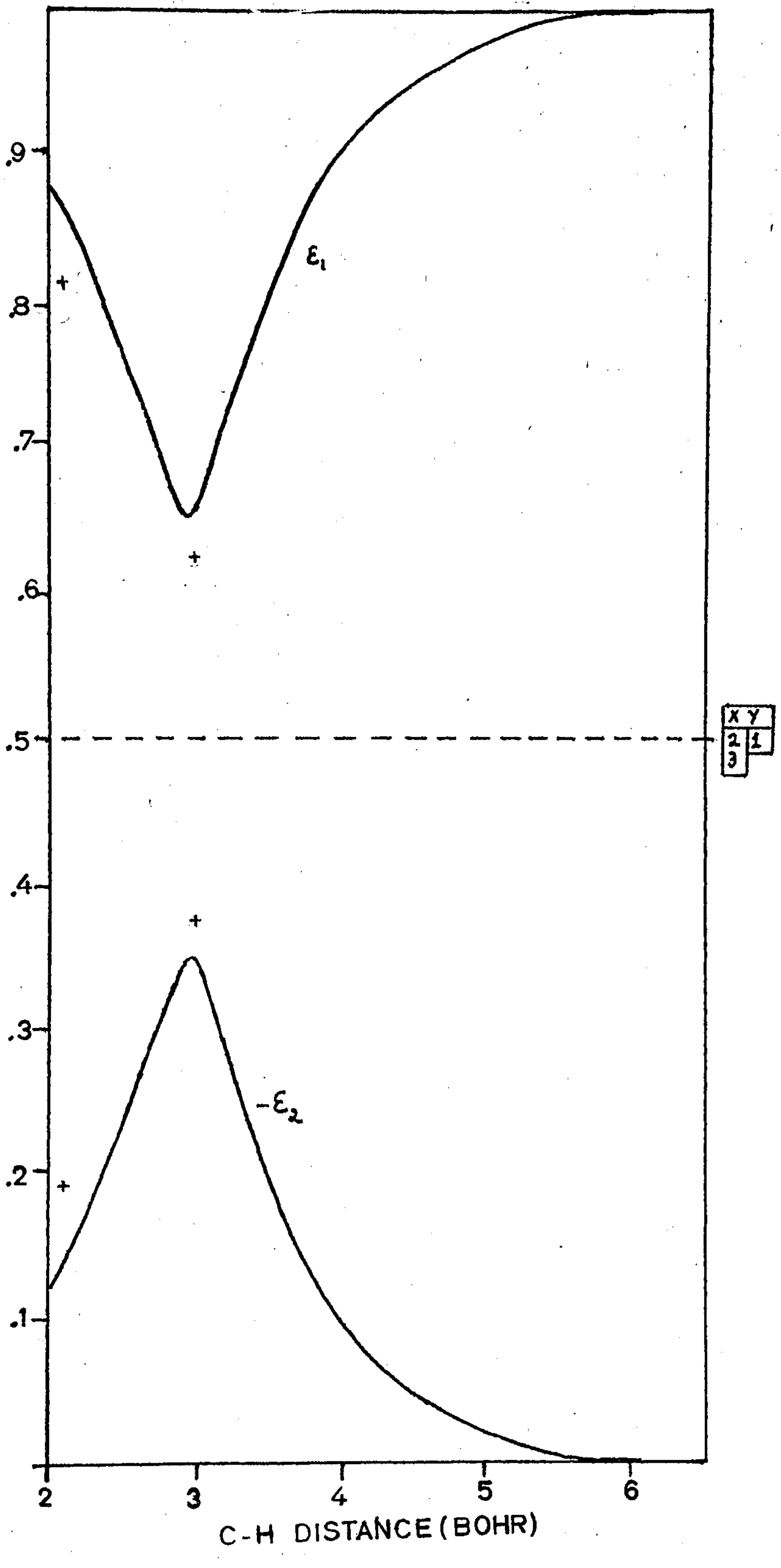


FIG. 11

VII. THE $^4\Sigma^-$ STATE

Qualitative Considerations

The $^4\Sigma^-$ state of CH can be envisioned to result when a hydrogen ^2S atom approaches a carbon ^3P atom along the axis of hybridization (Fig. 12). At infinite separation, atomic coupling must prevail. This corresponds to singlet pairing of orbitals s_z and $s_{\bar{z}}$, and quartet coupling between orbitals p_x, p_y and s_H(i.e. orbitals p_z and p_y are triplet coupled):

$$\Psi_\infty = \begin{array}{|c|c|}\hline s_z & s_{\bar{z}} \\ \hline s_H & \multicolumn{1}{c}{} \\ p_x & \multicolumn{1}{c}{} \\ p_y & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = \mathcal{A}\, s_z s_{\bar{z}} s_H p_x p_y (\alpha\beta-\beta\alpha)\alpha\alpha\alpha$$

If the orbitals remain localized during molecule formation, the C-H bond should be described by singlet pairing of orbitals s_z and s_H:

$$\Psi_e = \begin{array}{|c|c|}\hline s_z & s_H \\ \hline s_{\bar{z}} & \multicolumn{1}{c}{} \\ p_x & \multicolumn{1}{c}{} \\ p_y & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = \mathcal{A}\, s_z s_H s_{\bar{z}} p_x p_y (\alpha\beta-\beta\alpha)\alpha\alpha\alpha$$

Thus, the simplest localized orbital wavefunction needed to describe formation of this molecule would be a linear combination of these atomic and molecular couplings.

However, this is analogous to formation of the $^2\Delta$ state in that all that is essentially involved is singlet-pair transfer. The only difference is that now orbitals p_x and p_y are triplet coupled whereas they are singlet paired in the $^2\Delta$ state. Therefore, we can expect that orbitals $s_{\bar{z}}$ and s_H will not remain localized, but will gradually delocalize (as triplet coupling between them becomes more pronounced) and then relocalize so as to effectively exchange original identities. Therefore, we expect the general wavefunction to be:

$$\Psi_{{}^4\Sigma^-} = |\varepsilon_1| \begin{array}{|l|l|}\hline s_z & \phi_2 \\ \hline \multicolumn{1}{|l|}{\phi_3} \\ \multicolumn{1}{|l|}{p_x} \\ \multicolumn{1}{|l|}{p_y} \\ \cline{1-1}\end{array} - |\varepsilon_2| \begin{array}{|l|l|}\hline s_z & \phi_3 \\ \hline \multicolumn{1}{|l|}{\phi_2} \\ \multicolumn{1}{|l|}{p_x} \\ \multicolumn{1}{|l|}{p_y} \\ \cline{1-1}\end{array}$$

where ϕ_2 and ϕ_3 are initially the carbon $s_{\bar{z}}$ and hydrogen 1s orbitals respectively.

GVB Results:

Results of GVB calculations are summarized in Table 3. From the potential energy curve in Fig.3a, we obtain a binding energy of 0.095 a.u. at 2.09 a_0. While this state has not been observed experimentally, these results are in good agreement with other studies which have placed it somewhat above the $^2\pi$ ground state. Also, we see that the potential barrier which would have been expected by our analogy to the $^2\Delta$ state never materializes.

As plots of the sigma orbitals in Figs. 13 and 14 show, these orbitals behave just as in formation of the $^2\Delta$ state. Orbital ϕ_1 remains essentially localized throughout. Orbital ϕ_2 ($s_{\bar{z}}$) gradually delocalizes into the internuclear region while maintaining high overlap with ϕ_1 and then relocalizes as the hydrogen centered bonding orbital. Simultaneously, ϕ_3 moves in the other direction, achieving small overlap with ϕ_1 and ϕ_2 through formation of a nodal plane. As expected, orbitals p_x and p_y (not shown) remain virtually unchanged during molecule formation. The only significant difference between these orbital changes and those found for the $^2\Delta$ state is that increased delocalization of orbitals ϕ_2 and ϕ_3 occurs at larger internuclear distances.

Plots of the coupling coefficients in Fig. 15 are also analogous to those for the $^2\Delta$ state with the exception that antisymmetric (triplet) coupling between ϕ_2 and ϕ_3 is now more pronounced at large internuclear separations. In addition, however, we see that a third coupling develops which was not considered previously. This corresponds to quintet coupling between orbitals p_x, p_y, ϕ_2 and ϕ_3. That this coupling contributes to the wavefunction is not too surprising since it allows for very favorable exchange interactions between these orbitals.(Note that the orbital coupling designations in Fig. 14b are compatible with development of this coupling since all four of these orbitals have (α) labels). However, the simultaneously required symmetric coupling of ϕ_1 with p_z and p_y is highly unfavorable. As a consequence, this coupling is never of any great significance.

Discussion

The GVB description of formation of the $^4\Sigma^-$ state is qualitatively the same as that for formation of the $^2\Delta$ state. However, while both involve the same singlet-pair transfer mechanism, the $^2\Delta$ state has a potential barrier while the $^4\Sigma^-$ state does not. Obviously, this must be due to favorable interactions that can develop between the sigma orbitals and the triplet coupled p-orbitals which are not possible in the $^2\Delta$ state since these p-orbitals are singlet paired. In formation of the $^2\Delta$ state we saw that the barrier could be qualitatively attributed to repulsive interactions developing between the atomiclike sigma orbitals as the internuclear separation decreased. In response to these increasingly unfavorable interactions, orbitals $\phi_2(s_{\bar{z}})$ and ϕ_3 (s_H) began to delocalize. However, owing to the excessive ionic character which would have otherwise increasingly developed, this delocalization could not continue to any significant extent and still lead to binding unless these two orbitals became increasingly triplet coupled. As we have seen, in formation of the $^4\Sigma^-$ state, orbital delocalization occurs before the atomic orbitals come close enough to repulsively interact. In addition, ϕ_2 and ϕ_3 are also significantly triplet coupled at these distances. Therefore, the potential can remain attractive at all distances.

The reason why orbital delocalization and enhanced recoupling occur at larger distances than in the $^2\Delta$ state can be attributed mainly to the favorable exchange interactions which can develop by having three orthogonal quartet coupled orbitals centered about the carbon nucleus. This, of course, is the same reason for the fairly large binding energy of this molecule at equilibrium. Even ignoring the question of orbital recoupling, the system can take on some of this character at large distances through delocalization, as this allows ϕ_3 (quartet coupled to p_x and p_y) to develop character on carbon. The extent to which this can occur is naturally limited by the attendant increase in ionic character. Enhanced orbital recoupling can also achieve this effect since increased quartet coupling between orbitals p_x, p_y and $\phi_2(s_{\bar{z}})$ results when symmetric (singlet) coupling between ϕ_1 and ϕ_3 is increased. In addition, increased triplet coupling between ϕ_2 and ϕ_3 is favored on the whole since this can lead to favorable exchange interactions between all four orbitals p_x, p_y, ϕ_2 and ϕ_3. Thus, taking all of these factors into account, it is not surprising that we do not find a potential barrier for this state, despite the fact that the singlet-pair transfer involved is in itself an endothermic process.

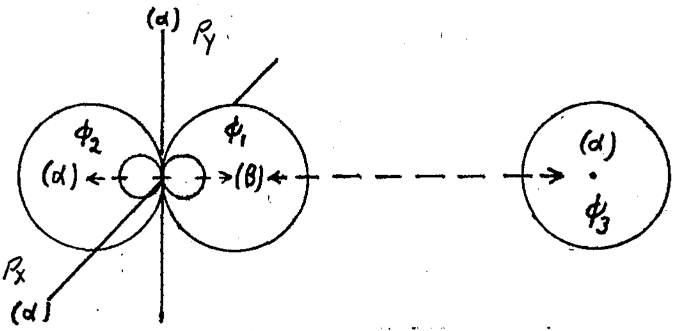
TABLE 3: $^4\Sigma^-$ RESULTS

Distance R(bohr)	Energy -E(a.u.)	Binding Energy B.E. (a.u.)	Coupling Coefficients ϵ_1	ϵ_2	ϵ_3
6.00	38.20364	0.00003	0.9823	0.0145	0.0032
5.00	38.20353	0.0001	0.9172	0.0688	0.0140
4.00	38.20547	0.0019	0.6908	0.2583	0.0509
3.50	38.21275	0.0091	0.5489	0.3787	0.0724
3.00	38.23469	0.0311	0.6628	0.2606	0.0766
2.40	38.28064	0.0770	0.7543	0.1669	0.0788
2.124	38.29620	0.0926	0.7893	0.1343	0.0763
1.90	38.28659	0.0830	0.8061	0.1193	0.0746
Complete GVB					
6.00	38.20364	0.00003	0.9928	0.1436	0.0028
3.50	38.21518	0.01158	0.5280	0.3998	0.0722
2.124	38.29818	0.09458	0.7474	0.1595	0.0940
HF:[14]					
2.00	38.28967	0.10119			
CI:[14]					
2.00	38.38058	0.10524			

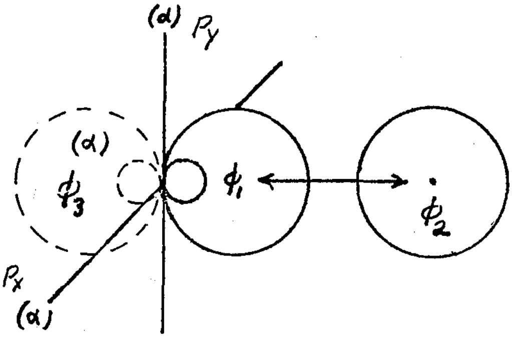
$$\Psi_{{}^4\Sigma^-} = \varepsilon_1 \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \multicolumn{1}{c}{} \\ p_x & \multicolumn{1}{c}{} \\ p_y & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} - \varepsilon_2 \begin{array}{|c|c|}\hline \phi_1 & \phi_3 \\ \hline \phi_2 & \multicolumn{1}{c}{} \\ p_x & \multicolumn{1}{c}{} \\ p_y & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \varepsilon_3 \begin{array}{|c|c|}\hline \phi_2 & \phi_1 \\ \hline \phi_3 & \multicolumn{1}{c}{} \\ p_x & \multicolumn{1}{c}{} \\ p_y & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

CH $^4\Sigma$ FORMATION

a. Infinite Separation

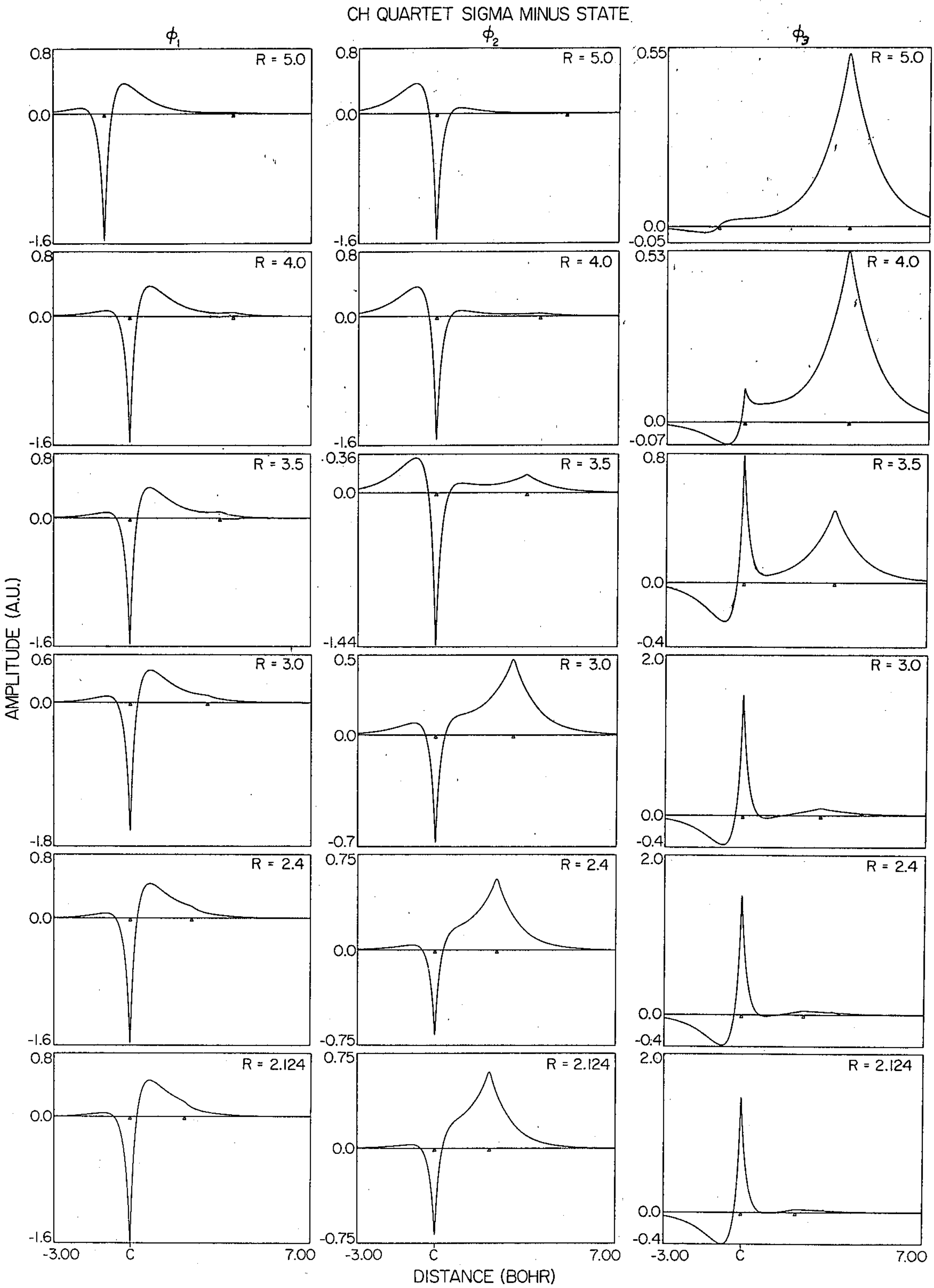


b. Intermediate Separation



c. Equilibrium

FIG. 12



CH QUARTET SIGMA MINUS STATE
ϕ_1
ϕ_2
ϕ_3
R = 5.0
R = 4.0
R = 3.5
R = 3.0
R = 2.4
R = 2.124
0.8
0.0
-1.6
0.55
-0.05
0.53
-0.07
0.36
-1.44
0.6
-1.8
0.5
-0.7
2.0
-0.4
0.75
-0.75
AMPLITUDE (A.U.)
-3.00
C
7.00
DISTANCE (BOHR)

FIG. 13

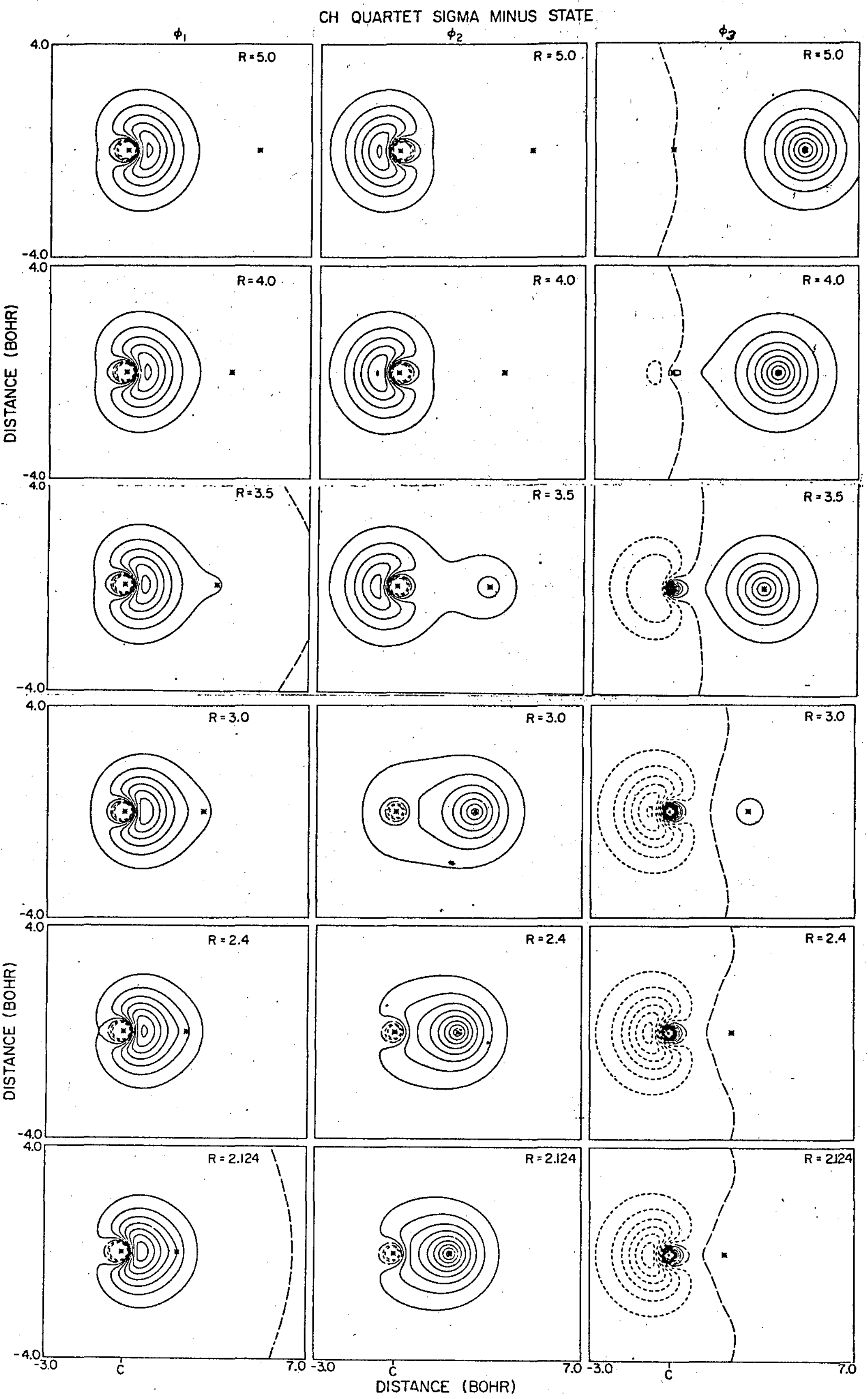

CH QUARTET SIGMA MINUS STATE
ϕ_1
ϕ_2
ϕ_3
R = 5.0
R = 4.0
R = 3.5
R = 3.0
R = 2.4
R = 2.124
4.0
-4.0
DISTANCE (BOHR)
-3.0
C
7.0
DISTANCE (BOHR)

FIG. 14

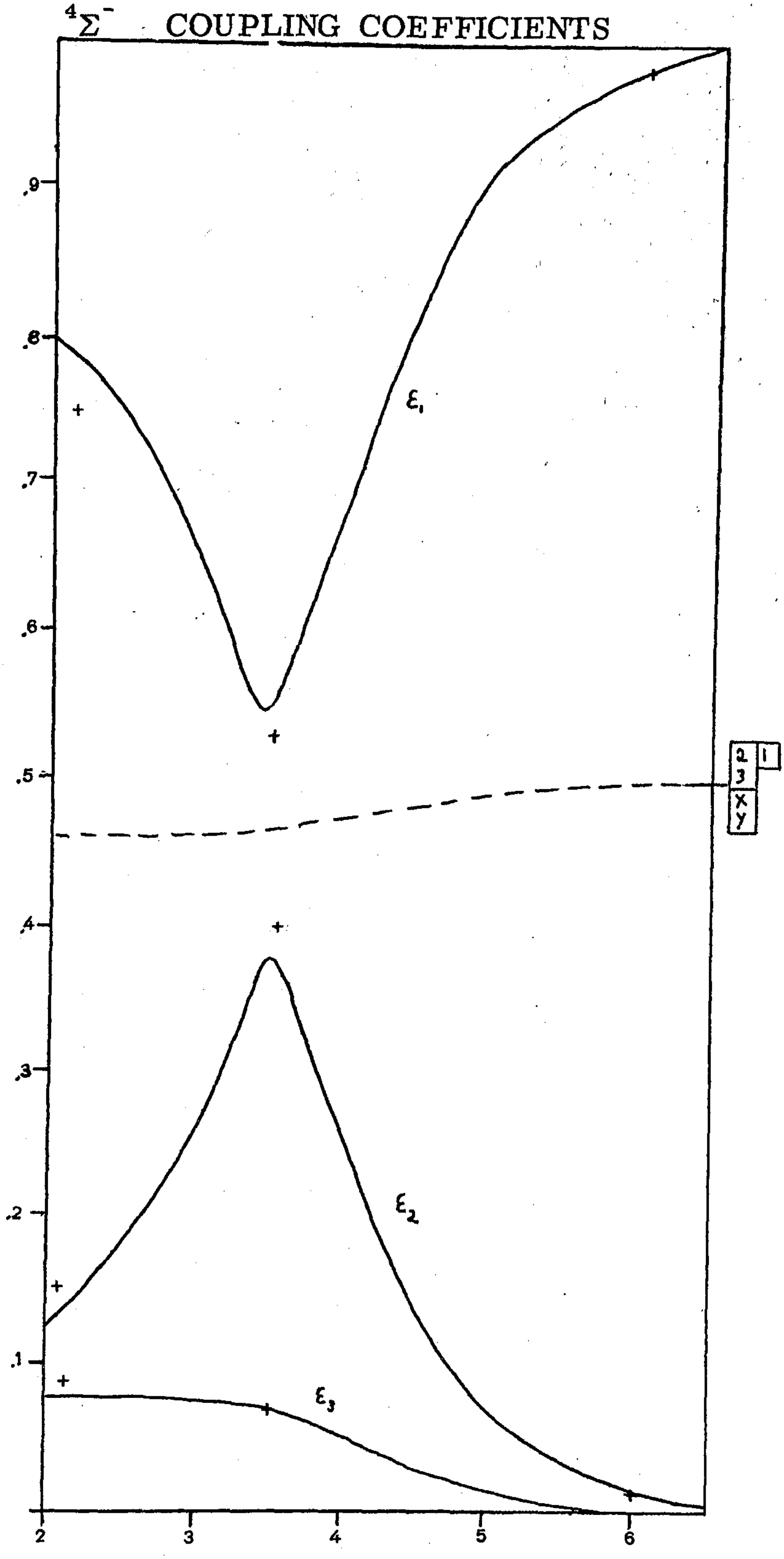

$^4\Sigma^-$ COUPLING COEFFICIENTS
.9
.8
.7
.6
.5
.4
.3
.2
.1
2
3
4
5
6
C-H DISTANCE (BOHR)
ε_1
ε_2
ε_3
2
1
3
X
Y

FIG. 15

VIII. CONCLUSION

GVB descriptions for the formation of the low-lying $^2\pi$, $^2\Delta$, and $^4\Sigma^-$ states of the CH molecule have been presented. These GVB wavefunctions have been found to behave properly at all internuclear distances and lead to a clear physical picture of these simple molecule-formation reactions. The observed orbital and orbital-coupling changes have been found to be consistent with simple Valence-Bond arguments once they have been modified to allow for orbital optimization as well.

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PART TWO

Evaluation of Spin-Eigenfunction Configuration Interaction Matrices

Abstract

A procedure for calculating Spin-Eigenfunction Configuration Interaction matrices utilizing the U matrices which form the irreducible representations of $\mathcal{S}_N$ is presented. In addition, an improved determinant method is summarized. By combining both of these U-matrix and Determinant methods, it has been possible to formulate a practical and yet highly efficient procedure for generating such CI matrices.

I. INTRODUCTION

Calculation of spin-eigenstate Configuration Interaction (CI) wavefunctions can be facilitated by using configurations which are themselves eigenstates of spin. The simplest such basic unit is an orbital-product wavefunction of the form:

$$\psi = \mathcal{A}\,[\text{Core}]\,\Phi^{(N)}\chi^{(N)}$$

$$\text{Core} = \prod_{i}^{ND} \bar{\phi}_i^{2}\,\alpha\beta$$

$$\Phi^{(N)} = \prod_{i}^{N} \phi_i$$

$$\chi^{(N)} = \sum_{j} d_j\,\chi_j(\alpha,\beta\cdots)$$

where $\mathcal{A}$ is the antisymmetrizer (determinant operator). Core consists of a set of doubly occupied (closed-shell) orbitals $\{\bar{\phi}\}$, each of which is associated with an $\alpha\beta$ spin term. $\Phi^{(N)}$ is a product of the N singly-occupied (open-shell) orbitals with which the spin function $\chi^{(N)}$ is associated. $\chi^{(N)}$ is a linear combination of appropriate N-electron spin $(\alpha\beta)$ products and is required to be an eigenfunction of spin:

$$\hat{S}^2\chi^{(N)} = S(S+1)\,\chi^{(N)}$$

For N electrons, there are generally several linearly independent spin-eigenfunctions of multiplicity S. Hence, corresponding to each spatial configuration (defined simply as a set of doubly- and singly-occupied orbitals) there are usually several independent Spin-Eigenfunction Configurations (SECs):

$$\psi_i^I = \mathcal{A}\,[\text{core}]_I\,\Phi^{(NI)}\chi_i^{(NI)}$$

where $(\text{core})_I$ and $\Phi_I^{(NI)}$ contain the closed- and open-shell orbitals of spatial configuration I and $\chi_i^{(NI)}$ is the i$^{\text{th}}$ linearly independent spin-eigenfunction (SEF) of multiplicity S for NI electrons. A convenient set of orthonormal SEFs for N electrons can be obtained from the appropriate SEFs for (N-1) electrons using the recursion relationships:

If $S^{(N)} > S^{(N-1)}$: $\chi^{(N)} = \chi^{(N-1)}\alpha$

If $S^{(N)} < S^{(N-1)}$: $\chi^{(N)} = 2S^{(N-1)}\chi^{(N-1)}\beta - [\hat{S}^-_{N-1}\chi^{(N-1)}]\alpha$

where $\chi^{(N-1)}$ is an (N-1)-electron SEF of multiplicity $S^{(N-1)}$ and $\hat{S}^-_{N-1}$ is the spin lowering operator for (N-1) electrons. If in ψ_i^I the orbitals of Φ_I are arranged in increasing order and χ_i is one of these standard orthogonal SEFs, then ψ_i^I is said to be a standard SEC.*

In terms of standard SECs, an N_e-electron CI wavefunction of multiplicity S constructed from a set of NF spatial configurations is:

$$\Psi_{CI} = \sum_{I=1}^{NF}\sum_{i=1}^{NSI} c_i^I\,\psi_i^I$$

where each of the NSI SECs of multiplicity S for spatial configuration I contain the same NI open-shell orbitals and NDI = $\frac{1}{2}(N_e\text{-NI})$ closed-shell orbitals. Assuming all orbitals are orthonormal, the energy is:

$$E = \sum_{I,J=1}^{NF}\sum_{i}^{NSI}\sum_{j}^{NSJ} c_i^I c_j^J \langle\psi_i^I|H|\psi_j^J\rangle \Big/ \sum_{I}^{NF}\sum_{i}^{NSI} c_i^{I\,2}$$

---

*See Appendix 2

Hence, the solutions of this wavefunction are obtained by simply diagonalizing the CI matrix $\underline{H}$ where:

$$H_{ij}^{IJ} = \langle \Psi_i^I | H | \Psi_j^J \rangle$$

The remaining sections of this paper will be devoted to development of a practical yet highly efficient procedure for generating these SEC CI matrices. First, evaluation of such matrix elements by expressing each SEC as a linear combination of Slater determinants will be discussed. This method is the basis of the procedure employed by R. Ladner in which CI matrix elements between all required determinants of all spatial configurations are independently calculated and transformed to give the desired results.[1] Next, a method based upon the irreducible representations of $\mathscr{S}_N$ which permits direct evaluation of SEC CI matrix elements will be derived. Finally it will be shown that using both this latter approach and a more refined determinant method, in which unnecessary and redundant computations are eliminated, leads to a procedure which has typically been found to generate SEC CI matrices an order of magnitude more rapidly than the previously employed independent-determinant procedure.

II. THE DETERMINANT METHOD OF EVALUATING SEC CI MATRIX ELEMENTS

CI matrix elements between the SECs of multiplicity S for a set of spatial configurations involving orthonormal orbitals can straightforwardly be evaluated by expressing each SEC as a linear combination of Slater determinants. If $\{D^I\}$ are the NDETI determinants needed to construct all SECs of multiplicity S for spatial configuration I, then the mth SEC is:

$$\Psi^I_m = \sum_i^{NDETI} C^{NI}_{im}\, D^I_i$$

where, for given S, C^{NI}_{im} is the coefficient of the ith determinant in the mth SEC of a spatial configuration containing NI singly occupied orbitals. Choosing the SECs to be the standard couplings, these coefficients can readily be obtained from the standard orthonormal spin-eigenfunctions for NI electrons of multiplicity S, $\{\chi\}$, by simply expanding:

$$\Psi^I_m = \mathcal{A}\left[\prod_i^{NI} \phi_i(i)\right] \chi_m$$

in terms of these determinants. Hence, the CI matrix element between the mth SEC of configuration I and the nth SEC of configuration J is simply:

$$\langle \Psi^I_m | H | \Psi^J_n \rangle = \sum_i^{NDETI} \sum_j^{NDETJ} C^{NI}_{im}\, C^{NJ}_{jn}\, \langle D^I_i | H | D^J_j \rangle$$

A. Determinant Definitions:

If configuration I consists of NI singly occupied orbitals, the required NDETI determinants having spin projection $S_z = S$ correspond to the unique number of ways these orbitals can be associated with $NA = \frac{1}{2}(NI + 2S)$ α spins and $NB = (NI-NA)$ β spins. Thus, the i^th determinant can be written as:

$$D_i^I = \mathcal{A}\, \Theta_i^I(\alpha)\, \Theta_i^I(\beta)$$

where $\Theta_i^I(\alpha)$ is a product of the NA α spin orbitals (written in increasing order) in the ith determinant. $\Theta_i^I(\beta)$ is defined analogously. For example, if configuration I consists of orbitals ϕ_1, ϕ_2, ϕ_3, and ϕ_4 then the six $S_z = 0$ determinants are defined by:

$$\begin{aligned}
\Theta_1^I(\alpha)\, \Theta_1^I(\beta) &= \phi_1\alpha\, \phi_2\alpha\, \phi_3\beta\, \phi_4\beta \\
\Theta_2^I(\alpha)\, \Theta_2^I(\beta) &= \phi_1\alpha\, \phi_3\alpha\, \phi_2\beta\, \phi_4\beta \\
\Theta_3^I(\alpha)\, \Theta_3^I(\beta) &= \phi_1\alpha\, \phi_4\alpha\, \phi_2\beta\, \phi_3\beta \\
\Theta_4^I(\alpha)\, \Theta_4^I(\beta) &= \phi_2\alpha\, \phi_3\alpha\, \phi_1\beta\, \phi_4\beta \\
\Theta_5^I(\alpha)\, \Theta_5^I(\beta) &= \phi_2\alpha\, \phi_4\alpha\, \phi_1\beta\, \phi_3\beta \\
\Theta_6^I(\alpha)\, \Theta_6^I(\beta) &= \phi_3\alpha\, \phi_4\alpha\, \phi_1\beta\, \phi_2\beta
\end{aligned}$$

If configuration I also contains NDI closed-shell (doubly-occupied) orbitals, the i^th determinant can be written as:

$$D_i^I = \mathcal{A}\, \Theta_c^I(\alpha)\, \Theta_i^I(\alpha)\, \Theta_c^I(\beta)\, \Theta_i^I(\beta)$$

where Θ_c^I is a product of the NDI closed shell orbitals in increasing order. In $\Theta_c^I(\alpha)$, these orbitals are associated with α spins and in $\Theta_c^I(\beta)$ they are associated with β spins. Finally, if $\Phi_i^I(\alpha)$ is the product of all α spin orbitals in the i^{th} determinant written in increasing order and $\Phi_i^I(\beta)$ is the product of all β spin orbitals also in increasing order:

$$\Phi_i^I(\alpha) = \tau_{i\alpha}^I \, \Theta_c^I(\alpha) \, \Theta_i^I(\alpha)$$
$$\Phi_i^I(\beta) = \tau_{i\beta}^I \, \Theta_c^I(\beta) \, \Theta_i^I(\beta)$$

then:

$$D_i^I = \zeta_i^I \, \mathcal{A} \, \Phi_i^I(\alpha) \, \Phi_i^I(\beta)$$

where ζ_i^I is the parity of permutation $\tau_{i\alpha}^I \tau_{i\beta}^I$.

Defining the determinants in this manner is not only computationally convenient, but, more importantly, gives rise to compatible determinants for all spatial configurations. Thus, all the standard couplings for these configurations can be constructed using a single set of coefficients which, for given multiplicity, depend only upon the number of singly occupied orbitals involved.

B. Evaluation of Determinant Matrix Elements:

Since all spatial configurations are for the same number of electrons and since all determinants have the same S_z, all determinants have the same number of α spin orbitals and β spin orbitals. Therefore, if all orbitals are orthonormal, the CI matrix element between the i^{th} determinant of configuration I and the j^{th} determinant of configuration J can be nonzero only when:

1) $\Phi_i^I(\gamma)$ and $\Phi_j^J(\gamma)$ differ by no more than a double excitation and $\Phi_i^I(\epsilon) = \Phi_j^J(\epsilon)$, where $\gamma(\epsilon) = \alpha(\beta)$ or $\beta(\alpha)$

or

2) $\Phi_i^I(\alpha)$ and $\Phi_j^J(\alpha)$ differ by a single excitation as does $\Phi_i^I(\beta)$ and $\Phi_j^J(\beta)$.

These give rise to the four possibilities:

1) α (or β) single excitations

2) $\alpha\alpha$ (or $\beta\beta$) double excitations

3) $\alpha\beta$ double excitations

4) Zero excitations

1. α (or β) Single Excitations:

Assume $\Phi_i^I(\alpha)$ and $\Phi_j^J(\alpha)$ differ by orbitals ϕ_I and ϕ_J which occupy positions I_1 and J_1 in their respective lists. Rearranging $\Phi_i^I(\alpha)$ via the cyclic permutation which positions ϕ_I before all other orbitals:

$$\phi_I\alpha\ \Phi_i^{I'}(\alpha) = \Upsilon_{(1,2\cdots I_1)}\ \Phi_i^I(\alpha)$$

gives:

$$D_i^I = \zeta_i^I (-1)^{I_1-1} \mathcal{A}\ \phi_I\alpha\ \Phi_i^{I'}(\alpha)\ \Phi_i^I(\beta)$$

Similarly:

$$D_j^J = \zeta (-1)^{J_1-1} \mathcal{A}\ \phi_J\alpha\ \Phi_j^{J'}(\alpha)\ \Phi_j^J(\beta)$$

Since $\Phi_i^{I'}(\alpha) = \Phi_j^{J'}(\alpha)$ and $\Phi_i^I(\beta) = \Phi_j^J(\beta)$:

$$\langle D_i^I | H | D_j^J \rangle = \zeta_i^I \zeta_j^J (-1)^{I_1+J_1} \langle \mathcal{A}\, \phi_I \alpha\, \Phi_i^{I'}(\alpha)\, \Phi_i^I(\beta) | H | \mathcal{A}\, \phi_J \alpha\, \Phi_i^{I'}(\alpha)\, \Phi_i^I(\beta) \rangle$$

$$= \zeta_i^I \zeta_j^J (-1)^{I_1+J_1} \Big[\langle \phi_I \alpha\, \Phi_i^{I'}(\alpha)\, \Phi_i^I(\beta) | H | \phi_J \alpha\, \Phi_i^{I'}(\alpha)\, \Phi_i^I(\beta) \rangle + \sum_{\phi_\nu \in \Phi_i^{I'}(\alpha)} \langle \phi_I | K_\nu | \phi_J \rangle \Big]$$

Hence:

$$\langle D_i^I | H | D_j^J \rangle = \zeta_i^I \zeta_j^J (-1)^{I_1+J_1} \Big[h_{IJ} + \sum_{\phi_\nu \in \Theta_c^I} \langle I | 2J_\nu - K_\nu | J \rangle + \sum_{\phi_\nu \in \Theta_I} \langle I | J_\nu | J \rangle - \sum_{\phi_\nu \in \Theta_i^I(\gamma)} \langle I | K_\nu | J \rangle \Big]$$

where $\Theta^I = \Theta_i^I(\alpha)\Theta_i^I(\beta)$ and $\gamma = \alpha$

$$h_{IJ} = \langle I | h | J \rangle = \langle \phi_I | \mathcal{T} + \mathcal{V}_n | \phi_J \rangle$$

$$\langle I | J_\nu | J \rangle = \langle \phi_I \phi_\nu | \tfrac{1}{r_{12}} | \phi_J \phi_\nu \rangle$$

$$\langle I | K_\nu | J \rangle = \langle \phi_I \phi_\nu | \tfrac{1}{r_{12}} | \phi_\nu \phi_J \rangle$$

Had the excitation been within the β list, this same equation would apply, but with $\gamma = \beta$.

2. $\alpha\alpha$ (or $\beta\beta$) Double Excitations:

Assume $\Phi_i^I(\alpha)$ differs from $\Phi_j^J(\alpha)$ by orbitals ϕ_I and ϕ_I' which occupy positions I_1 and I_2 ($I_2 > I_1$) respectively in $\Phi_i^I(\alpha)$ and $\Phi_j^J(\alpha)$ differs from $\Phi_i^I(\alpha)$ by orbitals ϕ_J and ϕ_J' which occupy positions J_1 and J_2 ($J_2 > J_1$) in $\Phi_j^J(\alpha)$. Rearranging $\Phi_i^I(\alpha)$ via the two cyclic permutations which position ϕ_I and ϕ_I' before all other orbitals:

$$\phi_I \alpha\, \phi_I' \alpha\, \Phi_i^{I'}(\alpha) = \Upsilon_{(1,2 \cdots I_1+1)}\, \Upsilon_{(1,2 \cdots I_2)}\, \Phi_i^I(\alpha)$$

gives:

$$D_i^I = \zeta_i^I (-1)^{I_1+I_2-1} \mathcal{A}\, \phi_I \alpha\, \phi_I' \alpha\, \Phi_i^{I'}(\alpha)\, \Phi_i^I(\beta)$$

Similarly:

$$D_j^J = \zeta_j^J (-1)^{J_1+J_2-1} \mathcal{A}\, \phi_J \alpha\, \phi_J' \alpha\, \Phi_j^{J'}(\alpha)\, \Phi_j^J(\beta)$$

Since $\Phi_i^{I'}(\alpha) = \Phi_j^{J'}(\alpha)$ and $\Phi_i^I(\beta) = \Phi_j^J(\beta)$:

$$\begin{aligned}\langle D_i^I | H | D_j^J \rangle &= \zeta_i^I \zeta_j^J (-1)^{I_1+I_2+J_1+J_2} \langle \mathcal{A}\, \phi_I \alpha\, \phi_I' \alpha\, \Phi_i^{I'}(\alpha)\, \Phi_i^I(\beta) | H | \\ &\qquad\qquad \mathcal{A}\, \phi_J \alpha\, \phi_J'\, \Phi_i^{I'}(\alpha)\, \Phi_i^I(\beta) \rangle \\ &= \zeta_i^I \zeta_j^J (-1)^{I_1+I_2+J_1+J_2} \langle \mathcal{A}\, \phi_I \alpha\, \phi_I' \alpha | H | \mathcal{A}\, \phi_J \alpha\, \phi_J' \alpha \rangle \\ &= \zeta_i^I \zeta_j^J (-1)^{I_1+I_2+J_1+J_2} \left[\langle \phi_I \phi_I' | \tfrac{1}{r_{12}} | \phi_J \phi_J' \rangle - \langle \phi_I \phi_I' | \tfrac{1}{r_{12}} | \phi_J' \phi_J \rangle \right]\end{aligned}$$

Had the excitation been in the β list, the same result would have been obtained.

3. <u>$\alpha\beta$ Double Excitations:</u>

Assume $\Phi_i^I(\alpha)$ and $\Phi_j^J(\alpha)$ differ by orbitals ϕ_I and ϕ_J which occupy positions I_α and J_α in their respective lists and, $\Phi_i^I(\beta)$ and $\Phi_j^J(\beta)$ differ by orbitals ϕ_I' and ϕ_J' which occupy positions I_β and J_β in their respective lists. Rearranging $\Phi_i^I(\alpha)$ and $\Phi_i^I(\beta)$ by the cyclic permutations such that:

$$\phi_I \alpha\, \Phi_i^{I'}(\alpha)\, \phi_I' \beta\, \Phi^{I'}(\beta) = \Upsilon_{(1,2\cdots I_\alpha)}\, \Phi_i^I(\alpha)\, \Upsilon_{(1,2\cdots I_\beta)}\, \Phi_i^I(\beta)$$

gives:

$$D_i^I = \zeta_i^I (-1)^{I_\alpha+I_\beta} \mathcal{A}\, \phi_I \alpha\, \Phi_i^{I'}(\alpha)\, \phi_I' \beta\, \Phi_i^{I'}(\beta)$$

Similarly:

$$D_j^J = \zeta_j^J (-1)^{J_\alpha + J_\beta} \mathcal{A}\, \phi_J \alpha\, \Phi_j^{J'}(\alpha)\, \phi'_J \beta\, \Phi_j^{J'}(\beta)$$

Since $\Phi_i^{I'}(\alpha) = \Phi_j^{J'}(\alpha)$ and $\Phi_i^{I'}(\beta) = \Phi_j^{J'}(\beta)$:

$$\begin{aligned} \langle D_i^I | H | D_j^J \rangle &= \zeta_i^I \zeta_j^J (-1)^{I_\alpha + I_\beta + J_\alpha + J_\beta} \langle \mathcal{A}\, \phi_I \alpha\, \Phi_i^{I'}(\alpha)\, \phi'_I \beta\, \Phi_i^{I'}(\beta) | \\ &\qquad H | \mathcal{A}\, \phi_J \alpha\, \Phi_i^{I'}(\alpha)\, \phi'_J \beta\, \Phi_i^{I'}(\beta) \rangle \\ &= \zeta_i^I \zeta_j^J (-1)^{I_\alpha + I_\beta + J_\alpha + J_\beta} \langle \phi_I \phi'_I | \tfrac{1}{r_{12}} | \phi_J \phi'_J \rangle \end{aligned}$$

4. Zero Excitation:

Since $\Phi_i^I(\alpha) = \Phi_j^J(\alpha)$ and $\Phi_i^I(\beta) = \Phi_j^J(\beta)$, $D_i^I = D_j^J$

$$\begin{aligned} \langle D_i^I | H | D_i^I \rangle &= \langle \mathcal{A}\, \Phi_i^I(\alpha)\, \Phi_i^I(\beta) | H | \mathcal{A}\, \Phi_i^I(\alpha)\, \Phi_i^I(\beta) \rangle \\ &= \langle \Phi_i^I(\alpha)\, \Phi_i^I(\beta) | H | \Phi_i^I(\alpha)\, \Phi_i^I(\beta) \rangle \\ &\quad - \sum_{\phi_\mu > \phi_\nu \in \Phi_i^I(\alpha)} K_{\mu\nu} - \sum_{\phi_\mu > \phi_\nu \in \Phi_i^I(\beta)} K_{\mu\nu} \end{aligned}$$

Hence:

$$\begin{aligned} \langle D_i^I | H | D_j^J \rangle &= \sum_{\phi_\nu \in \Theta_c^I} 2 h_{\nu\nu} + \sum_{\phi_\nu \in \Theta^I} h_{\nu\nu} + \sum_{\phi_\mu, \phi_\nu \in \Theta_c^I} (2 J_{\mu\nu} - K_{\mu\nu}) \\ &+ \sum_{\phi_\mu > \phi_\nu \in \Theta^I} J_{\mu\nu} + \sum_{\phi_\nu \in \Theta_c^I} \sum_{\phi_\mu \in \Theta^I} (2 J_{\mu\nu} - K_{\mu\nu}) - \sum_{\phi_\mu > \phi_\nu \in \Theta_i^I(\alpha)} K_{\mu\nu} - \sum_{\phi_\mu > \phi_\nu \in \Theta_i^I(\beta)} K_{\mu\nu} \end{aligned}$$

where $\Theta^I = \Theta_i^I(\alpha)\Theta_i^I(\beta)$

$$J_{\mu\nu} = \langle \phi_\mu | J_{\phi_\nu} | \phi_\mu \rangle$$

$$K_{\mu\nu} = \langle \phi_\mu | K_{\phi_\nu} | \phi_\mu \rangle$$

III. THE U-MATRIX METHOD OF EVALUATING SEC CI MATRIX ELEMENTS

Equations which permit direct evaluation of the CI matrix elements between the standard SECs of two N_e-electron spatial configurations will now be derived. It will be assumed that all SECs correspond to the same spin multiplicity and involve only real orthonormal orbitals.

It is convenient to partition the two spatial configurations I and J into orbital products as follows: All orbitals which are doubly occupied in both configurations are placed in Φ_c^I and Φ_c^J. Φ_c^I and Φ_c^J are then filled equally with remaining doubly occupied orbitals which are not singly occupied in the other configuration until this is no longer possible. Remaining orbitals are placed in Φ^I and Φ^J with doubly occupied orbitals in increasing order preceding the singly occupied orbitals also in increasing order.

Example:

$$\left.\begin{aligned} I &= \phi_1^2\phi_2^2\phi_4\phi_5\phi_8^2\phi_9\phi_{11} \\ J &= \phi_2^2\phi_4\phi_5^2\phi_6^2\phi_7\phi_{11}^2 \end{aligned}\right\} \qquad \begin{aligned} \Phi_c^I &= \phi_2^2\phi_1^2 \qquad & \Phi^I &= \phi_8^2\phi_4\phi_5\phi_9\phi_{11} \\ \Phi_c^J &= \phi_2^2\phi_6^2 \qquad & \Phi^J &= \phi_5^2\phi_{11}^2\phi_4\phi_7 \end{aligned}$$

The m^{th} SEC of configuration I can then be written as:

$$\psi_m^I = \mathcal{A}\,\Phi_c^I\,(\theta_m\Phi^I)\chi$$

where $\mathcal{A}$ is the antisymmetrizer, θ_m is an operator which acts on Φ^I to generate its m^{th} linearly independent orthonormal SEC, and χ is an appropriate product spin function (e.g. $\alpha\beta\alpha\beta\cdots$)

The CI matrix element between the mth SEC of I and nth SEC of J is:

$$\langle \psi^I_m | H | \psi^J_n \rangle = \frac{\langle \mathcal{A}\Phi^I_c\, \theta_m \Phi^I \chi | H | \mathcal{A}\Phi^J_c\, \theta_n \Phi^J \chi \rangle}{\langle \mathcal{A}\Phi^I_c\, \theta_m \Phi^I \chi | \mathcal{A}\Phi^I_c\, \theta_m \Phi^I \chi \rangle^{\frac{1}{2}} \langle \mathcal{A}\Phi^J_c\, \theta_n \Phi^J \chi | \mathcal{A}\Phi^J_c\, \theta_n \Phi^J \chi \rangle^{\frac{1}{2}}}$$

$$= \frac{\langle \Phi^I_c\, \theta_m \Phi^I | H | N_\alpha N_\beta \Phi^J_c\, \theta_n \Phi^J \rangle}{\langle \Phi^I_c\, \theta_m \Phi^I | N_\alpha N_\beta \Phi^I_c\, \theta_m \Phi^I \rangle^{\frac{1}{2}} \langle \Phi^J_c\, \theta_n \Phi^J | N_\alpha N_\beta \Phi^J_c\, \theta_n \Phi^J \rangle^{\frac{1}{2}}}$$

where $N_\alpha (N_\beta)$ is the antisymmetric sum of all permutations involving electrons associated with $\alpha(\beta)$ spins in χ.

Since:

$$\langle \Phi^I_c\, \theta_m \Phi^I | N_\alpha N_\beta \Phi^I_c\, \theta_m \Phi^I \rangle = \langle \Phi^I_c | N_\alpha N_\beta \Phi^I_c \rangle \langle \theta_m \Phi^I | N_\alpha N_\beta \theta_m \Phi^I \rangle = 1:$$

we obtain

$$\langle \psi^I_m | H | \psi^J_n \rangle = \langle \Phi^I_c \theta_m \Phi^I | H | N_\alpha N_\beta \Phi^J_c\, \theta_n \Phi^J \rangle$$

Letting $H = H_c + H_o + H_{co}$

where H_c operates on the 2M electrons of Φ_c.

H_o operates on the N electrons of Φ, and

$$H_{co} = \sum_{i=1}^{2M} \sum_{j>2M}^{N_e} \frac{1}{r_{ij}} \quad ,$$

we find

$$\langle \Phi^I_c\, \theta_m \Phi^I | H_c | N_\alpha N_\beta \Phi^J_c\, \theta_n \Phi^J \rangle = \langle \Phi^I_c | H_c | N_\alpha N_\beta \Phi^J_c \rangle \langle \theta_m \Phi^I | N_\alpha N_\beta \theta_n \Phi^J \rangle$$

$$= \langle \Phi^I_c | H_c | N_\alpha N_\beta \Phi^J_c \rangle\, \delta_{mn}\, \delta_{\Phi^I \Phi^J}$$

$$\langle \Phi_c^I \theta_m \Phi^I | H_o | N_\alpha N_\beta \Phi_c^J \theta_n \Phi^J \rangle = \langle \Phi_c^I | N_\alpha N_\beta \Phi_c^J \rangle \langle \theta_m \Phi^I | H_o | N_\alpha N_\beta \theta_n \Phi^J \rangle$$

$$= \delta_{\Phi_c^I \Phi_c^J} \langle \theta_m \Phi^I | H_o | N_\alpha N_\beta \theta_n \Phi^J \rangle$$

$$\langle \Phi_c^I \theta_m \Phi^I | H_{co} | N_\alpha N_\beta \Phi_c^J \theta_n \Phi^J \rangle = \delta_{\Phi_c^I \Phi_c^J} \langle \theta_m \Phi^I | \sum_{i=1}^{N} \sum_{\phi_\kappa \in \Phi_c^I}^{M} (2J_k - K_k)_{(i)} | N_\alpha N_\beta \theta_n \Phi^J \rangle$$

If:

$$H' \equiv E_c + \delta_{\Phi_c^I \Phi_c^J} \left\{ \sum_{i=1}^{N} \left[h(i) + \sum_{\phi_k \in \Phi_c^I} [2J_k(i) - K_k(i)] \right] + \sum_{i > j=1}^{N} \frac{1}{r_{ij}} \right\};$$

where $E_c \equiv \langle \Phi_c^I | H_c | N_\alpha N_\beta \Phi_c^J \rangle$

then the CI matrix elements are:

$$\langle \psi_m^I | H | \psi_n^J \rangle = \langle \theta_m \Phi^I \chi | H' | N_\alpha N_\beta \theta_n \Phi^J \chi \rangle$$

$$= \langle \mathcal{A} \theta_m \Phi^I | H' | \mathcal{A} \theta_n \Phi^J \rangle$$

which is effectively a matrix element only over N electrons.

If $\Phi_c^I \neq \Phi_c^J$:

$$E_c = K_{\phi_i \phi_j} \delta_{\Phi_c^{I'} \Phi_c^{J'}}$$

where ϕ_i and ϕ_j are orbitals not held in common by Φ_c^I and Φ_c^J respectively and $\Phi_c^{I'}$ and $\Phi_c^{J'}$ are what is left of Φ_c^I and Φ_c^J after removal of these orbitals. Therefore, if $\Phi_c^I \neq \Phi_c^J$:

$$\langle \psi_m^I | H | \psi_n^J \rangle = K_{\phi_j \phi_i} \delta_{\Phi_c^{I'} \Phi_c^{J'}} \delta_{\Phi^I \Phi^J} \delta_{mn}$$

Since all matrix elements will be zero if the configurations differ by more than a double excitation, all other cases to be considered must have $\Phi_c^I = \Phi_c^J$ in which case the core energy is:

$$E_c = \langle \Phi_c^I | H | N_\alpha N_\beta \Phi_c^I \rangle = \sum_{\phi_k \in \Phi_c^I}^{M} 2\, h_{kk} + \sum_{\phi_k, \phi_\ell \in \Phi_c^I}^{M} (2J_{k\ell} - K_{k\ell})$$

Choosing the set of SECs to correspond to the standard GI couplings, we obtain

$$\mathcal{O}\theta_m\, \Phi^I\chi = \frac{L_i \mathcal{Y}_i \Phi^I \chi}{\langle \mathcal{Y}_i \Phi^I \chi | \mathcal{Y}_i \Phi^I \chi \rangle^{\frac{1}{2}}}$$

where $\mathcal{Y}_i$ is the Group operator generating the i^{th} standard SEC for a system containing N electrons with spin multiplicity S and L_i is an arbitrary phase factor.[2] Since Φ^I can contain doubly occupied orbitals, i can only take on certain values (the others either vanish or are redundant). Hence the m^{th} SEC of configuration I corresponds to the i^{th} standard SEC for the N electrons of Φ^I where $i \geqslant m$. Likewise, the n^{th} SEC of configuration J corresponds to the j^{th} standard SEC for the N electrons of Φ^J.

Therefore:

$$\langle \psi_m^I | H | \psi_n^J \rangle = \frac{L_i L_j \langle \mathscr{G}_i \Phi^I \chi | H' | \mathscr{G}_j \Phi^J \chi \rangle}{\langle \mathscr{G}_i \Phi^I \chi | \mathscr{G}_i \Phi^I \chi \rangle^{\frac{1}{2}} \langle \mathscr{G}_j \Phi^J \chi | \mathscr{G}_j \Phi^J \chi \rangle^{\frac{1}{2}}}$$

$$\equiv GG(i, j)$$

If O_p is a spin-independent hermitian operator:

$$\langle \mathscr{G}_i \Phi^I \chi | O_p | \mathscr{G}_j \Phi^J \chi \rangle = f^{\nu} \langle \Phi^I | O_p | O_{ij} \Phi^J \rangle \langle \chi | \omega_{\bar{i}\bar{j}} \chi \rangle$$

where O_{ij} and $\omega_{\bar{i}\bar{j}}$ are the usual Wigner projection operators.[2]

Thus

$$GG(i, j) = \frac{L_i L_j \quad \langle \Phi^J | H' | O_{ij} \Phi^J \rangle \langle \chi | \omega_{\bar{i}\bar{j}} \chi \rangle}{[\langle \Phi^I | O_{ii} \Phi^I \rangle \langle \Phi^J | O_{jj} \Phi^J \rangle \langle \chi | \omega_{\bar{i}\bar{i}} \chi \rangle \langle \chi | \omega_{\bar{j}\bar{j}} \chi \rangle]^{\frac{1}{2}}}$$

Letting $L_{ij} = L_i L_j \quad \langle \chi | \omega_{\bar{i}\bar{j}} \chi \rangle / [\langle \chi | \omega_{\bar{i}\bar{i}} \chi \rangle \langle \chi | \omega_{\bar{j}\bar{j}} \chi \rangle]^{\frac{1}{2}}$, (it can be shown that $L_{ij} = \pm 1$) leads to:

$$GG(i, j) = \frac{L_{ij} \langle \Phi^I | H' | O_{ij} \Phi^J \rangle}{[\langle \Phi^I | O_{ii} \Phi^I \rangle \langle \Phi^J | O_{jj} \Phi^J \rangle]^{\frac{1}{2}}}$$

Since

$$O_{ij} = \frac{1}{\theta} \sum_{\tau \in \mathscr{S}_N} U_{ij}(\tau) \, \tau$$

where $\{U_{ij}(\tau)\}$ are the well-known U matrix elements forming the irreducible representations of $\mathscr{S}_N$, we obtain:[3]

$$GG(i,j) = \frac{L_{ij} \langle \Phi^I | H' | \sum_{\tau} U_{ij}(\tau) \tau \Phi^J \rangle}{\left[\langle \Phi^I | \sum_{\tau} U_{ii}(\tau) \tau \Phi^I \rangle \langle \Phi^J | \sum_{\tau} U_{jj}(\tau) \tau \Phi^J \rangle \right]^{\frac{1}{2}}}$$

If Φ^J contains D_J double occupations, there are 2^{D_J} permutations $\{\tau_s\}$ which do not alter Φ^J. By definition, j can only take on values such that $U_{ij}(\tau_s) = \delta_{ij}$. Therefore:

$$\langle \Phi^J | \sum_{\tau} U_{jj}(\tau) \tau \Phi^J \rangle = \sum_{\tau_s}^{2^{D_J}} U_{jj}(\tau_s) = 2^{D_J}.$$

Thus,

$$GG(i,j) = 2^{-(D_I + D_J)/2} L_{ij} \langle \Phi^I | H' | \sum_{\tau} U_{ij}(\tau) \tau \Phi^J \rangle$$

Factoring the sum over τ as

$$\sum_{\tau'} \sum_{\tau_s}^{2^{D_J}} \tau' \tau_s = \sum_{\tau} \tau$$

and noting the τ_s does not affect Φ^J we obtain

$$GG(i,j) = 2^{-(D_I + D_J)/2} L_{ij} \langle \Phi^I | H' | \sum_{\tau'} \sum_{\tau_s}^{2^{D_J}} U_{ij}(\tau' \tau_s) \tau' \tau_s \Phi^J \rangle$$

$$= 2^{-(D_I + D_J)/2} L_{ij} \langle \Phi^I | H' | \sum_{\tau'} \Big[\Big(\sum_{\tau_s}^{2^{D_J}} U^{\nu}_{ij}(\tau' \tau_s) \Big] \tau' \Phi^J \rangle$$

Since

$$U_{ij}(\tau' \tau_s) = \sum_t U_{it}(\tau')U_{tj}(\tau_s) \text{ and } U_{tj}(\tau_s) = \delta_{tj}$$

for all allowed values of j, we obtain

$$U_{ij}(\tau' \tau_s) = U_{ij}(\tau').$$

Hence:

$$GG(i, j) = 2^{(D_J - D_I)/2} L_{ij} \langle \Phi^I | H' | \sum_{\tau'} U_{ij}(\tau') \tau' \Phi^J \rangle$$

If $\{\tau_{s'}\}$ are the 2^{D_I} permutations which leave Φ^I unchanged and if it is assumed that $D_I \leqslant D_J$. Then

$$\sum_{\tau'} \tau' = \sum_{\tau'''} \tau''' + \sum_{\tau''} \sum_{\tau_s'}^{2^{D_I}} \tau_{s'} \tau''$$

where $\{\tau'''\}$ are those permutations in $\{\tau'\}$ which leave a double occupation of Φ^J in coincidence with a double occupation of Φ^I. By the definitions of Φ^I and Φ^J it follows that:

$$\langle \Phi^I | H' | \tau''' \Phi^J \rangle = 0$$

Thus

$$GG(i, j) = 2^{(D_J - D_I)/2} L_{ij} \langle \Phi^I | H' | \sum_{\tau''} \sum_{\tau_{s'}}^{2^{D_I}} U_{ij}(\tau_{s'} \tau'') \tau_{s'} \tau'' \Phi^J \rangle$$

Since $\langle \Phi^I | H' | \tau_{s'}, \tau'' \Phi^J \rangle = \langle \Phi^I | H' | \tau'' \Phi^J \rangle$ and $U_{it}(\tau_{s'}) = \delta_{it}$ for all allowed values of i, we obtain

$$GG(i, j) = 2^{(D_I + D_J)/2} L_{ij} \langle \Phi^I | H' | \sum_{\tau''} U_{ij}(\tau'') \tau'' \Phi^J \rangle$$

If σ_m is a permutation which brings Φ^J into maximum coincidence with Φ^I (all common orbitals have the same position numbers):

$$GG(i, j) = 2^{(D_I + D_J)/2} L_{ij} \langle \Phi^I | H' | \sum_{\tau''} U^{\nu}_{ij}(\tau'') \tau'' \sigma_m^{-1} \Phi^J_I \rangle$$

$$= 2^{(D_I + D_J)/2} L_{ij} \langle \Phi^I | H' | \sum_{T} U_{ij}(T \sigma_m) T \Phi^J_I \rangle$$

where $\phi^J_I \equiv \sigma_m \Phi^J$ and $\{T\} = \{\tau'' \sigma_m^{-1}\}$.

Since Φ^I and Φ^J_I are in maximum coincidence, the only permutations in $\{T\}$ which can possibly give rise to nonzero terms are the identity and the allowed transpositions $\{\tau_{k\ell}\}$, (the allowed transpositions in $\{T\}$ are those which do not interchange identical orbitals in either Φ^I or Φ^J_I), hence

$$GG(i, j) = 2^{(D_I + D_J)/2} L_{ij} [\langle \Phi^I | H' | \Phi^J_I \rangle U_{ij}(\sigma_m)$$

$$+ \sum_{\tau_{k\ell}} U_{ij}(\tau_{k\ell} \sigma_m) \langle \Phi^I | H' | \tau_{k\ell} \Phi^J_I \rangle]$$

At this point, the various possible types of excitations must be considered:

I. One Orbital Double Excitation:

If the configurations differ by a double excitation in which the mismatched orbitals of one configuration (J) are identical (ϕ_J), only the identity survives:

$$GG(i,j) = 2^{(D_I+D_J)/2} L_{ij} U_{ij}(\sigma_m) \langle \phi_{I_1} | K_{\phi_J} | \phi_{I_2} \rangle$$

where ϕ_{I_1} and ϕ_{I_2} are the mismatched orbitals of configuration I with ϕ_{I_1} coming before ϕ_{I_2} in Φ^I.

II. Two Orbital Double Excitation:

If the configurations differ by a double excitation in which the mismatched orbitals of both configurations are different (ϕ_{I_1} and ϕ_{I_2} for configuration I; ϕ_{J_1} and ϕ_{J_2} for configuration J) only the identity and the transposition interchanging ϕ_{I_1} and ϕ_{I_2} in Φ^I survive

$$GG(i,j) = 2^{(D_I+D_J)/2} L_{ij} \Big[U_{ij}(\sigma_m) \langle \phi_{I_1} \phi_{I_2} | \frac{1}{r_{12}} | \phi_{J_1} \phi_{J_2} \rangle$$

$$+ U_{ij} (\tau_{\phi_{I_1} \phi_{I_2}} \sigma_m) \langle \phi_{I_2} \phi_{I_1} | \frac{1}{r_{12}} | \phi_{J_1} \phi_{J_2} \rangle \Big]$$

where ϕ_{I_1} comes before ϕ_{I_2} in Φ^I and ϕ_{J_1} comes before ϕ_{J_2} in Φ^J_I .

III. Single Excitation

If configurations I and J differ by orbitals ϕ_I and ϕ_J the only surviving transpositions are those which interchange ϕ_I with another orbital other than ϕ_I (double occupation) or ϕ_J(ϕ_J doubly occupied in Φ^J) in Φ^I. These other orbitals are of course singly occupied:

$$GG(i,j) = 2^{(D_I+D_J)/2} L_{ij} \left[U_{ij}(\sigma_m) \langle \Phi^I | H' | \Phi^J_I \rangle \right.$$

$$\left. + \sum_{\phi_\ell \in \Phi^I \neq \phi_I, \phi_J} U_{ij}(\tau_{\phi_I \phi_\ell} \sigma_m) \langle \phi_I | K_{\phi_\ell} | \phi_J \rangle \right]$$

where:

$$\langle \Phi^I | H' | \Phi^J_I \rangle = \langle \phi_I | h + \sum_c (2J_{\phi'_c} - K_{\phi'_c}) | \phi_J \rangle$$

$$+ \sum_{\phi_\ell \in \Phi^I \neq \phi_I} \langle \phi_I | J_{\phi_\ell} | \phi_J \rangle$$

where $\{\phi'\}$ are all the doubly occupied orbitals of configuration I.

IV. Zero Excitations:

Since $\Phi^I = \Phi^J$:

$$\sigma_m = e$$

$$DI = DJ = 0$$

Therefore:

$$GG(i,j) = L_{ij} \left[\langle \Phi^I | H' | \Phi^I \rangle + \sum_{\phi_i \rangle \phi_\ell \in \Phi^I} U_{ij}(\tau_{\phi_k \phi_\ell}) K_{\phi_k \phi_\ell} \right],$$

where:

$$\langle \Phi^I | H' | \Phi^I \rangle = E_c + \sum_{\phi_\ell \in \Phi^I} h_{\phi_\ell \phi_\ell} + \sum_{\phi_k \rangle \phi_\ell \in \Phi^I} J_{\phi_k \phi_\ell} + \sum_{\phi_\ell \in \Phi^I} \sum_{\phi_c \in \Phi_c^I} (2J_{\phi_\ell \phi_c} - K_{\phi_\ell \phi_c})$$

IV. COMPUTATIONAL CONSIDERATIONS

Comparing the U-matrix and Determinant methods for generating standard SEC CI matrices for sets of spatial configurations involving orthonormal orbitals, the former method is obviously more efficient since all matrix elements involving two configurations can simultaneously be directly evaluated using the same subset of U matrices. The Determinant method is generally much more time consuming since large numbers of determinant CI matrix elements must first be calculated and then transformed to give the desired SEC CI matrix elements.

Unfortunately, however, it has not been possible to design a practical program for generating SEC CI matrices based solely upon the U-matrix method. This is because of the huge number of U matrix elements which must generally be available. If Φ^I and Φ^J are orbital products of what is left of spatial configurations I and J after deletion of all common closed-shell orbitals and if in Φ^I and Φ^J all doubly occupied orbitals (in increasing order) precede the singly occupied orbitals (in increasing order), then U matrices must generally be available for all the permutations:

$$\tau = \tau_{k\ell}\,\sigma_{IJ}$$

where $\tau_{k\ell}$ is that transposition interchanging the k^{th} and ℓ^{th} orbitals of Φ^I and σ_{IJ} is that permutation which brings Φ^J into maximum coincidence with Φ^I (common orbitals are in the same positions in Φ^I and $\sigma_{IJ}\Phi^J$). In general, the set of σ_{IJ}s needed to align all possible pairs of configurations which differ by no more than a double excitation can be quite large. Moreover, if $\sigma_{IJ} \neq e$, Φ^I and Φ^J can contain up to N+4 orbitals, where N is the maximum number of singly occupied orbitals allowed in any spatial configuration. Therefore, even for relatively small values of N, the number of generally required U matrix elements is horrendous.

However, the number of elements comprising the (symmetric) transposition U matrices for N electrons (matrices for less electrons are subsets of these) falls well within the bounds of practicality even for reasonably large values of N (e.g. N=8). Accepting the limitation that only these U matrices can be available during CI matrix generation, CI matrix elements involving aligned configurations ($\sigma_{IJ} = e$) can still be evaluated using the rapid U-matrix method since only these U matrices are needed. CI matrix elements involving misaligned configurations ($\sigma_{IJ} \neq e$), for which the required U matrices are not available, can be evaluated using the Determinant method, for which only a small number of transformation coefficients need be known.

Hence, by using both the U-matrix and Determinant methods during SEC CI matrix generation a practical program can be designed which strikes a reasonable compromise between optimal efficiency in the generation of the CI matrix and minimal storage requirements for the U matrices.

V. COMPUTATIONAL SUMMARY

The currently employed approach for generating SEC CI matrices will now be summarized. If:

I = the ith N_e-electron spatial configuration consisting of a set of NDI closed-shell orbitals in increasing order followed by a set of NI singly occupied orbitals also in increasing order

H^{IJ}_{mn} = CI matrix element between the mth standard SEC of spatial configuration I and the nth standard SEC of spatial configuration J

D^{IJ}_{ij} = CI matrix element between the ith determinant of configuration I and the jth determinant of configuration J ($S_z = S$) ignoring ζ^I_i and ζ^J_j

Θ^I_c = the product of all closed-shell orbitals in configuration I in increasing order (each orbital appears only once in Θ^I_c whereas it appears twice in I)

Θ^I = the product of all singly occupied orbitals in configuration I in increasing order

$\Theta^I_i(\gamma)$= the product of all γ-spin ($\gamma = \alpha, \beta$) singly occupied orbitals in the ith determinant of configuration I in increasing order

$\Phi^I_i(\gamma)$= the product of all γ-spin ($\gamma = \alpha, \beta$) orbitals in the ith determinant of configuration I in increasing order

$U_{ij}(\tau)$= the known U-matrix element for transposition τ between the ith and jth standard SECs of multiplicity S for NI singly occupied orbitals

$\tau_{\phi_k \phi_\ell}$ = the transposition interchanging orbitals ϕ_k and ϕ_ℓ in Θ^I

C_{im}^{NI} = the known coefficient of D_i^I in ψ_m^I

ζ_i^I = the parity of the permutation τ_i^I, where:

$$\Phi_i^I(\alpha)\,\Phi_i^I(\beta) = \tau_i^I\,\Theta_c^I(\alpha)\Theta_i^I(\alpha)\,\Theta_c^I(\beta)\,\Theta_i^I(\beta)$$

σ_{IJ} = the permutation which brings configuration J into maximum coincidence with configuration I after deleting common closed shell orbitals

the CI matrix elements involving spatial configurations I and J, where NI ≥ NJ, are evaluated as follows:

A. Zero Excitation (NEX=0)

If I = J:

$$H_{mn}^{II} = \delta_{mn} V_{II} + \sum_{\phi_\nu > \phi_\mu \in \Theta^I} U_{mn}(\tau_{\phi_\nu\phi_\mu})\, K_{\phi_\nu\phi_\mu}$$

$$V_{II} = \sum_{\phi_\nu \in \Theta_c^I} 2h_{\phi_\nu\phi_\nu} + \sum_{\phi_\nu \in \Theta^I} h_{\phi_\nu\phi_\nu} + \sum_{\phi_\nu, \phi_\mu \in \Theta_c^I} (2J_{\phi_\nu\phi_\mu} - K_{\phi_\nu\phi_\mu}) + \sum_{\phi_\nu \in \Theta_c^I} \sum_{\phi_\nu \in \Theta^I} (2J_{\phi_\nu\phi_\mu} - K_{\phi_\nu\phi_\mu}) + \sum_{\phi_\nu > \phi_\mu \in \Theta^I} J_{\phi_\nu\phi_\mu}$$

B. Single Excitation (NEX = 1)

Assume I and J differ by orbitals ϕ_I and ϕ_J

1. I and J are aligned ($\sigma_{IJ} = e$):

$$H_{mn}^{IJ} = 2^{(NOI-NOJ)/2}\Big[\delta_{mj} V_{IJ} + \sum_{\substack{\phi_\nu \in \Theta^I \\ \phi_\nu \neq \phi_I, \phi_J}} U_{mj}(\tau_{\phi_I\phi_\nu}) \langle \phi_I | K_{\phi_\nu} | \phi_J \rangle$$

$$V_{IJ} = h_{\phi_I\phi_J} + \sum_{\phi_\nu \in \Theta_c^I} \langle \phi_I | 2J_{\phi_\nu} - K_{\phi_\nu} | \phi_J \rangle + \sum_{\phi_\nu \in \Theta^I \neq \phi_I} \langle \phi_I | J_{\phi_\nu} | \phi_J \rangle$$

where j is the n^{th} allowed NI-electron standard SEC for configuration J:

If NI = NJ, j = n

If NI > NJ, this corresponds to the n^{th} standard SEC for which $U_{jj}(12) = 1$

2. I and J are misaligned ($\sigma_{IJ} \neq e$):

$$H^{IJ}_{mn} = \sum_{i}^{NDETI} \sum_{j}^{NDETJ} \zeta^{I}_{i} \zeta^{J}_{j} C^{NI}_{im} C^{NJ}_{jn} D^{IJ}_{ij}$$

where nonzero D^{IJ}_{ij} elements are either γ single excitations ($\gamma = \alpha, \beta$) or $\alpha\beta$ excitations

a) γ Excitations

$$D^{IJ}_{ij} = \zeta_{\gamma} \left[V_{II} - \sum_{\substack{\phi_\nu \in \Theta^{I}_{i}(\gamma) \\ \phi_\nu \neq \phi_I}} \langle \phi_I | K_{\phi_\nu} | \phi_J \rangle \right]$$

where

$\zeta_{\gamma} = (-1)^{I_1 + J_1}$

I_1 = position of ϕ_I in $\Phi^{I}_{i}(\gamma)$

J_1 = position of ϕ_J in $\Phi^{J}_{j}(\gamma)$

b) $\alpha\beta$ Excitation

$$D^{IJ}_{ij} = \zeta_{\alpha\beta} \langle \phi_I | K_{\phi_k} | \phi_J \rangle$$

where $\phi_k \in \Theta^{I}$ but $\phi_k \neq \phi_I, \phi_J$. If ϕ_k appears in $\Phi^{I}_{i}(\gamma)$:

$\zeta_{\alpha\beta} = (-1)^{I_\gamma + I_\epsilon + J_\gamma + J_\epsilon}$

I_γ = position of ϕ_k in $\Phi^{I}_{i}(\gamma)$

J_ϵ = position of ϕ_k in $\Phi^{J}_{j}(\epsilon)$

I_ϵ = position of ϕ_I in $\Phi^{I}_{i}(\epsilon)$

J_ϵ = position of ϕ_J in $\Phi^{J}_{j}(\gamma)$

where $\gamma(\epsilon) = \alpha(\beta), \beta(\alpha)$

C. Double Excitation (NEX = 2):

1. One Orbital Double

Assume I differs from J by orbitals ϕ_{I_1} and ϕ_{I_2} (it is possible that $\phi_{I_1} = \phi_{I_2}$) and that J differs from U by doubly occupied orbital ϕ_J

a) I and J are aligned ($\sigma_{IJ} = e$)

$$H^{IJ}_{mn} = 2^{(NDJ-NDI)/2} \delta_{mj} \langle \phi_{I_1} | K_{\phi_J} | \phi_{I_2} \rangle$$

where j is the nth allowed NI-electron standard SEC for configuration J :

If NI = NJ, $j = n$

If NI $>$ NJ, this corresponds to the nth standard SEC for which $U_{jj}(12) = 1$

b) I and J are misaligned ($\sigma_{IJ} \neq e$):

$$H^{IJ}_{mn} = \sum_{i}^{NDETI} \sum_{j}^{NDETJ} \gamma_i^I \gamma_j^J C^{NI}_{im} C^{NJ}_{jn} D^{IJ}_{ij}$$

where all nonzero D^{IJ}_{ij} elements are $\alpha\beta$ excitations:

$$D^{IJ}_{ij} = (-1)^{J_\alpha + J_\beta + I_\gamma + I_\epsilon} \langle \phi_{I_1} | K_{\phi_J} | \phi_{I_2} \rangle$$

$J_\alpha + J_\beta$ = number of singly occupied orbitals in J less than ϕ_J

If ϕ_{I_1} in the mismatched orbital of $\Phi^I_i(\gamma)$:

I_γ = position of ϕ_{I_1} in $\Phi^I_i(\gamma)$

I_ϵ = position of ϕ_{I_2} in $\Phi_i^I(\epsilon)$

where $\gamma(\epsilon) = \alpha(\beta), \beta(\alpha)$

2. Two Orbital Double

Assume I differs from J by orbitals ϕ_{I_1} and ϕ_{I_2} where ϕ_{I_1} comes before ϕ_{I_2} in I and that J differs from I by orbitals ϕ_{J_1} and ϕ_{J_2} where ϕ_{J_1} comes before ϕ_{J_2} in J

a) I and J are aligned ($\sigma_{IJ} = e$):

$$H_{mn}^{IJ} = 2^{(NOJ-NOI)/2}\left[\delta_{mj}\langle\phi_{I_1}\phi_{I_2}|\tfrac{1}{r_{12}}|\phi_{J_1}\phi_{J_2}\rangle + U_{mj}(\tau_{\phi_{I_1}\phi_{I_2}})\langle\phi_{I_1}\phi_{I_2}|\tfrac{1}{r_{12}}|\phi_{J_2}\phi_{J_1}\rangle\right]$$

where j is the nth allowed NI-electron standard SEC for configuration J:

If NI = NJ, j = n

If NI - NJ = 2, this corresponds to the nth standard SEC for which $U_{jj}(12) = 1$

If NI - NJ = 4 this corresponds to the nth standard SEC for which $U_{jj}(12) = U_{jj}(34) = 1$

b) I and J are misaligned ($\sigma_{IJ} \neq e$):

$$H_{mn}^{IJ} = \sum_{i}^{NDETI}\sum_{j}^{NDETJ} \zeta_i^I \zeta_j^J C_{im}^{NI} C_{jn}^{NJ} D_{ij}^{IJ}$$

where all nonzero D_{ij}^{IJ} elements are either $\gamma\gamma$ double excitations ($\gamma = \alpha, \beta$) or are $\alpha\beta$ excitations

1) $\gamma\gamma$ Excitations

$$D_{ij}^{IJ} = \zeta_{\gamma\gamma}\left[\langle\phi_{I_1}\phi_{I_2}|\tfrac{1}{r_{12}}|\phi_{J_1}\phi_{J_2}\rangle - \langle\phi_{I_1}\phi_{I_2}|\tfrac{1}{r_{12}}|\phi_{J_2}\phi_{J_1}\rangle\right]$$

$\zeta_{\gamma\gamma} = (-1)^{\delta_I + \epsilon_I + \delta_J + \epsilon_J}$

δ_I = number of orbitals between ϕ_{I_1} and ϕ_{I_2} in $\Phi_i^I(\gamma)$

$\epsilon_I = 0$ if ϕ_{I_1} preceeds ϕ_{I_2} in $\Phi_i^I(\gamma)$. If not, $\epsilon_I = 1$

δ_J = number of orbitals between ϕ_{J_1} and ϕ_{J_2} in $\Phi_j^J(\gamma)$

$\epsilon_J = 0$ if ϕ_{J_1} preceeds ϕ_{J_2} in $\Phi_j^J(\gamma)$. If not, $\epsilon_J = 1$

2) $\alpha\beta$ Excitations

$$D_{ij}^{IJ} = \zeta_{\alpha\beta} \langle \phi_{I_1} \phi_{I_2} | \tfrac{1}{r_{12}} | \phi_{J_\gamma} \phi_{J_\epsilon} \rangle$$

If ϕ_{I_1} and ϕ_{J_γ} are the mismatched γ spin orbitals and ϕ_{I_2} and ϕ_{J_ϵ} are the mismatched ϵ spin orbitals where $\gamma(\epsilon) = \alpha(\beta), \beta(\alpha)$ and $\phi_{J_\gamma}(\phi_{J_\epsilon}) = \phi_{J_1}(\phi_{J_2}), \phi_{J_2}(\phi_{J_1})$:

$\zeta_{\alpha\beta} = (-1)^{I_\gamma + I_\epsilon + J_\gamma + J_\epsilon}$

I_γ = position of ϕ_{I_1} in $\Phi_i^I(\gamma)$

I_ϵ = position of ϕ_{I_2} in $\Phi_i^I(\epsilon)$

J_γ = position of ϕ_{J_γ} in $\Phi_j^J(\gamma)$

J_ϵ = position of ϕ_{J_ϵ} in $\Phi_j^J(\epsilon)$

D. Higher Excitations (NEX $>$ 2):

If I and J differ by more than a double excitation, all matrix elements are zero.

N.B.

The U-matrix method phase factors (ζ_{mj}) are omitted since a compatible set of SECs can still be obtained by simply redefining the Determinant method transformation coefficient $\{c\}$. At most, these

SECs differ only in sign from the standard couplings.

VI. PROGRAMMING

The program is currently capable of generating moderately sized singlet, doublet and triplet SEC CI matrices for spatial configurations containing up to six singly occupied orbitals. Input 1- and 2-electron integrals are assumed to already be for the desired orthonormal orbital basis. Only modestly sized bases can be accommodated (around 20 orbitals) as the full canonical 2-electron integral list is required to be in core during matrix generation.

Prior to matrix generation, the determinant transformation coefficients and triangular transposition U matrices corresponding to the desired spin multiplicity are defined. In addition, determinant lists giving the α- and β- spin orbitals in each determinant of each input spatial configuration are constructed based upon the spin multiplicity and the number of singly occupied orbitals involved. Initially, these are conveniently generated in $\{\Theta_c^I\Theta_i^I(\alpha); \Theta_c^I\Theta_i^I(\beta)\}$ form. However, prior to actual usage, these lists are converted to the more useful $\{\zeta_i^I; \Phi_i^I(\alpha); \Phi_i^I(\beta)\}$ form.

The triangular CI matrix is generated considering two spatial configurations at a time taken in triangular order. Once the SEC CI matrix elements for a pair have been evaluated, they are stored on disc for later retrieval and reorganization prior to diagonalization. The following flow chart outlines the essentials of the procedure used in evaluating the CI matrix elements between spatial configurations I and J, where it is assumed that $NI \geq NJ$. The notation used in this chart is the same as above. In addition:

NEX(γ) = γ-spin ($\gamma = \alpha, \beta$) excitation number between two determinants

MK = sum of occupation numbers of the mismatched orbitals in each configuration + NJ-NI

IE1, IE2 = open-shell position numbers of ϕ_{I_1} and ϕ_{I_2} (when appropriate) in configuration I

JE1, JE2 = open-shell position numbers of ϕ_{J_1} and ϕ_{J_2} (when appropriate) in configuration J

IO(k) = kth open-shell orbital in configuration I

NSI, NSJ = number of SECs from configuration I and J

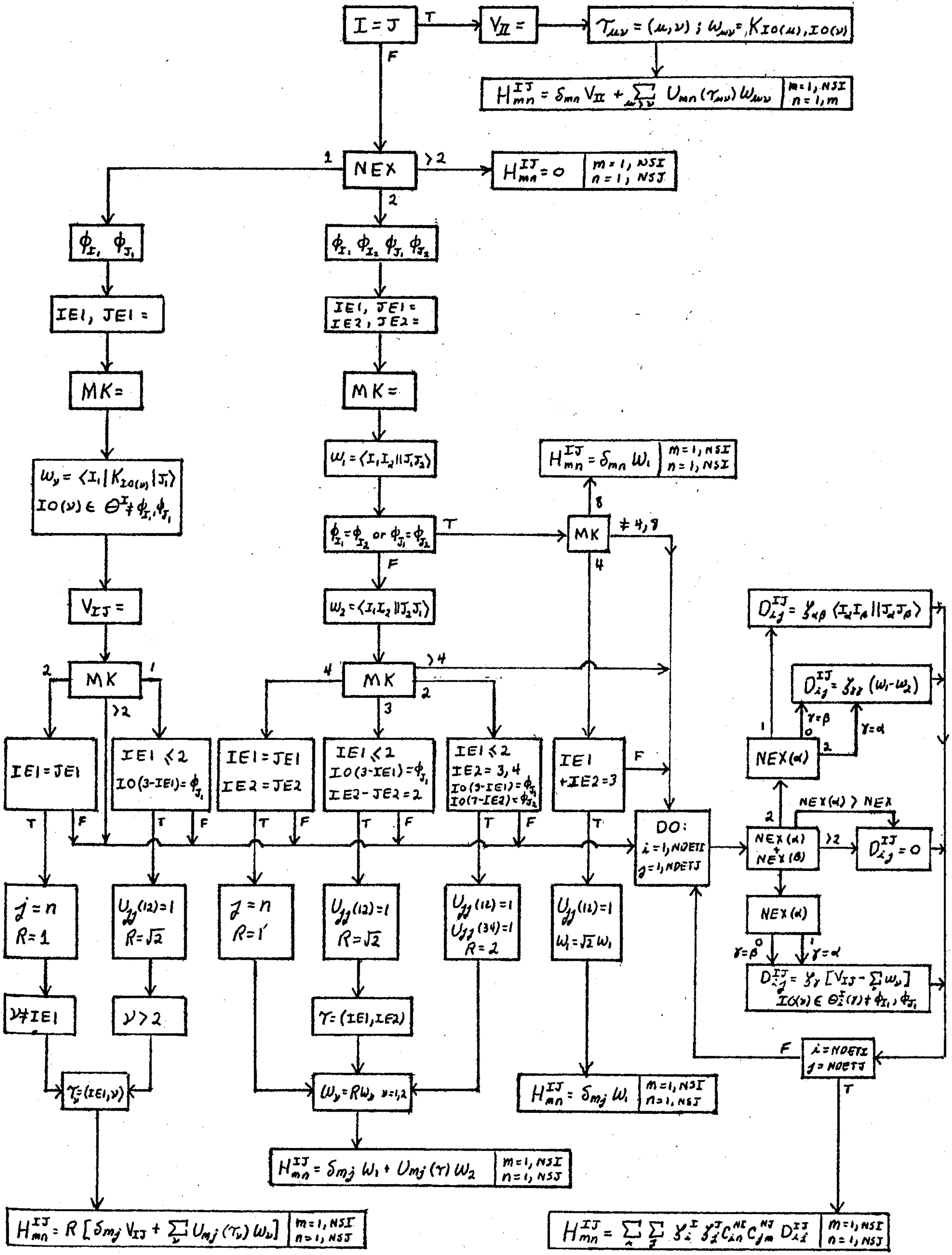


FIG. 1 SEF CI Matrix Generation

VII. CONCLUSION

Computational details for calculating Spin-Eigenfunction Configuration Interaction CI matrices via a method utilizing the U matrices which form the irreducible representations of $\mathcal{S}_N$ have been presented. When combined with an improved Determinant method, a practical and yet highly efficient procedure for generating CI matrices can be formulated. This approach is employed in our current CI program; being much more rapid than the previously employed independent-determinant method.

APPENDIX 1

Definition of the CI Program Spin-Couplings Used in Terms of the Standard Couplings

When constructing Spin-Eigenfunction Configuration (SEC) CI matrix elements via the determinant method, it is most convenient to have all alpha spin orbitals preceding all beta spin orbitals in each determinant. Thus, the j^th SEC for a given spatial configuration for N_e electrons is:

$$
\begin{aligned}
\psi_j &= \sum_{i}^{NDET} C_{ij}^{N} \mathcal{A}\, \Theta_c(\alpha)\, \Theta_i(\alpha)\, \Theta_c(\beta)\, \Theta_i(\beta) \\
&= \sum_{i}^{NDET} C_{ij}^{N} \mathcal{A} \Big[\prod_{n}^{ND} \phi_{n_\alpha}\Big]\Big[\prod_{n}^{NA} \phi'_{n_i\alpha}\Big]\Big[\prod_{n}^{ND} \phi_{n_\beta}\Big]\Big[\prod_{n}^{NB} \phi''_{n_i\beta}\Big]
\end{aligned} \tag{1}
$$

where $\phi_{\ell_\alpha} = \phi_\ell \alpha$ and $\phi_{\ell_\beta} = \phi_\ell \beta$. $\{\phi_n\}$ are the ND doubly-occupied orbitals, $\{\phi'_{ni}\}$ are the NA singly occupied orbitals having alpha spins in determinant i and $\{\phi''_{ni}\}$ are the NB=(N-NA) singly occupied beta spin orbitals.

However, it is more consistent to express ψ_j as:

$$
\begin{aligned}
\psi_j &= \zeta \mathcal{A} \Big[\prod_{n}^{ND} \phi_{n_\alpha} \phi_{n_\beta}\Big] \sum_{i}^{NDET} C_{ij}^{N} \Big[\prod_{n}^{NA} \phi'_{n_i\alpha}\Big]\Big[\prod_{n}^{NB} \phi''_{n_i\beta}\Big] \\
&= \zeta \mathcal{A} \,[\mathrm{core}]_{ND} \sum_{i}^{NDET} C_{ij}^{N}\, \Theta_i(\alpha)\, \Theta_i(\beta)
\end{aligned}
$$

Therefore, the phase factor ζ must be evaluated:

(a) First rearrange (1) to:

$$
\psi_j = \zeta' \mathcal{A}\, \Theta_c(\alpha)\, \Theta_c(\beta) \sum_{i} C_{ij}^{N}\, \Theta_i(\alpha)\, \Theta_i(\beta)
$$

This is done by performing the permutation:

$$
\prod_{\ell=1}^{ND} (1,2,3\cdots L) \quad \text{on} \quad \Theta_i(\alpha)\cdot\Theta_c(\beta)
$$

Since this permutation has a parity of $[(-1)^{L-1}]^{ND}$ and L = NA + ND:

$$
\zeta' = (-1)^{NA\cdot ND + ND(ND-1)} = (-1)^{NA\cdot ND}
$$

(b) Reorder doubly-occupied orbitals:

Since:

$$\prod_{i=1}^{ND-1} \zeta_i \; (2i, 2i+1, \cdots ND+i) \; \Theta_c(\alpha) \, \Theta_c(\beta) = \zeta'' \, [core]_{ND}$$

and $\zeta_i = (-1)^{ND-i}$:

$$\zeta'' = (-1)^{\sum_{i=1}^{ND-1} (ND-i)} = (-1)^{ND(ND-1)/2}$$

Thus:

$$\zeta = \zeta' \zeta'' = (-1)^{NA \cdot ND + ND(ND-1)/2}$$

Explicit dependence upon the number of doubly-occupied orbitals can be removed as follows:

$$ND = \frac{N_e - (NA+NB)}{2} \quad ; \quad NB = NA - 2S$$

Therefore:

$$ND = \frac{N_e + 2S - 2NA}{2} = D_m - NA$$

where $D_m = \frac{N_e}{2} + S$ is a constant which depends upon the number of electrons (N_e) and the spin multiplicity (S).

Hence:

$$NA \cdot ND + ND(ND-1)/2 = D_m(D_m-1)/2 - NA(NA-1)/2$$

Thus:

$$\zeta = (-1)^{D_m(D_m-1)/2} \, (-1)^{NA(NA-1)/2} = \zeta_m \, \zeta_{NA}$$

Since D_m is a constant for a given CI wavefunction, ζ_m is irrelevant so that:

$$\Psi_J = (-1)^{NA(NA-1)/2} \, \mathcal{A} \, [core]_{ND} \sum_i^{NDET} C_{iJ}^N \, \Theta_i(\alpha) \, \Theta_i(\beta)$$

In terms of the standard couplings, the various

$$a \sum_{i}^{NDET} C_{ij}^{N} \Theta_i(\alpha)\, \Theta_i(\beta)$$

(in which the orbitals of $\Theta_i(\alpha)$ and $\Theta_i(\beta)$ are arranged in increasing order) allowed in our now current CI program are (See Appendix 2):

(I) Singlets:

2 open shells: G1

4 open shells: -G1, G2

6 open shells: -G1, G2, G3, -G4, G5

(II) Doublets:

1 open shell: G1

3 open shells: -G1, G2

5 open shells: -G1, G2, G3, -G4, G5

(III) Triplets:

2 open shells: G1

4 open shells: G1, -G2, G3

6 open shells: -G1, G2, G3, -G4, G5, -G6, G7, -G8, G9

For a given multiplicity, all open shell SECs can be made consistent with each other by multiplying by ζ (if necessary, subsequent readjustment is made so that the SEC for the smallest number of open shells is always +G1):

(I) Singlets:

2 open shells: G1

4 open shells: G1, -G2

6 open shells: G1, -G2, -G3, G4, -G5

(II) Doublets:

1 open shell: G1

3 open shells: G1, -G2

5 open shells: G1, -G2, -G3, G4, -G5

(III) Triplets:

2 open shells: G1

4 open shells: G1, -G2, G3

6 open shells: G1, -G2, -G3, G4, -G5, G6, -G7, G8, -G9

Thus, for a given multiplicity, the SECs of our CI program can be taken to be:

$$\psi_j = \zeta_j^N \mathcal{A} [\mathrm{core}] \Phi^N \chi_j^N$$

where the phase ζ_j^N is given above (coefficient of G_j for a given N). Φ^N is the product of the N singly occupied orbitals in increasing order and χ_j^N is the jth standard SEF of multiplicity S for N electrons.

APPENDIX 2

Spin-Eigenfunctions and SEF Diagrams

For an N-electron system having multiplicity S_N where $N > 2$ and $S_N \neq S_N(\mathrm{MAX})$, there are several linearly independent spin-eigenfunctions (SEFs). A convenient set of orthogonal SEF s can be generated from the appropriate (N-1)-electron functions using the recursion relationships:

1) If $S_N > S_{N-1}$:
$$\chi_N = \chi_{N-1}\,\alpha$$

2) If $S_N < S_{N-1}$:
$$\chi_N = 2\,S_{N-1}\,\chi_{N-1}\beta - (\hat{S}^-_{N-1}\chi_{N-1})\alpha$$

where χ_{N-1} is the parent SEF whose multiplicity number is S_{N-1}. $\hat{S}^-_{N-1}$ is the spin lowering operator for (N-1) electrons.

If two horizontally contiguous electron numbers inscribed within a rectangle implies singlet coupling and vertically contiguous electron numbers inscribed within a rectangle signifies multiplet coupling, the 2-electron singlet and triplet SEFs are:

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

$$\boxed{\begin{matrix}1\\2\end{matrix}} = \alpha\alpha$$

From these, two independent 3-electron doublet SEFs are obtained:

$$\begin{array}{|ll}\hline 1 & \multicolumn{1}{l|}{2} \\ \hline \multicolumn{1}{|l|}{3} & \\ \cline{1-1}\end{array} = \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\alpha \qquad G_1$$

$$\begin{array}{|l|l|}\hline 1 & 3 \\ \cline{2-2} 2 & \multicolumn{1}{l}{} \\ \cline{1-1}\end{array} = \frac{1}{\sqrt{6}}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) \quad G_2$$

As the representations imply, the G_1 function preserves the (1, 2) singlet couple and the G_2 function preserves the (1, 2) triplet couple.

As the number of electrons increases, the resulting spin eigenfunctions soon become too complicated to write down. However, the SEF diagrams, which convey all the pertinent information about the functions, are easy to construct:

1) If the multiplicity increases, add an electron number to the bottom of the left hand column of the appropriate (N-1)-electron diagram.
2) If the multiplicity decreases, the electron number is added to the bottom of the right-hand column.
3) Extend rectangles to inscribe all vertically or horizontally contiguous numbers.

The resultant diagrams are interpreted as follows:

1) Horizontally contiguous positions are singlet coupled.
2) Vertically contiguous positions are multiplet coupled.
3) Positions 1 to (N-1) remain coupled just as in the parent function.

These diagrams can also be used to represent product orbital wavefunctions having these SEF spin functions by simply placing orbitals in the desired positions. For example, the 3-electron doublet in which orbitals ϕ_1 and ϕ_2 are singlet coupled is:

$$\begin{array}{|cc|}\hline \phi_1 & \phi_2 \\ \hline \multicolumn{1}{|c|}{\phi_3} & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} = \mathcal{A}\; \phi_1\phi_2\phi_3 \left(\frac{\alpha\beta - \beta\alpha}{\sqrt{2}}\right) \alpha$$

Notice that this coupling is distinctly different from:

$$\begin{array}{|c|c|}\hline \phi_2 & \phi_3 \\ \hline \phi_1 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} = \mathcal{A}\,\phi_2\phi_3\phi_1\left(\frac{\alpha\beta-\beta\alpha}{\sqrt{2}}\right)\alpha$$

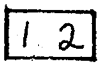
in which orbitals ϕ_2 and ϕ_3 are singlet coupled rather than ϕ_1 and ϕ_2.

The standard SEFs for up through six electrons are given in the following table. The corresponding SEF diagrams are also given. In the spin terms, a 1 is used for α spins and a 0 is used for β spins. A (**) preceding a normalization coefficient indicates that our CI program employs the negative of that SEF. These functions were obtained using the generating program SEFGEN.

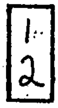
Spin-Eigenfunction Listing

```
1E DOUBLET
   COEFFICIENT          SPIN TERM
        1                1
     NORMALIZATION COEF IS 1/SQRT(      1 )
```

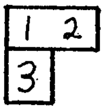
```
2E SINGLET
   COEFFICIENT          SPIN TERM
        1                10
       -1                01
     NORMALIZATION COEF IS 1/SQRT(      2 )
```



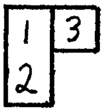
```
2E TRIPLET
   COEFFICIENT          SPIN TERM
        1                11
     NORMALIZATION COEF IS 1/SQRT(      1 )
```



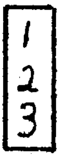
```
3E DOUBLET G1
   COEFFICIENT          SPIN TERM
        1                101
       -1                011
     NORMALIZATION COEF IS 1/SQRT(      2 )
```



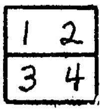
```
3E DOUBLET G2
   COEFFICIENT          SPIN TERM
        2                110
       -1                011
       -1                101
  ** NORMALIZATION COEF IS 1/SQRT(      6 )
```



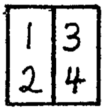
```
3E QUARTET
   COEFFICIENT          SPIN TERM
        1                111
     NORMALIZATION COEF IS 1/SQRT(      1 )
```



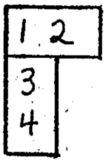
```
4E SINGLET G1
   COEFFICIENT          SPIN TERM
        1                1010
       -1                1001
       -1                0110
        1                0101
     NORMALIZATION COEF IS 1/SQRT(      4 )
```



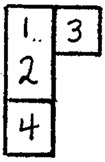
```
4E SINGLET G2
   COEFFICIENT          SPIN TERM
        2                1100
       -1                0101
       -1                1001
       -1                1010
        2                0011
       -1                0110
  ** NORMALIZATION COEF IS 1/SQRT(     12 )
```



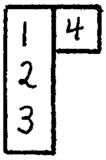
```
4E TRIPLET G1
   COEFFICIENT        SPIN TERM
        1              1011
       -1              0111
     NORMALIZATION COEF IS 1/SQRT(      2 )
```



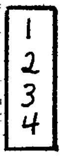
```
4E TRIPLET G2
   COEFFICIENT        SPIN TERM
        2              1101
       -1              1011
       -1              0111
   **NORMALIZATION COEF IS 1/SQRT(      6 )
```



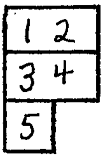
```
4E TRIPLET G3
   COEFFICIENT        SPIN TERM
        3              1110
       -1              0111
       -1              1011
       -1              1101
     NORMALIZATION COEF IS 1/SQRT(     12 )
```



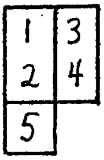
```
4E QUINTET
   COEFFICIENT        SPIN TERM
        1              1111
     NORMALIZATION COEF IS 1/SQRT(      1 )
```



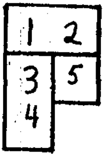
```
5E DOUBLET G1
   COEFFICIENT        SPIN TERM
        1              10101
       -1              10011
       -1              01101
        1              01011
     NORMALIZATION COEF IS 1/SQRT(      4 )
```



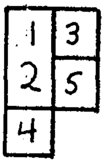
```
5E DOUBLET G2
   COEFFICIENT        SPIN TERM
        2              11001
       -1              01011
       -1              10011
       -1              10101
        2              00111
       -1              01101
   **NORMALIZATION COEF IS 1/SQRT(     12 )
```



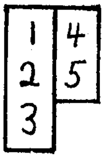
```
5E DOUBLET G3
   COEFFICIENT       SPIN TERM
        2             10110
       -1             10011
       -1             10101
       -2             01110
        1             01011
        1             01101
  ** NORMALIZATION COEF IS 1/SQRT(    12 )
```



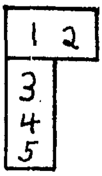
```
5E DOUBLET G4
   COEFFICIENT       SPIN TERM
        4             11010
       -1             01011
       -1             10011
       -2             11001
       -2             10110
        2             00111
        1             10101
       -2             01110
        1             01101
    NORMALIZATION COEF IS 1/SQRT(    36 )
```



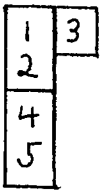
```
5E DOUBLET G5
   COEFFICIENT       SPIN TERM
        6             11100
       -2             01101
       -2             10101
       -2             11001
       -2             01110
        2             00111
        2             01011
       -2             10110
        2             10011
       -2             11010
  **NORMALIZATION COEF IS 1/SQRT(    72 )
```



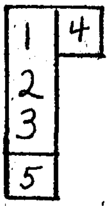
```
5E QUARTET G1
   COEFFICIENT       SPIN TERM
        1             10111
       -1             01111
    NORMALIZATION COEF IS 1/SQRT(     2 )
```



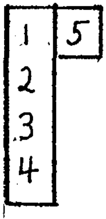
```
5E QUARTET G2
   COEFFICIENT       SPIN TERM
        2             11011
       -1             10111
       -1             01111
    NORMALIZATION COEF IS 1/SQRT(     6 )
```



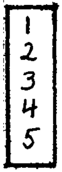
```
5E QUARTET G3
   COEFFICIENT         SPIN TERM
        3                11101
       -1                01111
       -1                10111
       -1                11011
     NORMALIZATION COEF IS 1/SQRT(      12 )
```



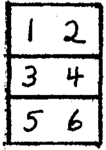
```
5E QUARTET G4
   COEFFICIENT         SPIN TERM
        4                11110
       -1                01111
       -1                10111
       -1                11011
       -1                11101
     NORMALIZATION COEF IS 1/SQRT(      20 )
```



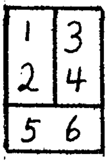
```
5E HEXTET
   COEFFICIENT         SPIN TERM
        1                11111
     NORMALIZATION COEF IS 1/SQRT(       1 )
```



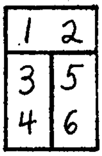
```
6E SINGLET G1
   COEFFICIENT         SPIN TERM
        1                101010
       -1                101001
       -1                100110
        1                100101
       -1                011010
        1                011001
        1                010110
       -1                010101
     NORMALIZATION COEF IS 1/SQRT(       8 )
```



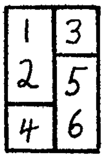
```
6E SINGLET G2
   COEFFICIENT         SPIN TERM
        2                110010
       -2                110001
       -1                010110
        1                010101
       -1                100110
        1                100101
       -1                101010
        1                101001
        2                001110
       -2                001101
       -1                011010
        1                011001
  **NORMALIZATION COEF IS 1/SQRT(      24 )
```



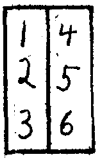
```
6E SINGLET G3
   COEFFICIENT        SPIN TERM
         2             101100
        -1             100101
        -1             101001
        -1             100110
         2             100011
        -1             101010
        -2             011100
         1             010101
         1             011001
         1             010110
        -2             010011
         1             011010
   **NORMALIZATION COEF IS 1/SQRT(    24 )
```



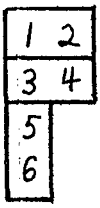
```
6E SINGLET G4
   COEFFICIENT        SPIN TERM
         4             110100
        -1             010101
        -1             100101
        -2             110001
        -1             010110
         2             010011
        -1             100110
         2             100011
        -2             110010
        -2             101100
         2             001101
         1             101001
         2             001110
        -4             001011
         1             101010
        -2             011100
         1             011001
         1             011010
     NORMALIZATION COEF IS 1/SQRT(    72 )
```



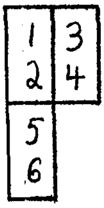
```
6E SINGLET G5
   COEFFICIENT        SPIN TERM
        6              111000
       -2              011001
       -2              101001
       -2              110001
       -2              011010
        2              001011
        2              010011
       -2              101010
        2              100011
       -2              110010
       -2              011100
        2              001101
        2              010101
        2              001110
       -6              000111
        2              010110
       -2              101100
        2              100101
        2              100110
       -2              110100
  **NORMALIZATION COEF IS 1/SQRT(   144 )
```



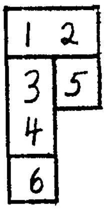
```
6E TRIPLET G1
   COEFFICIENT        SPIN TERM
        1              101011
       -1              100111
       -1              011011
        1              010111
    NORMALIZATION COEF IS 1/SQRT(     4 )
```



```
6E TRIPLET G2
   COEFFICIENT        SPIN TERM
        2              110011
       -1              010111
       -1              100111
       -1              101011
        2              001111
       -1              011011
  **NORMALIZATION COEF IS 1/SQRT(    12 )
```



```
6E TRIPLET G3
   COEFFICIENT        SPIN TERM
        2              101101
       -1              100111
       -1              101011
       -2              011101
        1              010111
        1              011011
  **NORMALIZATION COEF IS 1/SQRT(    12 )
```



```
6E TRIPLET G4
   COEFFICIENT        SPIN TERM
        4              110101
       -1              010111
       -1              100111
       -2              110011
       -2              101101
        2              001111
        1              101011
       -2              011101
        1              011011
     NORMALIZATION COEF IS 1/SQRT(    36 )
```

1	3
2	5
4	
6	

```
6E TRIPLET G5
   COEFFICIENT        SPIN TERM
        6              111001
       -2              011011
       -2              101011
       -2              110011
       -2              011101
        2              001111
        2              010111
       -2              101101
        2              100111
       -2              110101
   **NORMALIZATION COEF IS 1/SQRT(    72 )
```

1	4
2	5
3	
6	

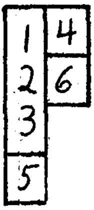
```
6E TRIPLET G6
   COEFFICIENT        SPIN TERM
        3              101110
       -1              100111
       -1              101011
       -1              101101
       -3              011110
        1              010111
        1              011011
        1              011101
     NORMALIZATION COEF IS 1/SQRT(    24 )
```

1	2
3	6
4	
5	

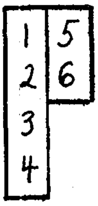
```
6E TRIPLET G7
   COEFFICIENT        SPIN TERM
        6              110110
       -1              010111
       -1              100111
       -2              110011
       -2              110101
       -3              101110
        2              001111
        1              101011
        1              101101
       -3              011110
        1              011011
        1              011101
   **NORMALIZATION COEF IS 1/SQRT(    72 )
```

1	3
2	6
4	
5	

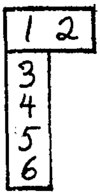
```
6E TRIPLET G8
   COEFFICIENT        SPIN TERM
         9              111010
        -2              011011
        -2              101011
        -2              110011
        -3              111001
        -3              011110
         2              001111
         2              010111
         1              011101
        -3              101110
         2              100111
         1              101101
        -3              110110
         1              110101
     NORMALIZATION COEF IS 1/SQRT(   144 )
```



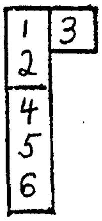
```
6E TRIPLET G9
   COEFFICIENT        SPIN TERM
        12              111100
        -3              011101
        -3              101101
        -3              110101
        -3              111001
        -3              011110
         2              001111
         2              010111
         2              011011
        -3              101110
         2              100111
         2              101011
        -3              110110
         2              110011
        -3              111010
  **NORMALIZATION COEF IS 1/SQRT(   240 )
```



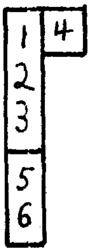
```
6E QUINTET G1
   COEFFICIENT        SPIN TERM
         1              101111
        -1              011111
     NORMALIZATION COEF IS 1/SQRT(     2 )
```



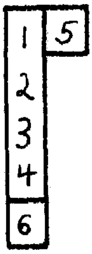
```
6E QUINTET G2
   COEFFICIENT        SPIN TERM
         2              110111
        -1              101111
        -1              011111
     NORMALIZATION COEF IS 1/SQRT(     6 )
```



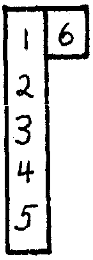
```
6E QUINTET G3
   COEFFICIENT       SPIN TERM
        3             111011
       -1             011111
       -1             101111
       -1             110111
     NORMALIZATION COEF IS 1/SQRT(    12 )
```



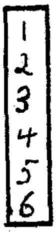
```
6E QUINTET G4
   COEFFICIENT       SPIN TERM
        4             111101
       -1             011111
       -1             101111
       -1             110111
       -1             111011
     NORMALIZATION COEF IS 1/SQRT(    20 )
```



```
6E QUINTET G5
   COEFFICIENT       SPIN TERM
        5             111110
       -1             011111
       -1             101111
       -1             110111
       -1             111011
       -1             111101
     NORMALIZATION COEF IS 1/SQRT(    30 )
```



```
6E HEPTET
   COEFFICIENT       SPIN TERM
        1             111111
     NORMALIZATION COEF IS 1/SQRT(     1 )
```



References

1) R. C. Ladner, Thesis, California Institute of Technology (1972)

2) W. A. Goddard III, Phys. Rev. **157**, 73 (1967)

3) D. E. Rutherford, Substitutional Analysis, Hafner Publishing Co. (1968)

PART THREE

The GVBTWO SCF Program

Abstract

Even for relatively simple Hartree-Fock (HF) or Perfect-Pairing Generalized Valence-Bond (PPGVB) many-electron wavefunctions, self-consistent calculations can be prohibitively expensive for many chemically interesting systems. Considerable effort has been devoted toward developing highly efficient computational techniques for solving for such wavefunctions. The results of this research, as embodied in the GVBTWO program, have made such calculations on relatively large systems a practical reality.

I. INTRODUCTION

GVBTWO is a fully optimized program written by F. Bobrowicz and W. R. Wadt for performing PPGVB[1] calculations. It can also handle open- and closed-shell Hartree-Fock calculations, among others. This program has brought PPGVB calculations of relatively large systems into the realm of practicality as it is well over an order of magnitude faster than its predecessor (GVBONE) written by J. Hay and W. Hunt (1971). Moreover, GVBTWO converges more rapidly and has a much wider radius of convergence than GVBONE.

The program is specifically designed to solve self-consistently for wavefunctions involving N real orthonormal orbitals of the form:

$$\Psi = \mathcal{A}\left[\prod_{i}^{NC} \bar{\phi}_i^2 \alpha\beta\right]\left[\prod_{m}^{NP}\left(\lambda_{m_1}\phi_{m_1}^2 - \lambda_{m_2}\phi_{m_2}^2\right)\alpha\beta\right]\Phi\chi \qquad (1)$$

where $\mathcal{A}$ is the antisymmetrizer (determinant operator). $\{\bar{\phi}\}$ is a set of closed-shell orbitals. The PPGVB pair:

$$\left(\lambda_{m_1}\phi_{m_1}^2 - \lambda_{m_2}\phi_{m_2}^2\right)\alpha\beta$$

is the natural orbital representation for two nonorthogonal singlet coupled orbitals ϕ'_{m_1} and ϕ'_{m_2}:

$$\mathcal{A}\cdots\left(\lambda_{m_1}\phi_{m_1}^2 - \lambda_{m_2}\phi_{m_2}^2\right)\alpha\beta\cdots = \mathcal{A}\cdots\phi'_{m_1}\phi'_{m_2}(\alpha\beta-\beta\alpha)\cdots$$

where:

$$\phi'_{m_1} = N'\left(\sqrt{\lambda_{m_1}}\,\phi_{m_1} + \sqrt{\lambda_{m_2}}\,\phi_{m_2}\right)$$

$$\phi'_{m_2} = N'\left(\sqrt{\lambda_{m_1}}\,\phi_{m_1} - \sqrt{\lambda_{m_2}}\,\phi_{m_2}\right)$$

$$\langle\phi'_{m_1}|\phi'_{m_2}\rangle = (\lambda_{m_1} - \lambda_{m_2})/(\lambda_{m_1} + \lambda_{m_2})$$

Φ is a fixed function of the remaining orbitals having the general form:

$$\Phi = \prod_i \left[\sum_j \gamma_{ji} \phi_{ji}^2 \right] \prod_\nu \phi_\nu$$

and X is the fixed spin function associated with these orbitals.

The energy of this wavefunction involves only diagonal 1-electron integrals and the usual coulomb and exchange 2-electron integrals:

$$E = \sum_i^N \left[2f_i h_{ii} + a'_{ii} J_{ii} \right] + 2 \sum_{i>j}^N \left[a'_{ij} J_{ij} + b'_{ij} K_{ij} \right] \qquad (2)$$

where:

$$h_{ii} = \langle \phi_i | h | \phi_i \rangle = \langle \phi_i | t + v_n | \phi_i \rangle$$
$$J_{ij} = \langle \phi_i | J_j | \phi_i \rangle = \langle \phi_i \phi_j | \tfrac{1}{r_{12}} | \phi_i \phi_j \rangle = (\phi_i \phi_i | \phi_j \phi_j)$$
$$K_{ij} = \langle \phi_i | K_j | \phi_i \rangle = \langle \phi_i \phi_j | \tfrac{1}{r_{12}} | \phi_j \phi_i \rangle = (\phi_i \phi_j | \phi_i \phi_j)$$

The coefficients $\{f, a', b'\}$ are functions of the pair coefficients $\{\lambda\}$ and the forms of Φ and X. The coefficients associated with closed shell orbital ϕ_ν are always:

$$f_\nu = a'_{\nu\nu} = 1$$
$$a'_{i\nu} = 2f_i$$
$$b'_{i\nu} = -f_i$$

whereas those associated with paired orbitals ϕ_{m_1} and ϕ_{m_2} are always:

$$f_{m_i} = a'_{m_i m_i} = \lambda_{m_i}^2 / (\lambda_{m_1}^2 + \lambda_{m_2}^2) \qquad i = 1,2$$
$$a'_{m_1 m_2} = 0$$
$$\left.\begin{aligned} b'_{m_1 m_2} &= -\lambda_{m_1} \lambda_{m_2} / (\lambda_{m_1}^2 + \lambda_{m_2}^2) \\ a'_{j m_i} &= 2 f_j f_{m_i} = -2 b'_{j m_i} \end{aligned}\right\} \quad \begin{aligned} &i = 1,2 \\ &j \neq m_1, m_2 \end{aligned}$$

Definitions of the remaining coefficients depend upon the form of ΦX.

Actually, GVBTWO is capable of solving for the orbitals involved in (2) for any arbitrary set of $\{f, a', b'\}$ coefficients, even if they do not define a wavefunction of form (1). However, for wavefunctions of this form, it can optimize for the pair coefficients $\{\lambda\}$ as well as for the orbitals themselves.

Casting (2) in terms of the more computationally convenient operators:

$$\mathcal{J}_i = \tfrac{1}{2}\left(J_i - \tfrac{1}{2}K_i\right)$$
$$\mathcal{K}_i = \tfrac{1}{4}\,K_i$$

$$E = \sum_{i}^{N}\left[2f_i h_{ii} + a_{ii}\mathcal{J}_{ii}\right] + 2\sum_{i>j}^{N}\left[a_{ij}\mathcal{J}_{ij} + b_{ij}\mathcal{K}_{ij}\right]$$

where $a_{ii} = 4a'_{ii}$, $a_{ij} = 2a'_{ij}$ and $b_{ij} = 4b'_{ij} + 2a'_{ij}$, the coefficients associated with closed shell orbital ϕ_ν become:

$$a_{j\nu} = 4f_j \quad ; \quad b_{j\nu} = 0 \qquad j = 1, N$$

and for paired orbitals ϕ_{m_1} and ϕ_{m_2} they are:

$$\begin{aligned} a_{m_i m_i} &= 2f_{m_i} && i = 1,2 \\ a_{m_1 m_2} &= 0 \\ b_{m_1 m_2} &= -4\lambda_{m_1}\lambda_{m_2} / (\lambda_{m_1}^2 + \lambda_{m_2}^2) \\ a_{jm_i} &= 4f_j f_{m_i} && \left.\begin{matrix} \\ \\ \end{matrix}\right\} \begin{matrix} i = 1,2 \\ j \neq m_1, m_2 \end{matrix} \\ b_{jm_i} &= 0 \end{aligned}$$

Applying the Variational Principle to this expression yields the usual variational condition for the optimum orbitals:

$$0 = \sum_{i}^{N} \langle \delta_i | H_i | \phi_i \rangle$$

where the orbital variations $\{\delta\}$ are constrained so as to maintain orbital orthogonality at least through first order. The one-particle hamiltonians are:

$$\begin{aligned} H_i &= f_i h + a_{ii} \mathcal{J}_i + \sum_{j \neq i}^{N} \left[a_{ji} \mathcal{J}_j + b_{ji} \mathcal{K}_j \right] \\ &= f_i \left[h + A_{ii} \mathcal{J}_i + \sum_{j \neq i}^{N} \left(A_{ji} \mathcal{J}_j + B_{ji} \mathcal{K}_j \right) \right] \end{aligned}$$

where $A_{ji} = a_{ji}/f_i$ and $B_{ji} = b_{ji}/f_i$. Since for closed-shell orbital ϕ_ν:

$$A_{j\nu} = A_{\nu j} = 4 \quad ; \quad B_{j\nu} = B_{\nu j} = 0$$

if

$$\mathscr{h} = h + 4 \sum_{\phi_\nu \in \{\phi\}}^{\text{closed}} \mathcal{J}_\nu$$

then:

$$H_i = f_i \left[\mathscr{h} + \sum_{j \neq \text{closed}} \left(A_{ji} \mathcal{J}_j + B_{ji} \mathcal{K}_j \right) \right]$$

In terms of these hamiltonians, the energy is:

$$E = \sum_{i}^{N} \left[f_i h_{ii} + \langle \phi_i | H_i | \phi_i \rangle \right]$$

These equations form the basis from which the self-consistent set of orbitals and pair coefficients are found.

II DISCUSSION

GVBTWO is a Fortran program written for the IBM 370-155 system. It is linearly dimensioned and takes full advantage of zero coefficients whenever possible. Maximum efficiency is attained through elimination of virtually all redundant computations. All symmetric matrices are stored and used in triangular form with diagonal elements $\frac{1}{2}$ value. The iterative cycle is optimized as thoroughly as possible through liberal use of initially defined indexing arrays and by initial preparation of input integrals.

The program requires a POLYPAIR preprocessed integral input (see Appendix) in which the usual 2-electron integrals are replaced by the pairs:

$$VK(IJKL) = \frac{1}{4}\left[(IK|JL) + (IL|JK)\right]$$

$$VJ(IJKL) = (IJ|KL) - VK(IJKL)$$

$$IJKL = IJ*(IJ-1)/2 + KL \qquad IJ \geqslant KL$$

$$IJ = I*(I-1)/2 + J \qquad I \geqslant J$$

where $(IJ|KL)$ is a 2-electron integral written in $(11|22)$ form. Use of these quantities makes possible much more rapid generation of the required $\mathscr{h}$, $\mathscr{J}$ and $\mathscr{K}$ matrices than is possible using raw integrals.

The hamiltonian coefficients $\{f, A, B\}$ for the most common forms of wavefunction (1) in which:

$$\Phi\chi = 0$$

$$\Phi\chi = \phi_i\phi_j(\alpha\beta - \beta\alpha)$$ HF open-shell singlet

$$\Phi\chi = \prod_i \phi_i(i)\,\alpha(i)$$ HF open-shell multiplet

are preprogrammed. For all other possibilities, these coefficients must be read in. Since several orbitals can have the same hamiltonian, the orbitals are grouped into shells. Thus, only the $\{f, A, B\}$ coefficients which define each shell are required. The program makes full use of the fact that mixing between orbitals of the same shell does not affect the energy.

The orbitals are defined in terms of a set of primitive basis functions $\{\chi\}$:

$$\phi_w = \sum_i c_{iw}\chi_i$$

subject to the constraint that $\langle\phi_w|\phi_\nu\rangle = \delta_{w\nu}$. Hence, orbital optimization consists of self-consistently determining the optimal $\{c\}$ within the constraint of orbital orthogonality. Symmetry restrictions can be placed upon these orbitals by initially partitioning the space scanned by $\{\chi\}$ into the desired symmetry types. Each orbital is optimized only with respect to the space having the proper symmetry. The program takes full advantage of these restrictions and of the construction of the symmetry partitioned space in terms of the primitive bases.

For purposes of discussion, the program can be partitioned into the following sections:

Initialization:

A) Input - Read in data and set initial parameters

B) Formation of the initial MO transformation matrix and determination of symmetry type basis set information

C) Preparation of input integrals and generation of initial $\mathscr{h}$, $\mathscr{g}$ and $\mathscr{K}$ matrices

The Iterative Cycle:

D) Hamiltonian Optimization -

Optimization of pair coefficients

E) Orbital mixing -

Optimization of orbitals with respect to each other through independent rotations

F) OCBSE orbital optimization -

Optimization of orbitals with respect to the space orthogonal to them (the virtual space)

Termination:

G) Output - print and punch final results

The individual tasks involved in each of these sections will now be discussed in detail. Whenever appropriate, an outline of the computational procedure employed will be given.

A. INPUT

GVBTWO requires the following input data:

1. TITLE
FORMAT (10A8)
TITLE = case description (molecule, basis, etc.)

2. NBF, NPAIR, MAXIT, ITERO, IWRITE, IPUNCH, IPRINT, IOVLP, IVIRT, IEXTRP, IELOW
FORMAT (16I5)
NBF = number of basis functions (maximum is 50)
NPAIR = number of PPGVB pairs (maximum is 12)
MAXIT = maximum number of SCF iterations to be permitted in calculating the new pair coefficients for the PPGVB pairs. (If zero is read in , ITERO = 1.) A reasonable choice for ITERO is 5.
(IWRITE. LT. 0) ⩾ no intermediate print out
(IWRITE. EQ. 0) ⩾ intermediate print out
(IWRITE. EQ. 1) ⩾ rotation matrix and MO transformation matrix after orbital rotations are also printed
(IWRITE. EQ. 1) ⩾ $h, \mathcal{J}$ and $\mathcal{K}$ matrices over primitives and orbitals are printed out for each iteration. (Make sure the PRT parameter on your SET card is large, e.g., PRT = 20.)
(IPUNCH. LT. 0) ⩾ no punch
(IPUNCH. EQ. 0) ⩾ MO transformation matrix punched out
(IPUNCH. EQ. 1) ⩾ MO transformation matrix and occupied orbitals are punched out
(IPUNCH . EQ. 2) ⩾ occupied orbitals are punched out
(IPRINT. LT. 0) ⩾ extra final output printed out (see IPRINT . LT. 0). Program tries to read basis set information off the integrals tape and then prints it out. If basis set information is not there, the program continues, but gives an IHC213 error.

(IOVLP.LT.0) ⩾ after diagonalization of a hamiltonian, the OCBSE transformation matrix is ordered by overlap with previous orbitals. Good for trying to solve for excited states that are not the lowest energy states of that symmetry. It is also good when ordering by eigenvalue leads to wild oscillation of the energy (a bad guess), where virtual and occupied orbitals switch positions from iteration to iteration.

(IOVLP.EW.0) ⩾ after diagonalization of a hamiltonian, the OCBSE transformation matrix is ordered by eigenvalue

(IOVLP.GT.0) ⩾ after diagonalization of a hamiltonian, the OCBSE transformation matrix is ordered by eigenvalue for the first IOVLP iterations and then by overlap with the previous orbitals for the remaining iterations. Good for bad starting guesses.

(IVIRT.EQ.0) ⩾ virtuals are obtained from Schmidt orthogonalization to the occupied orbitals obtained from diagonalization of the hamiltonian matrix. These virtuals, therefore, have <u>no</u> physical meaning and their orbital energies are set equal to zero.

(IVIRT.NE.0) ⩾ virtuals are obtained from diagonalization of the hamiltonian matrix. This procedure is, of course, used when the orbitals are ordered by overlap.

(IEXTRP.GT.0) ⩾ 2-point extrapolation of the transformation matrix is performed every IEXTRP iterations starting with the first iteration.

(IEXTRP.LT.0) ⩾ 2-point extrapolation of the transformation matrix is performed on iteration I+1 whenever the condition |(SQCDF(I)-SQCDF (I+IEXTRP))/SQCDF(I)|<(0.7)**|IEXTRP| is met. (N.B. Extrapolation is also performed on the first iteration.)

(IELOW.NE.0) ⩾ orbital rotation coefficients selected by eigenvalue rather than overlap.

3. CONVG, ZERO, SKIP, ROTTST
   FORMAT (5D15.8)

CONVG = convergence criterion, which is compared with the sum of the squares of the differences (SQCDF) between <u>all</u> the occupied orbital coefficients for the past iteration and the current one. (If zero is read in, 1.D-8 is used.)

ZERO = coefficient criterion, i.e., all coefficients in the transformation matrix LT ZERO are set equal to 0.D0. (If zero is read in. 1.D-8 is used.)

SKIP = orbital skip criterion, i.e., if the sum of the squares of the differences between an occupied orbitals coefficients for the past and present iterations is LT SKIP then the primitive J and K matrices for this orbital are not regenerated. This does not apply for closed-shell orbitals (If zero is read in, CONVG/NBF is used.)

ROTTST = rotations shut-off parameter. If SQCDF from the previous iteration is greater than ROTTST, then the rotations of the occupied orbitals belonging to different hamiltonians are shut off. N.B. If zero is read in for ROTTST then ROTTST is set equal to 1.D6, so that the rotations are always performed. On the other hand, by setting ROTTST to a value less than zero, the rotations will be shut off entirely.

4. NSYTYP
FORMAT (1615)

NSYTYP = number of irreducible representations of the point group to be used in the calculation, i.e., number of symmetry types (maximum is 15).

5. DO 5 I=1,
NSYTYP SYM(I),
NOCC(I) FORMAT
(A8,2X,215)

SYM(I) = symmetry name for the I symmetry type, e.g., A1G or SIGMA.

NTOT(I) = number of I symmetry functions, i.e., number of independent functions of the I^{th} symmetry type that can be formed from the basis set.

NOCC(I) = number of occupied orbitals for the I^{th} symmetry type.

6. ASPIN, IOPEN, INHAM
FORMAT (A8, 2X. 215)

ASPIN = spin name, e.g., singlet, doublet, triplet, etc., left-adjusted.

IOPEN = number of open-shell HF orbitals, if INHAM = 0. If INHAM ≠0, shell for which the hamiltonian is to be read in

(INHAM.EQ.0) $\geqslant$ no hamiltonians are to be read in
(INHAM.NE.0) $\geqslant$ INHAM hamiltonians will be read in (NB. The closed shell hamiltonians, #1, is not read in)

7. IF(IOPEN.EQ.0) GO TO 10 IF(INHAM.NE.0) GO TO 8 (IORB(I),I=1, IOPEN)
FORMAT (16I5)
GO TO 10
IORB(I) = list of occupied orbitals appearing in the HF open shell.

8. (F(I),I=2,INHAM+1
FORMAT(5D15.8)
F(I) = occupation number for shell I (i.e. fi)

9. DO 9 J=2, INHAM+1
(JORB(I,J,), I=1, IOPEN)
FORMAT (16I5)
(AJ(I,J),I=2,INHAM+1)
FORMAT (5D15.8)
AK(I,J),I=2, INHAM+1)
FORMAT (5D15.8)
JORB(I,J) = Ith orbital of Jth shell (0 signals end of list)
AJ(I,J) = shell J $\mathcal{J}$ operator coefficient for orbitals in shell I (ie. Aij).
AK(I,J) = shell J $\mathcal{K}$ operator coefficient for orbitals in shell I(i.e. B j).

10. IF(NPAIR.EQ.0) GO TO 11 DO 10 I=1, NPAIR
K1(I),K2(I),C1(I),C2(I)
FORMAT (2I5,5X,2D15,8)
K1(I)} K2(I)} = the two occupied orbitals involved in the Ith PPGVB pair.
C1(I)} C2(I)} = pair coefficients for the occupied orbitals K1(I) and K2(I), respectively, that form the Ith PPGVB pair. (i.e. $\lambda_{I_1} + \lambda_{I_2}$)

11. NIN
FORMAT (16I5)
NIN = number of starting vector to be read in. If NIN= NSOS (the number of occupied orbitals plus virtuals), then no symmetry vectors are read in. If NIN=0, then the symmetry vectors are used as starting guesses. If NIN=NORB (numbered orbitals) NIN set to NORB, but symmetry vectors are still read in.

N.B. Vectors are to be read in by symmetry type. Within each symmetry type, the orbitals (with closed-shell orbitals preceding the others) precede the virtuals (if NIN=NSOS).

12. IF(NIN.EQ.0) GO TO 14
FMT
FORMAT (10A8)
FMT = format for reading in starting vectors

13. DO 13 J=1,NIN
TRLAB(J)
FORMAT (10A8)
TRANS(I,J),I=1,NBF)
FORMAT (FMT)
TRLAB(J) = label for the J^{th} starting vector.
TRANS(I,J), I=1,NBF) = J^{th} starting vector

14. IF(NIN.EQ.NSOS) GO TO 16
NREAD,IDENT
FORMAT (16I5)
NREAD = largest number of basis functions with nonzero coefficients for any one symmetry vector
(IDENT.NE.0) = the unit matrix will be used as the symmetry matrix. (Normally used when there is no symmetry.)

15. IF(IDENT.NE.0) GO TO 16
DO 15 J=1,NSOS
((KX(I,J),KY(I,J),I=1,NREAD)
FORMAT (16I5)
KX(I,J) KY(I,J) = J^{th} symmetry vector defined by pairs of numbers, the first (KX) being the number of a basis function that has a nonzero coefficient in this symmetry orbital, while the second (KY) is the value of that coefficient. (If KY is zero, KY is set equal to 1.) N.B.: If KY.GT.4, then the coefficient is treated as sin KY, where KY is in degrees. This is convenient for molecules with C_3 or higher axes of symmetry.

16. IGO
FORMAT (16I5)
IF(IGO.NE.0) GO TO 1
(IGO.NE.0) ⩾ program starts over reading a new data set, but using the same integral set

In addition to these variables and initialization of hamiltonian coefficients, the following indexing arrays are established:

ISNX(I) = $I \times (I-1)/2,\ I \le NBF+1$ position prior to beginning of the I^{th} triangular array row

NCONF(I) = shell number of orbital I

NHORB(I) = number of orbitals in shell I

MSYMPR(I) = linear position in the MO transformation matrix prior to the beginning of the column defining orbital I

IDIAG(I) = position of the diagonal element of the I^{th} orbital in a symmetry packed triangular array over the orbitals

IORB = sequential list of nonclosed-shell orbital number by shell number

B. The Initial MO Transformation Matrix and Symmetry Type Basis Set Information

The initial MO transformation matrix is constructed from the inputed initial orbitals, the primitive overlap integrals, and the symmetry vectors. This matrix defines the orthonormal occupied orbitals and virtuals (defined simply as those functions which scan the available space orthogonal to the orbitals) in terms of the primitive basis set $\{\chi\}$. The matrix is partitioned into symmetry blocks, with the occupied orbitals preceding the virtuals in each block. The orbitals of each symmetry type are arranged with closed-shell orbitals preceding all others. Throughout the iterative cycle, this matrix will continually be revised so as to define the current MO basis (orbitals plus virtuals) in terms of the primitive basis.

The primitive basis functions used by each symmetry type are determined, as this information can significantly reduce the operation count for computations involving the MO transformation matrix. Since primitive operator matrices are always transformed to an MO basis in symmetry blocks prior to use, primitive matrix elements between basis functions I and J need only be calculated and stored if I and J are simultaneously used by some symmetry type. Therefore, the triangular indices:

$$IJ = I \times (I-1)/2 + J \qquad I \geq J$$

of the needed primitive matrix elements are determined. Using this information, operations involving these matrices can be performed on packed (unneeded elements deleted) matrices. Moreover, this information permits deletion of unneeded VJK pairs from the input POLYPAIR integral list

Procedure:

After Schmidt orthogonalizing the input symmetry vectors, the initial MO transformation matrix is constructed a symmetry block at a time. Before doing so, however, the M input orbitals of a given symmetry type are first purged of any possible symmetry contamination by projecting each orbital into the N symmetry vectors (orthogonalized) of that symmetry type $\{ w \}$ on the basis of overlap:

$$\phi_\nu = \sum_{j=1}^{N} \langle \phi_\nu^\circ | W_j \rangle W_j$$

Since:

$$\phi_\nu^\circ = \sum_{i=1}^{NBF} c_{i\nu}^\circ \chi_i \quad ; \quad W_\mu = \sum_{i=1}^{NBF} d_{i\mu} \chi_i$$

the symmetry-pure orbital is:

$$\phi_\nu = \sum_{i=1}^{NBF} c_{i\nu} \chi_i$$

where:

$$c_{i\nu} = \sum_{j=1}^{NBF} \langle \phi_\nu^\circ | W_j \rangle d_{ij}$$

$$\langle \phi_\nu^\circ | W_\mu \rangle = \sum_{i \geq j}^{NBF} \left[c_{i\nu}^\circ d_{j\mu} + c_{j\nu}^\circ d_{i\mu} \right] S_{ij}$$

$$S_{ij} = \langle \chi_i | \chi_j \rangle / (1 + \delta_{ij})$$

While doing so, the M symmetry vectors having maximal overlap with these orbitals are noted. The symmetry block is then constructed by Schmidt orthogonalization of the resulting orbitals and the (N-M) symmetry vectors of that type having minimal overlap with these orbitals.

After the matrix has been constructed, each symmetry block is scanned to determine the primitive basis functions used by that symmetry type. The triangular indices associated with these basis functions are also determined. Once all blocks have been scanned, a list of the unique required triangular indices is constructed in increasing order.

<u>N.B.</u>

1) If a complete MO transformation matrix was inputed, this matrix is simply Schmidt orthogonalized unless these are no virtuals. In this case the input orbitals may be purged of symmetry contamination using input symmetry vectors if desired.
2) If no initial orbitals were inputed, the initial MO transformation matrix consists of the orthogonalized symmetry vectors.

C. Input Integral Preparation and Initial Matrix Generation

The input POLYPAIR VJK pair list is in packed IJKL canonical order (zero pairs deleted) where:

$$VK(IJKL) = \frac{1}{4}\left[(IK|JL) + (IL|JK)\right]$$

$$VJ(IJKL) = (IJ|KL) - VK(IJKL)$$

$$IJKL = IJ*(IJ-1)/2 + KL \qquad IJ \geqslant KL$$

$$IJ = I*(I-1)/2 + J \qquad I \geqslant J$$

Packed into the lower two bytes of the VK element of a pair is the KL (column) number. A separate array indicates the number of pairs having the same I J (row) value. A detailed description of this input list is given in Appendix 2.

As explained in Appendix 1, a pair whose row or column number corresponds to an unneeded primitive matrix triangular index is of no value. Consequently, such pairs are deleted from the list at the onset. Since the number of operations involved in generation of primitive $\mathcal{h}$, $\mathcal{J}$, and $\mathcal{K}$ matrices is directly proportional to the number of VJK pairs, this can reduce iteration times significantly. To further increase the efficiency of matrix generation, the list of needed pairs is stored on disc in packed canonical order in records of the form:

IST, IEND, VJ, VK

where VJ(LTH) and VK(LTH) are REAL * 8 arrays containing the pairs. IST and IEND are the number of the first and last occupied rows for which there are pairs in the record. A separate array holds the actual IJ values of each occupied row. Packed into the lower two bytes of the first VJ element of a row in the record is the number of the last pair of that row in the record. The column (KL) number of each pair is packed into the lower two bytes of the VK element. Finally, the input T (kinetic energy) and V (nuclear potential energy) 1-electron integrals are added to form the primitive h matrix. This is also stored on disc after dividing diagonal elements by two

The initial primitive $\mathcal{J}$ and $\mathcal{K}$ matrices for all but closed-shell orbitals are then generated and stored on disc (with unneeded elements deleted and diagonal elements $\frac{1}{2}$ value). While efficient generation of such matrices using row 2-electron integrals is rather complicated, it is straightforward using VJK pairs:

$$\langle \chi_i | \mathcal{J}_\nu | \chi_j \rangle = \sum_{kl \leq ij} D^{\nu}_{kl}\, VJ(ijkl) + \sum_{kl > ij} D^{\nu}_{kl}\, VJ(klij)$$

$$\langle \chi_i | \mathcal{K}_\nu | \chi_j \rangle = \sum_{kl \leq ij} D^{\nu}_{kl}\, VK(ijkl) + \sum_{kl > ij} D^{\nu}_{kl}\, VK(klij)$$

where:

$$D^{\nu}_{kl} = c_{k\nu} c_{l\nu} / (1 + \delta_{kl}) \quad ; \quad \phi_\nu = \sum_{k=1} c_{k\nu} \chi_k$$

In addition, these matrices are transformed over the orbitals in symmetry blocks which are then stored on another disc unit.

Generation of the primitive $\mathfrak{h}$ matrix is also straightforward:

$$\langle \chi_i | \mathfrak{h} | \chi_j \rangle = \langle \chi_i | h | \chi_j \rangle + 4 \sum_{\nu}^{\text{closed}} \langle \chi_i | \mathcal{J}_\nu | \chi_j \rangle$$

$$= \langle \chi_i | h | \chi_j \rangle + \sum_{kl \leq ij} D^{c}_{kl}\, VJ(ijkl)$$

$$+ \sum_{kl > ij} D^{c}_{kl}\, VJ(klij)$$

where:

$$D^{c}_{kl} = \frac{4}{1+\delta_{kl}} \sum_{\nu}^{(\text{CLOSED})} C_{k\nu} C_{l\nu}$$

This matrix is also transformed over the orbitals in symmetry blocks and both the packed primitive and orbital transformed matrices are stored on disc.

Procedure:

From the list of required primitive matrix triangular indices an array indicating which indices correspond to needed and unneeded VJK pairs is constructed. Using this array, the input pair list is processed a row at a time, storing only the needed pairs in arrays VJ and VK sequentially. Since the input list is in packed canonical order, this can be done with only one input record at a time being held in core. Upon encountering the first needed pair for row IJ (there can, of course, be none), the number of 'occupied' rows is incremented by one and the IJ value is recorded (i.e. the k$^{\text{th}}$ occupied row has an actual row number of IJ). Once LTH pairs have been accumulated or the input list is exhausted, they are written on disc (IDISC) in records of the form described above. In order to do this, as the pairs for a given record are accumulated, the occupied row number of the first pair is noted (IST) as is the occupied row number of the last pair (IEND). In addition, once an occupied row has been processed, the number of the last pair of the row in this record is recorded. This information is automatically packed into the first VJ element of that row in this record through use of suitably equivalenced arrays. Since the input VK elements already have the pair column numbers packed into them, this information is automatically passed on. Finally, the number of such records is noted. Once the last pair record has been placed on disc, the primitive h matrix (diagonal elements $\frac{1}{2}$ value) which was formed from the input T and V integrals prior to processing the pair list is written twice on the same disc unit.

The initial primitive $\mathcal{J}$ and $\mathcal{K}$ matrices for the nonclosed-shell orbitals are then generated sequentially from this integral list using the algorithm given in Appendix 1. These matrices are purged of unnecessary (and meaningless) elements and stored on disc (JUNIT). Each record consists of the $\mathcal{J}$ and $\mathcal{K}$ matrices of a particular orbital along with the orbital number. In addition, these matrices are transformed over the orbitals in symmetry blocks and are likewise stored on another disc unit (IUNIT). Finally, the primitive $\mathscr{h}$ matrix is generated in an analogous fashion using the density matrix $\underline{D}^c$. This matrix is packed and stored on JUNIT along with the primitive $\mathcal{J}$ and $\mathcal{K}$ matrices. It is also transformed over orbitals and stored on IUNIT.

D. Hamiltonian Optimization

The energy contribution of the M^{th} PPGVB pairs:

$$(\lambda_{m_1}\phi_{m_1}^2 - \lambda_{m_2}\phi_{m_2}^2)\alpha\beta$$

is:

$$E_m = 2f_{m_1}h_{m_1m_1} + 2f_{m_2}h_{m_2m_2} + a_{m_1m_1}\mathcal{J}_{m_1m_1} + a_{m_2m_2}\mathcal{J}_{m_2m_2}$$
$$+ 2a_{m_1m_2}\mathcal{J}_{m_1m_2} + 2b_{m_1m_2}\mathcal{K}_{m_1m_2} + 2\sum_{\substack{i=1,2\\ j\neq m_1,m_2}}\left[a_{jm_i}\mathcal{J}_{jm_i} + b_{jm_i}\mathcal{K}_{jm_i}\right]$$

since:

$$f_{m_i} = \lambda_{m_i}/(\lambda_{m_1}^2+\lambda_{m_2}^2) \qquad i=1,2$$
$$a_{m_1m_2} = 0$$
$$b_{m_1m_2} = -4\lambda_{m_1}\lambda_{m_2}/(\lambda_{m_1}^2+\lambda_{m_2}^2)$$
$$\left.\begin{aligned} b_{jm_i} &= 0\\ a_{jm_i} &= 4f_j f_{m_i}\\ a_{m_im_i} &= 4f_{m_i}\end{aligned}\right\}\begin{aligned} &i=1,2\\ &j\neq m_1,m_2\end{aligned}$$

$$\epsilon_m(\lambda_{m_1}^2+\lambda_{m_2}^2) = \sum_{i=1}^{2}\lambda_{m_i}^2\left[\frac{1}{4}h_{m_im_i} + \frac{1}{2}\mathcal{J}_{m_im_i} + \sum_{j\neq m_1,m_2} f_j\mathcal{J}_{jm_i}\right]$$
$$- \lambda_{m_1}\lambda_{m_2}\mathcal{K}_{m_1m_2}$$

where $\epsilon_m = \frac{1}{8}E_m$. Thus if:

$$X_{m_i} = \frac{1}{4}h_{m_im_i} + \frac{1}{2}\mathcal{J}_{m_im_i} + \sum_{j\neq m_1,m_2} f_j\mathcal{J}_{m_ij}$$
$$= \frac{1}{4}h_{m_im_i} + \frac{1}{2}\mathcal{J}_{m_im_i} + \sum_{j\neq m_1,m_2,[\text{CLOSED}]} f_j\mathcal{J}_{m_ij}$$

$$\varepsilon_m = \lambda_{m_2}/\lambda_{m_1}$$

$$\epsilon_m = \left[X_{m_1} + \varepsilon_m^2 X_{m_2} - \varepsilon\mathcal{K}_{m_1m_2}\right]/\left[1+\varepsilon_m^2\right]$$

Requiring ϵ_m to be stationary with respect to $\mathcal{E}_m$ ($\frac{\partial \epsilon_m}{\partial \mathcal{E}_m} = 0$) gives:

$$\mathcal{E}_m = \frac{X_m}{Y_m} \pm \left[1 + \left(\frac{X_m}{Y_m}\right)^2 \right]^{1/2} \quad ; \quad Y_m = 0 \Rightarrow \mathcal{E}_m = 0$$

where:

$$X_m = X_{m_1} - X_{m_2}$$

$$Y_m = \mathcal{K}_{m_1 m_2}$$

Since $\mathcal{K}_{m_1 m_2} \geq 0$, the minimum ϵ_m invariably corresponds to the root for which $\mathcal{E}_m \geq 0$. Hence:

$$\mathcal{E}_m = \frac{X_m}{Y_m} + \left[1 + \left(\frac{X_m}{Y_m}\right)^2 \right]^{1/2} \quad ; \quad Y_m = 0 \Rightarrow \mathcal{E}_m = 0$$

Thus by solving this simple equation, the optimum pair coefficient and $\{f, A, B\}$ coefficients for the Mth PPGVB pair can be obtained. However, since X_m depends upon the f values of the other pair, $\{\mathcal{E}\}$ must be determined sequentially. Moreover, since these coefficients define the hamiltonians used in orbital optimization, their degree of validity within each iteration can have a significant effect upon overall convergence. Consequently, these parameters are continually evaluated through $\{X\}$ updating until self-consistency is attained.

Procedure:

Initial $\{X, Y\}$ values are calculated simultaneously from the orbital transformed h, $\mathcal{J}$, and $\mathcal{K}$ matrices stored on disc (one pass) using the current f values $\{ f^{\circ} \}$. In addition, the quantities:

$$\omega_n^{m_1} = g_{m_1 n_1} - g_{m_1 n_2}$$

$$\omega_n^{m_2} = g_{m_2 n_1} - g_{m_2 n_2} \qquad n \neq m$$

are also calculated for all pairs. Once $\mathcal{E}_m$ is determined from X_m and Y_m the other Xs are updated before calculating the next $\mathcal{E}$:

$$X_n = X_n^{\circ} + (f_{m_1} - f_{m_1}^{\circ})\,\omega_n^{m_1} + (f_{m_2} - f_{m_2}^{\circ})\,\omega_n^{m_2}$$

where $f_{m_2} = \varepsilon_m^2 f_{m_1} = \varepsilon_m^2/(1+\varepsilon_m^2)$

This extremely rapid process of $\mathcal{E}$ evaluation and X updating is continued until self-consistency is achieved. Finally, new pair and hamiltonian coefficients are calculated from the results.

E. Orbital Mixing

Optimizing the orbitals with respect to each other is most easily accomplished by considering only two orbitals at a time. If only orbitals ϕ_W and ϕ_ν are allowed to change, the variational condition is:

$$0 = \langle \delta_\omega | H_\omega | \phi_\omega \rangle + \langle \delta_\nu | H_\nu | \phi_\nu \rangle \quad ; \quad \langle \phi_\omega | \phi_\nu \rangle = 0$$

where $\phi_W + \delta_W$ and $\phi_\nu + \delta_\nu$ must be orthogonal at least through first order. Since optimization is to be with respect to occupied space, a quadratically convergent solution is required.[2]

If:

$$\phi_\omega = N_\omega(\phi_{\omega_0} + \Delta_\omega) \quad ; \quad \phi_\nu = N_\nu(\phi_{\nu_0} + \Delta_\nu)$$

where $\{ \phi_0 \}$ are the current guesses for the orbitals, the energy dependence upon these new orbitals is:

$$\epsilon_{\omega\nu} = \langle \omega | H_{\omega_0} | \omega \rangle + \langle \nu | H_{\nu_0} | \nu \rangle + \langle \Delta_\omega | \Delta H_\omega | \omega_0 \rangle + \langle \Delta_\nu | \Delta H_\nu | \nu_0 \rangle + \cdots$$

where ΔH_W (ΔH_ν) is the first-order change in H_W (H_ν) owing to the changes Δ_W and Δ_ν :

$$H_\omega = H_{\omega_0} + \Delta H_\omega + \cdots$$
$$H_\nu = H_{\nu_0} + \Delta H_\nu + \cdots$$

Since these orbitals are to be optimized only with respect to each other :

$$\Delta_\omega = \varepsilon_{\omega\nu} \phi_{\nu_0} \quad ; \quad \Delta_\nu = -\varepsilon_{\omega\nu} \phi_{\omega_0} \quad ; \quad N_\nu = N_\omega = (1 + \varepsilon_{\omega\nu}^2)^{1/2}$$

where the rotation coefficient is an adjustable parameter. Assuming $_{w\nu}$ will be small, it can be obtained in a quadratically convergent manner by solving:

$$\epsilon_{\omega\nu}\left(1+\varepsilon_{\omega\nu}^{2}\right) = \langle \omega_0 + \varepsilon_{\omega\nu}\nu_0 \,|\, H_{\omega_0} \,|\, \omega_0 + \varepsilon_{\omega\nu}\nu_0 \rangle$$
$$+ \langle \nu_0 - \varepsilon_{\omega\nu}\omega_0 \,|\, H_{\nu_0} \,|\, \nu_0 - \varepsilon_{\omega\nu}\omega_0 \rangle$$
$$+ \varepsilon_{\omega\nu} \langle \omega_0 \,|\, \Delta H_\omega - \Delta H_\nu \,|\, \nu_0 \rangle$$

Since $H_\nu = f_\nu h_\nu + a_{\nu\nu}\mathcal{J}_\nu + \sum_{i\neq\nu}\left(a_{i\nu}\mathcal{J}_i + b_{i\nu}\mathcal{K}_i\right)$:

$$H_{\nu_0} = f_\nu \left[h_0 + \sum_{i\neq[\text{CLOSED}]} \left(A_{i\nu}\mathcal{J}_{i_0} + B_{i\nu}\mathcal{K}_{i_0} \right) \right]$$

and

$$\Delta H_\nu = a_{\nu\nu}\Delta\mathcal{J}_\nu + a_{\omega\nu}\Delta\mathcal{J}_\omega + b_{\omega\nu}\Delta\mathcal{K}_\omega$$

Hence:

$$\langle \nu_0 \,|\, \Delta H_\omega - \Delta H_\nu \,|\, \omega_0 \rangle = \langle \nu_0 \,\big|\, (a_{\omega\omega} - a_{\omega\nu})\Delta\mathcal{J}_\omega + (a_{\nu\omega} - a_{\omega})\Delta\mathcal{J}_\nu$$
$$+ b_{\nu\omega}\left(\Delta\mathcal{K}_\nu - \Delta\mathcal{K}_\omega\right) \,|\, \omega_0 \rangle$$
$$= \varepsilon_{\omega\nu}\left[X\,\mathcal{J}_{\omega_0\nu_0} + Y\,\mathcal{K}_{\omega_0\nu_0} \right]$$

where:

$$X = f_\omega\left(A_{\nu\omega} - B_{\nu\omega}\right) - \tfrac{1}{2}\left(f_\omega A_{\omega\omega} + f_\nu A_{\nu\nu}\right)$$
$$Y = \tfrac{5}{2}\left(f_\omega A_{\omega\omega} + f_\nu A_{\nu\nu}\right) - 5 f_\omega A_{\nu\omega} - 3 f_\omega B_{\nu\omega}$$

Thus:

$$\epsilon_{\omega\nu}\left(1+\varepsilon_{\omega\nu}^{2}\right) = \langle \omega_0 \,|\, H_{\omega_0} \,|\, \omega_0 \rangle + \langle \nu_0 \,|\, H_{\nu_0} \,|\, \nu_0 \rangle + 2\varepsilon_{\omega\nu} \langle \nu_0 \,|\, H_{\omega_0} - H_{\nu_0} \,|\, \omega_0 \rangle$$
$$+ \varepsilon_{\omega\nu}^{2}\left[\langle \nu_0 \,|\, H_{\omega_0} \,|\, \nu_0 \rangle + \langle \omega_0 \,|\, H_{\nu_0} \,|\, \omega_0 \rangle + X\,\mathcal{J}_{\omega_0\nu_0} + Y\,\mathcal{K}_{\omega_0\nu_0} \right]$$

Requiring $\epsilon_{w\nu}$ to be stationary with respect to $\varepsilon_{w\nu}$ ($\partial\epsilon_{\omega\nu}/\partial\varepsilon_{\omega\nu} = 0$) gives:

$$(1) \qquad \varepsilon_{\omega\nu} = \frac{C_{\omega\nu}}{2D_{\omega\nu}} \pm \left[1 + \left(\frac{C_{\omega\nu}}{2D_{\omega\nu}} \right)^2 \right]^{1/2} \quad ; \quad D_{\omega\nu} = 0 \Rightarrow \varepsilon_{\omega\nu} = 0$$

where:

$$C_{\omega\nu} = \langle \nu_0 \,|\, H_{\omega_0} - H_{\nu_0} \,|\, \nu_0 \rangle - \langle \omega_0 \,|\, H_{\omega_0} - H_{\nu_0} \,|\, \omega_0 \rangle + X\,\mathcal{J}_{\omega_0\nu_0} + Y\,\mathcal{K}_{\omega_0\nu_0}$$
$$D_{\omega\nu} = \langle \nu_0 \,|\, H_{\omega_0} - H_{\nu_0} \,|\, \nu_0 \rangle$$

As is required, this equation satisfies the variational condition $(D_{w\nu} = 0 = \mathcal{E}_{w\nu})$. Since $\epsilon_{w\nu}$ is independent of $\mathcal{E}_{w\nu}$ if ϕ_w and ϕ_ν are in the same shell $(H_w = H_\nu)$, such coefficients can always be taken to be zero. This, of course, simply reflects the fact that the total energy is invariant with respect to mixing between orbitals in the same shell. Since (1) is valid only for the root corresponding to $|\mathcal{E}_{w\nu}'| < 1$ (least change), this is the root normally selected. Whenever this root does not differ in sign from $D_{w\nu}$, it is indicative that convergence is toward high-energy orbitals. Hence, if lowest-energy orbitals are desired, the root which differs in sign from $D_{w\nu}$ may be more appropriate even if it corresponds to $|\mathcal{E}_{w\nu}| > 1$.

In theory, these 'rotations' should be performed sequentially, using updated orbitals based upon the results of the preceding rotations. However, this is not practical since new $\mathcal{J}$ and $\mathcal{K}$ or $\mathcal{h}$ matrices would have to be calculated after each rotation (simple transformations such as $\langle w_\circ | \mathcal{J}_{\nu_\circ} | \nu_\circ \rangle \Rightarrow \langle w | \mathcal{J}_{\nu_\circ} | \nu \rangle$ are insufficient). Instead, the rotations are performed independently. That is, the same set of original orbitals is used to calculate each rotation coefficient. Thus, while each coefficient is obtained quadratically, this procedure can approach an overall linearly convergent limit. This is compounded by the fact that the new orbitals defined by all of these coefficients are generally nonorthogonal. These nonorthogonalities could be removed by (arbitrary) Schmidt orthogonalization.

However, a more logical way of obtaining orthogonal orbitals is to apply the rotations defined by these coefficients sequentially to the original orbitals according to increasing coefficient magnitude. In doing so, high-order terms are kept to a minimum since they depend upon the smaller coefficients. Moreover, this approximates, as closely as possible, vigorous sequential rotations since if $\varepsilon_{w\nu}$ is small, subsequent rotation coefficients should be almost the same with or without orbital updating. However, if $\varepsilon_{w\nu}$ is large, this need not be the case.

Procedure:

The Coefficients:

$$C'_{\omega_0\nu_0} = \langle \omega_0 | H_{\nu_0} | \omega_0 \rangle + \langle \nu_0 | H_{\omega_0} | \nu_0 \rangle + x\,\mathcal{J}_{\omega_0\nu_0} + y\,\mathcal{K}_{\omega_0\nu_0}$$
$$D_{\omega_0\nu_0} = \langle \omega_0 | H_{\omega_0} - H_{\nu_0} | \nu_0 \rangle$$

for orbitals $\phi_W > \phi_\nu$ which are of the same symmetry but are in different shells are all calculated simultaneously from the orbital transformed h, $\mathcal{J}$, and $\mathcal{K}$ matrices stored on disc (one pass) using the $\{f, A, B\}$ hamiltonian coefficients. In addition, the quantities:

$$\epsilon_{\nu_0\nu_0} = \langle \nu_0 | H_{\nu_0} | \nu_0 \rangle$$

are determined for all orbitals. At this point, the current electronic energy is evaluated after first calculating the 1-electron energies

$$h_{\nu_0\nu_0} = \langle \nu_0 | h | \nu_0 \rangle$$

from the primitive 1-electron integrals stored on disc:

$$\underline{E = \sum_i \left[f_i h_{i_0 i_0} + \epsilon_{i_0 i_0} \right]}$$

Working with one symmetry type at a time, the rotation coefficients are found using (1) and the desired root selection criteria, where:

$$C_{\omega_0\nu_0} = C'_{\omega_0\nu_0} - \epsilon_{\omega_0\omega_0} - \epsilon_{\nu_0\nu_0}$$

The rotations defined by these coefficients are then performed sequentially according to increasing coefficient magnitude on an initial unit matrix. The resulting orthonormal orbital transformation matrix is then used to revise the appropriate columns of the MO transformation matrix. In addition, the change in each orbital and the total change in all orbitals (SQCDF) is evaluated.

Once a complete set of new orbitals has been so determined, control is passed to the next step (OCBSE) without generating new primitive $\mathscr{h}$, $\mathscr{J}$, and $\mathscr{K}$ matrices.

F. OCBSE Orbital Optimization

If only orbital ϕ_ν is allowed to change, the variational condition is:

$$0 = < \delta_\nu \mid H_\nu \mid \phi_\nu > \qquad (1)$$

where the variation δ_ν is orthogonal to all the orbitals and:

$$\begin{aligned} H_\nu &= f_\nu h + a_{\nu\nu} \mathcal{J}_\nu + \sum_{i \neq \nu} [a_{i\nu} \mathcal{J}_i + b_{i\nu} \mathcal{K}_i] \\ &= f_\nu [h + \sum_{i \neq \text{closed}} (A_{i\nu} \mathcal{J}_i + B_{i\nu} \mathcal{K}_i)] \\ &= f_\nu H'_\nu \end{aligned}$$

Therefore, the linearly convergent solution for ϕ_ν is obtained by solving:[3]

$$\epsilon_\nu = \langle \phi_\nu | H'_{\nu_0} | \phi_\nu \rangle / \langle \phi_\nu | \phi_\nu \rangle$$

where H'_{ν_0} is constructed using the current orbitals $\{\phi_0\}$. Letting:

$$\phi_\nu = C_0 \phi_{\nu_0} + \sum_i C_i \chi_i$$

where $\{\chi\}$ are the NV virtuals (functions orthogonal to the current orbitals) having the same symmetry as ϕ_ν. Hence:

$$\epsilon_\nu = \sum_{i,j=0} C_i C_j \mathcal{H}_{ij} / \sum_{i=0} C_i^2$$

where:

$$\begin{aligned} \mathcal{H}_{00} &= \langle \phi_{\nu_0} | H'_{\nu_0} | \phi_{\nu_0} \rangle \\ \mathcal{H}_{0i} &= \langle \phi_{\nu_0} | H'_{\nu_0} | \chi_i \rangle = \mathcal{H}_{i0} \\ \mathcal{H}_{ij} &= \langle \chi_i | H'_{\nu_0} | \chi_j \rangle \end{aligned}$$

Thus, ϕ_ν is obtained by solving (in matrix notation):

$$\underline{H}\,\underline{C} = \underline{\epsilon}\,\underline{C} \qquad (2)$$

This equation, of course, satisfies the variational condition (1).

If several orbitals have the same hamiltonian (are in the same shell), all such orbitals having the same symmetry can be obtained simultaneously in a linearly convergent manner by solving (2) in which the orbital expansion includes the current guesses for all these orbitals in addition to the virtuals. Each new orbital corresponds to a different (orthogonal) root of (2).

The choice of which root (s) corresponds to the orbital (s) can be made on the basis of overlap with the initial orbital(s) (least change) or on the basis of eigenvalue (lowest energy). If lowest-energy orbitals are desired, selection by eigenvalue is preferable. When conveying toward high-energy orbitals, selection by overlap is required.

The shells are optimized sequentially, using the new orbitals defined from optimization of preceding shells. This procedure, whereby orbitals are always optimized in the field of current orbitals, differs from the usual approach in which original orbitals are used in all hamiltonians. This method of 'continual updating' is no more time consuming and, in general, has been found to lead to more rapid overall convergence.

Procedure:

The orbitals are optimized a shell at a time in the following manner. The primitive hamiltonian matrix (H) is constructed from the packed primitive h, $\mathcal{J}$ and $\mathcal{K}$ matrices stored on disc using that shell's $\{A, B\}$ coefficients. Initially, these matrices are on a single disc unit (JUNIT) with the h matrix in the last record. Each other record contains the number and the $\mathcal{J}$ and $\mathcal{K}$ matrices of a particular orbital. For subsequent shells, revised $\mathcal{J}$ and $\mathcal{K}$ matrices (if any), which are to be used in place of the originals, are found on another disc unit (IUNIT) in records of the same form. Once completed, the hamiltonian matrix is transformed to MO basis for each symmetry type containing an orbital of that shell. For each symmetry type the basis consists of the current orbitals of the shell plus the virtuals (i.e. orbitals not of this shell are excluded). Each symmetry block is separately diagonalized to give the desired number of roots. This can be either the number of orbitals or the rank of the matrix. If the new orbitals are to be taken to be the lowest-energy eigenvectors, only the former number of roots are really needed. New virtuals are then rapidly obtained by simply Schmidt orthogonalizing to the new orbitals the NV original MOs having minimal overlap with them.

If the new orbitals are to be taken to correspond to the eigenvectors having maximal overlap with the original orbitals, all roots are obtained. The resulting eigenvector and eigenvalue arrays are then recorded with orbitals coming first. If desired, a 2-point extropolation of these results is performed (MO changes essentially cut in half). The total and relative (energy dependent) changes in each orbital are then determined and the SQCDF for the iteration is updated. Finally, the MO transformation matrix is revised for these new MOs.

Once the new orbitals of a shell have been determined, new primitive matrices associated with these orbitals are generated, if necessary, before continuing. After new closed-shell orbitals are obtained, a new primitive h matrix is always generated to replace the original on JUNIT. For other shells, new $\mathcal{J}$ and $\mathcal{K}$ matrices for an orbital are calculated only if the total change in the orbital since last matrix revision exceeds some (small) value. These new $\mathcal{J}$ and $\mathcal{K}$ matrices are packed and cumulatively stored on disc (IUNIT) in the usual form. When constructing subsequent hamiltonian matrices, these new matrices are used rather than the corresponding originals on JUNIT.

After a complete set of new orbitals has been obtained, $\mathcal{J}$ and $\mathcal{K}$ matrices for orbitals for which new matrices were not generated are transferred from JUNIT to IUNIT along with the current h matrix (last record). These matrices are then transformed over orbitals in symmetry blocks and stored on JUNIT in preparation for the next iteration (i.e. Hamiltonian Optimization)

G. Output

The iterative cycle is terminated after OCBSE whenever any one of the following is true:

1) Convergence is achieved
2) The maximum number of iterations has been performed
3) Insufficient compute time remains for another iteration.

Complete GVBTWO output consists of:

1) The case title
2) Energy summary
    a) electronic energy
    b) input nuclear repulsion energy
    c) total energy
    d) kinetic energy
    e) virial ratio (V/2T)
3) The energy and SQCDF for each iteration
4) The orbitals:
    a) primitive basis function coefficients
    b) symmetry type
    c) shell number
    d) orbital energy
    e) occupation number
5) The final MO transformation matrix
6) For each PPGVB pair:
    a) pair coefficients
    b) the nonorthogonal singlet coupled orbitals
    c) ionization potential
    d) energy splitting
    e) triplet and singlet excitation energies

III. CONCLUSION

Computational details for the GVBTWO SCF program have been presented. This program is capable of solving self-consistently for the orbitals of any wavefunction (actual or contrived) whose energy expression involves only diagonal 1-electron integrals and the usual coulomb and exchange 2-electron integrals. The program is specifically adapted to solving for PPGVB wavefunctions through provisions for optimizing the pair coefficients involved in such wavefunctions as well. This program has extended the practical limits of such calculations to include relatively large systems as it is more versatile and very much more rapid than its predecessors.

APPENDIX 1

Use of Preprocessed Integrals in SCF Calculations

Preprocessing 2-electron integrals to form the pairs:

$$VK(IJKL) = \frac{1}{4}\left[(IK|JL) + (IL|JK)\right]$$

$$VJ(IJKL) = (IJ|KL) - VK(IJKL)$$

$$IJKL = IJ*(IJ-1)/2 + KL \qquad IJ \geq KL$$

$$IJ = I*(I-1)/2 + J \qquad I \geq J$$

has been shown by Raffenetti[1] to allow for rapid generation of primitive matrices of the form:

$$\langle I \,|\, \frac{a}{2}(J_m - \frac{1}{2}K_m) + \frac{b}{4}K_m \,|\, J\rangle = \sum_{KL=1}^{IJ} D^m_{KL} * P(IJKL) + \sum_{IJ>KL} D^m_{IJ} * P(IJKL)$$

$$P(IJKL) = a \cdot VJ(IJKL) + b \cdot VK(IJKL)$$

$$D^m_{IJ} = C_{Im} * C_{Jm} / (1 + \delta_{I,J})$$

with C_{Im} being the coefficient of basis function I in orbital m.

Since generation of such matrices is the most time consuming step in most SCF calculations, they must be constructed as efficiently as possible from these pairs. This is accomplished in two ways. First of all, all pairs which aren't needed for a particular calculation are purged from the list at the onset. Secondly, the edited list is stored in a way that minimizes decision making during matrix construction and allows for optimization with respect to zero density matrix (D) elements.

(1) Deletion of Unneeded Pairs

The primitive matrices are invariably transformed to an MO basis. For example, in the GVB program these matrices (or primitive Hamiltonian matrices constructed from them) are transformed to an MO basis in symmetry blocks. Therefore, if basis functions I and J are never simultaneously used in any occupied symmetry type, the IJth element of all primitive matrices is never required. Hence, there is no need to calculate these elements.

Moreover, the corresponding density matrix elements are always zero. Consequently, a pair is not needed if either its row number (IJ) or its column number (KL) corresponds to two basis functions not appearing simultaneously in any symmetry type. In other programs, such as SOGVB, analogous deletion criteria prevail. Thus, before beginning the iterative cycle, the input pair list is purged of any pairs not needed for the particular calculation at hand.

(2) Optimizing Matrix Construction

The input pair list is required to be in packed canonical IJKL order. This order is of course unaffected by deletion of unneeded pairs with subsequent repacking. Having the pairs arranged in this manner allows matrices to be constructed with partial optimization for zero density matrix elements and decreases the number of array element lookups. In order to keep decision making to a minimum, as the input list is edited, it is stored on disc in records of the form

IST, LAST, VJ, VK

VJ and VK are REAL*8 arrays. IST is the occupied row number of the first pair in the record and LAST is the occupied row number of the last pair. The actual row numbers (IJ) of the occupied rows are stored in an array (IIJ) held in core. Packed into the lower two bytes of the first VJ element of a row in a record is the number of the last pair of the row in that record. The column number (KL) of a pair is packed into the lower two bytes of the VK element. Finally the number of such records is recorded (NBLK). As the following algorithm demonstrates, this formulation allows for very efficient matrix generation:

```
      SUBROUTINE JKMTRX(DJ,DK,D,TORB,IIJ)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION TORB(1),D(1),DJ(1),DK(1),VJK(1281)
      INTEGER*2 JN(4),KN(4),KSTOP,KL,IIJ(1)
      COMMON/INTS/IST,LAST,VJ(640),VK(640)
      COMMON/ISTUF/EE,SQCOF,EOLD,SKIP,ZERO,NORB,NBF,NBLK,MXSIZE
      EQUIVALENCE (IST,VJK(1))
      EQUIVALENCE (JN(1),V1),(KSTOP,JN(4)),(KN(1),V2),(KL,KN(4))
C
C     GENERATE A (J-K/2)/2 & A K/4 MATRIX OVER TORB WITH DIAGS 1/2
C
      DO 10 I=1,MXSIZE
      DJ(I)=0.0D 00
      DK(I)=0.0D 00
   10 D(I)=0.0D 00
      IJ=0
      DO 20 I=1,NBF
      DIJ=TORB(I)
      IF( DIJ .EQ. 0.0D 00 ) GO TO 20
      TORB(I)=DIJ*0.5D 00
      DO 30 K=1,I
   30 D(IJ+K)=DIJ*TORB(K)
      TORB(I)=DIJ
   20 IJ=IJ+I
C
      REWIND 11
      DO 200 KBLK=1,NBLK
      READ(11) VJK
      KSTOP=0
      DO 100 II=IST,LAST
      IJ=IIJ(II)
      DIJ=D(IJ)
      DJIJ=DJ(IJ)
      DKIJ=DK(IJ)
      KST=KSTOP+1
      V1=VJ(KST)
      IF( DIJ .EQ. 0.0D 00 ) GO TO 5
      DO 2 K=KST,KSTOP
      V2=VK(K)
      DKL=D(KL)
      DKIJ=DKIJ+V2*DKL
      DK(KL)=DK(KL)+V2*DIJ
      VT=VJ(K)
      DJIJ=DJIJ+VT*DKL
    2 DJ(KL)=DJ(KL)+VT*DIJ
      GO TO 101
    5 DO 3 K=KST,KSTOP
      V2=VK(K)
      DKL=D(KL)
      DKIJ=DKIJ+V2*DKL
    3 DJIJ=DJIJ+VJ(K)*DKL
```

```
  101 DJ(IJ)=DJIJ
  100 DK(IJ)=DKIJ
  200 CONTINUE
C
      IJ=0

      DO 400 I=1,NBF
      IJ=IJ+I
      DJ(IJ)=DJ(IJ)*0.5D 00
  400 DK(IJ)=DK(IJ)*0.5D 00
      RETURN
      END
```

APPENDIX 2

POLYPAIR Integral Preprocessing

The computing time required for many SCF calculations can be significantly reduced if the primitive basis 2-electron integrals are first preprocessed to form the pairs:

$$VK(IJKL) = \frac{1}{4}\left[(IK|JL) + (IL|JK) \right]$$

$$VJ(IJKL) = (IJ|KL) - VK(IJKL)$$

$$IJKL = IJ * (IJ-1)/2 + KL \qquad IJ \geqslant KL$$

$$IJ = I * (I-1)/2 + J \qquad I \geqslant J$$

where (I J|K L) is a 2-electron integral written in (11|22) form. Using these quantities, primitive coulomb-and exchange-type matrices can be generated much more rapidly than is possible using raw integrals. However, if preprocessing requires an inordinate amount of compute time or IO operations, overall savings may not be significant. Therefore, it is imperative that these pairs be generated as efficiently as possible.

Two-electron integrals are most efficiently generated in a random fashion. However, preprocessing of a random list is practical only if random access peripheral storage devices are available. This is because central storage must be partitioned so as to permit construction of both elements of a pair at the same time (so they can be outputed together) and three integrals must usually be simultaneously available in order to construct any one pair. If only sequential access peripheral storage is available, as in the case for the IBM 370/155 system, preprocessing of a random integral list must be done using highly inefficient multi-pass techniques

(DEFINE FILE is just as bad). Hence, overall savings are greatly decreased.

However, if the input list is ordered with all nonzero integrals from (I1|11) to (II|II) grouped together, preprocessing can be performed quite rapidly even without random access devices. This is because all pairs I 111 to II II involve only this relatively small number of integrals.

A POLYIJLK list in which the 2-electron integrals are in packed IJLK order (zeroed integrals deleted) fulfills this requirement. Thus, by using POLYIJLK integral input, preprocessing can be accomplished quite efficiently. Of course, formation of POLYIJLK involves sorting of the initial random (POLYATOM) 2-electron integral list. However this simple sorting can be done fairly rapidly via multi-pass techniques. Moreover, POLYIJLK is required input for our integral transformation program (FYBTRAN). Since integral transformations are invariably required before performing inevitable CI calculations on SCF results, this conversion would normally be done anyway.

The POLYPAIR program preprocesses an IJLK integral input list in the following manner. Integrals (I1|11) to (II|II) are preprocessed at the same time. As this group is read in, the integrals are stored on disc (IUNIT) along with their KL numbers. A separate array records the number of integrals having the same row (IJ) number (these are contiguous). The VK element indices associated with each integral are then calculated. As this is done, the first M (central storage allocation) VK x 4 elements are constructed from the appropriate integrals. Those integrals needed to construct elements N x M + 1 to (N + 1) M are gathered according to N value (category number) and are written on disc (JUNIT) along with the corresponding index numbers (if an integral is used twice in a given VK element, it is doubled before storing under that VK index) every time LTH integrals for a given category have been accumulated. The category number for this group is also written on the record and the number of records so far written for that category is noted. Once all these integrals have been so processed, the in core VK x 4 elements are scanned one row (IJ number) at a time and the nonzero elements are divided by -4. From these and the original integrals for this row read in from IUNIT, the VJ elements for the row are calculated. The nonzero pairs (VK $\neq$ 0 and/or VJ $\neq$ 0) are gathered and written on the output unit everytime KTH pairs are accumulated. Packed into the lower two bytes of the VK element is the KL number for the pair. A separate array records the number of pairs in a given row. Once these VK x 4 elements have been exhausted, the next group is constructed from those integrals stored on KUNIT belonging to the first category (N = 1). Since each record on KUNIT is labeled by category and since the number of records in each category is known, this retrieval can be accomplished with minimal effort. This process is then repeated until all categories have been processed and all pairs for this group of input integrals have been calculated.

Description of POLYPAIR Integral List

```
REAL*8 V(500), VJ(500), VK(500), REPNRG
INTEGER ITITLE (18)
INTEGER*2 IA(500), IB(500), IC(500), ID(500), IMU(500), IF(500),
                              NIJ(N*(N+1)/2)
                                              where N = number of basis functions
```

```
ITITLE (title with ITITLE(18) = 'JKPR')
Next three records either contain the usual basis set information or are dummy.
REPNRG, . . . . (nuclear repulsion energy and more basis set information)
Overlap integrals:
1  NINT, LAST, IA, IB, V
   IF(LAST.EQ.0) Go to 1
Kinetic energy integrals:
2  NINT, LAST, IA, IB, V
   IF(LAST.EQ.0) Go to 2
Potential energy integrals:
3  NINT, LAST, IA, IB, V
   IF(LAST.EQ.0) Go to 3
Pair List:
4  LAST, VJ, VK
   IF(LAST.EQ.0) Go to 4
NIJ
```

NINT = number of integrals in a given record.

(LAST.NE.0) ⇒ signals end of that particular list.

IA, IB = 1-electron integral indexing numbers.

VJ and VK are in packed [IJ] ⩾ [KL] order with [KL] packed into the lower two bytes of VK. NIJ ([IJ]) + 1 is the number of pairs having the same [IJ] number.

```
2-electron integral IJLK list (Optional):
5  NINT, LAST, IA, IB, IC, ID, IMU, IF, V
   IF(LAST.EQ.0) Go to 5.
                        These records are the same as in POLYIJLK
```

References

1) W. H. Hunt, P. J. Hay and W. A. Goddard III, *J. Chem. Phys.* **57**, 738 (1972).

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PART FOUR

The Strongly Orthogonal Generalized Valence-Bond Wavefunction

Abstract

The Generalized Valence-Bond (GVB) wavefunction has had considerable success in describing chemical reactions and molecular structure. Unfortunately, this method can only be applied to systems involving a few electrons. The Perfect-Pairing approximation to GVB (PPGVB) greatly simplifies the situation and is found to adequately describe the low-lying states of many molecules. However, in describing chemical reactions the restrictions of PPGVB are quite serious. The Strongly Orthogonal approximation (SOGVB) described here overcomes this problem by allowing the orbitals to recouple while still retaining the simplifying orbital restrictions of PPGVB. This intermediate method correctly describes many chemical reactions and is practical for treating relatively large systems.

I. INTRODUCTION

In recent years several methods have been developed which solve self-consistently for the orbitals of correlated wavefunctions. The primary objective of some procedures, such as MC-SCF, is to obtain orbitals that allow for construction of high quality, yet reasonably sized, Configuration Interaction wavefunctions. The aim of other approaches is to obtain wavefunctions that can be physically interpreted. From these, concepts explaining the nature of chemical bonding and the mechanisms of reactions can be developed. This is the objective of the Generalized Valence-Bond (GVB) Method.[1] The GVB wavefunction is an orbital product wavefunction in which each electron is allowed to have a different orbital. All orbitals are solved for self-consistently with no restrictions placed upon them or upon the coupling between them:

$$\Psi = \mathcal{A}\left[\prod_{i}^{N} \phi_i(i)\right] X_{(1,2\cdots N)} \qquad (1)$$

where X is the optimal spin function for the system and $\mathcal{A}$ is the antisymmetrizer (determinant operator). The wavefunction is taken to be an eigenstate of $\hat{S}^2$. As a result, X is required to be an eigenfunction of spin.

Unfortunately, this approach leads to an N! dependence upon the number of electrons and is impractical for large systems. However, it was found that in many instances the accuracy of the wavefunction was not significantly affected by placing simplifying restrictions on (1). This led to the Perfect-Pairing GVB (PPGVB) Method.[2] In this procedure, the spin function X is taken to be a fixed perfectly paired valence-bond function such as:

$$(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha),\ (\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)\alpha\alpha,\ \text{ETC}$$

In addition, only those two orbitals associated with an $(\alpha\beta - \beta\alpha)$ spin term are allowed to be nonorthogonal. Expressing the orbitals of each singlet pair in terms of natural orbitals leads to a total wavefunction that is a sum of closed-shell determinants and hence to very simple variational equations involving the same operators as in Hartree-Fock.

It was found that the restrictions of PPGVB are not significant for the ground and low-lying states of many molecules. However, it was found that the restriction placed upon the spin function X is particularly serious for describing reactions.[3] During a reaction, the spin-coupling (optimal form of X) changes significantly and is typically very different from a simple valence-bond coupling. A method intermediate between GVB and PPGVB will now be presented which overcomes this problem. In this approach, the orbitals are still grouped into nonorthogonal pairs (Strong Orthogonality). However, the coupling between the orbitals is optimized. That is, restrictions on X are relaxed. This method, denoted as SOGVB (SO for Strong Orthogonality) is found to lead to proper descriptions of reactions while retaining most of the computational simplifications of PPGVB.

II. DISCUSSION

A. THE GVB WAVEFUNCTION

The GVB wavefunction for N electrons can be written as an antisymmetrized product of a spatial function and a spin function

$$\Psi = \mathcal{A}\, \Phi_N X_{SN}$$

where: $\Phi_N = \prod_i^N \phi_i(i)$; $X_{SN} = \sum_j c_j \chi_j (1,2 \cdots N)$

$\mathcal{A}$ is the antisymmetrizer which guarantees that Pauli's Principle is obeyed. Φ_N is a product of N spatial orbitals $\{\phi\}$. X_{SN} is a linear combination of appropriate spin function (α, β) products $\{\chi\}$. Since we will be dealing with hamiltonians which are independent of spin, the wavefunction is required to be an eigenstate of $\hat{S}^2$. As a result, X_{SN} must satisfy

$$\hat{S}^2 X_{SN} = S(S+1) X_{SN}$$

With this one exception, no other restrictions are placed upon either the spatial orbitals or the spin function.

B. THE PPGVB WAVEFUNCTION

In the Perfect-Pairing approximation to GVB, restrictions are placed upon both the orbitals and the spin function. The orbitals are partitioned into singlet pairs whenever possible. That is, each such pair is required to be associated with an $(\alpha\beta-\beta\alpha)$ spin term:

$$\Psi = \mathcal{A}\left[\prod_{m}^{NP} \phi'_{m_1}\phi'_{m_2}(\alpha\beta-\beta\alpha)\right]\Phi\alpha\alpha\cdots$$

where Φ pertains to those remaining orbitals which cannot be singlet paired. The orbitals within a given pair can be nonorthogonal. This constraint whereby all orbitals, other than the two within a given pair, are orthogonal will be referred to as the Strong Orthogonality Restriction.

Expressing these pairs in terms of their orthogonal natural orbitals:

$$\phi'_{m_1} = N\left[\phi_{m_1} + \lambda_m \phi_{m_2}\right] \quad ; \quad \phi'_{m_2} = N\left[\phi_{m_1} - \lambda_m \phi_{m_2}\right]$$

where $\langle \phi_{m_1} | \phi_{m_2} \rangle = 0$, allows Ψ to be written in terms of orthogonal orbitals:

$$\Psi = \mathcal{A}\left[\prod_{m}^{NP} \left(\phi_{m_1}^2 - \lambda_m^2 \phi_{m_2}^2\right)\alpha\beta\right]\Phi\alpha\alpha\cdots$$

where the pair coefficients $\{\lambda\}$ are adjustable parameters. Setting all these coefficients to zero leads to the closed-shell Hartree-Fock wavefunction.

Upon expansion, Ψ consists of a set of determinant configurations involving orthonormal orbitals. Since these determinants differ by excitation of doubly occupied orbitals, the energy can be written in terms of diagonal 1-electron integrals and the usual coulomb and exchange 2-electron integrals:

$$E = 2\sum_{i}^{N} f_i h_{ii} + \sum_{i,j}^{N} \left[a_{ij} J_{ij} + b_{ij} K_{ij} \right]$$

where:

$$h_{ii} = \langle \phi_i | h | \phi_j \rangle = \langle \phi_i | \mathcal{T} + \mathcal{V}_n | \phi_j \rangle$$

$$J_{ij} = \langle \phi_i | J_j | \phi_i \rangle = \langle \phi_i \phi_j | \tfrac{1}{r_{12}} | \phi_i \phi_j \rangle = (\phi_i \phi_i | \phi_j \phi_j)$$

$$K_{ij} = \langle \phi_i | K_j | \phi_i \rangle = \langle \phi_i \phi_j | \tfrac{1}{r_{12}} | \phi_j \phi_i \rangle = (\phi_i \phi_j | \phi_i \phi_j)$$

$$\left.\begin{aligned} f_{m_1} &= a_{m_1 m_1} = 1/(1+\lambda_m^4) \\ f_{m_2} &= a_{m_2 m_2} = \lambda_m^4/(1+\lambda_m^4) \\ b_{m_1 m_2} &= -\lambda_m^2/(1+\lambda_m^4) \end{aligned}\right. \qquad m \leqslant NP$$

$$b_{m_1 m_1} = b_{m_2 m_2} = a_{m_1 m_2} = 0$$

$$\left.\begin{aligned} f_i &= 1/2 \\ a_{ii} &= b_{ii} = 0 \end{aligned}\right\} \quad i > 2*NP$$

$$\left.\begin{aligned} a_{ij} &= 2 f_i f_j \\ b_{ij} &= -f_i f_j \end{aligned}\right\} \quad \phi_i,\ \phi_j \text{ not in same pair}$$

$$a_{ij} = a_{ji}$$

$$b_{ij} = b_{ji}$$

The one-particle hamiltonians obtained by applying the variational principle therefore only involve the 1-electron operator h and the coulomb and exchange operators:

$$H_i = f_i h + \sum_{j}^{N} \left[a_{ji} J_j + b_{ji} K_j \right] \qquad i = 1, N$$

These equations are of the same form as for a general open-shell Hartree-Fock wavefunction. The only difference is that the coefficients $\{f, a, b\}$ are functions of the pair coefficients whereas in Hartree-Fock they are fixed. Since these coefficients can easily be found by diagonalizing trivial 2 x 2 matrices, it is almost as easy to calculate a PPGVB wavefunction as it is to obtain a Hartree-Fock solution.[4] Since all closed-shell orbitals have the same hamiltonian, calculation of PPGVB wavefunction is more time consuming as there are more hamiltonians to construct and diagonalize than in Hartree-Fock.

Since PPGVB removes the Double Occupancy Restriction of Hartree-Fock, it allows the singlet paired orbitals to correlate. This not only leads to better energies, but also gives a more satisfying orbital description as is evidenced by its ability to allow for bond dissociation. In Hartree-Fock this is generally not possible since a chemical bond must be described by a single doubly occupied orbital.

C. Spin Coupling

In PPGVB the spin function X_{SN} is fixed so as to allow for the maximum number of permissible singlet pairs. However, for systems not in maximum spin multiplicity which contain more than two electrons, this function is multidimensional. That is, there are several linearly independent spin eigenfunctions (SEFs) from which to choose. For example, a six electron singlet has five such SEFs. In instances where there are clearly defined chemical bonds, the optimal spin coupling usually corresponds closely to the PPGVB spin function. However, when this is not the case, X_{SN} must be allowed to be a general linear combination of these SEFs.

A convenient set of orthogonal SEFs for N electrons can be generated from the appropriate N-1 electron functions using two simple recursion relationships:

$$\text{If } S_N > S_{N-1} : \quad X_N = X_{N-1}\alpha$$

$$\text{If } S_N < S_{N-1} : \quad X_N = 2S_{N-1}X_{N-1}\beta - [\hat{S}^-_{N-1} X_{N-1}]\alpha$$

where X_{n-1} is the parent N-1 electron SEF(highest S_z projection) whose multiplicity number is S_{n-1} and $\hat{S}^-_{n-1}$ is the spin lowering operator for N-1 electrons.

In discussing spin eigenfunctions it is useful to use a pictorial representation illustrating the specific spin-coupling involved. To illustrate this, consider generation of the three electron doublet SEFs. The spins of two electrons can be coupled into either a singlet ($\alpha\beta - \beta\alpha$) or a triplet ($\alpha\alpha$, $\alpha\beta+\beta\alpha$, $\beta\beta$). Adopting the convention that two horizontally contiguous electron numbers inscribed within a rectangle implies a singlet (antisymmetric) spin couple and that vertically contiguous electron numbers inscribed within a rectangle signifies multiplet (symmetric) spin coupling, these functions can be represented as:

$$\boxed{1\ 2} = \frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha) \qquad \boxed{\begin{matrix}1\\2\end{matrix}} = \begin{cases}\alpha\alpha\\ \frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)\\ \beta\beta\end{cases}$$

From these, two 3-electron doublet SEFs are obtained:

$$\boxed{1\ 2} \rightarrow \begin{array}{l}\boxed{1\ 2}\\ \boxed{3}\end{array} \qquad \boxed{\begin{matrix}1\\2\end{matrix}} \rightarrow \boxed{\begin{matrix}1\\2\end{matrix}}\boxed{3}$$

$$G_1 = \frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)\alpha \qquad G_2 = \frac{1}{\sqrt{6}}(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)$$

As the diagrams imply, the G_1 function preserves the (1,2) singlet couple and the G_2 function preserves the (1,2) triplet couple.

As the number of electrons increases, the actual SEFs soon become too cumbersome to write down. However, the representations, which convey all the pertinent information about the functions, are easy to construct using the following rules:

1) If the multiplicity increases, an electron number is added to the bottom of the left-hand column of the appropriate N-1 electron diagrams.

2) If the multiplicity decreases, an electron number is added to the bottom of the right-hand column of the appropriate N-1 electron diagrams.

3) Rectangles are extended to inscribe all vertically or horizontally contiguous numbers.

(A listing of all the standard SEFs and their corresponding diagrams for up through six electrons is given in Appendix 2 of Part Two, this thesis)

These same diagrams can also be used to represent orbital product wavefunctions having standard spin functions by simply placing orbitals in the desired positions. Because of Pauli's Principle, there is a direct relationship between the spin coupling and spatial coupling of the orbitals. As a consequence, the resulting spin coupling schemes (SECs) can be interpreted as follows:

1) The two orbitals inscribed within the same horizontal rectangle are singlet coupled. That is, they are antisymmetrically spin coupled and symmetrically spatially coupled so that:

$$\boxed{\phi_i \phi_j} = \boxed{\phi_j \phi_i}$$

2) Orbitals inscribed within the same vertical rectangle are multiplet coupled. That is, they are symmetrically spin coupled and antisymmetrically spatially coupled so that:

$$\boxed{\begin{array}{c} \vdots \\ \phi_i \\ \vdots \\ \phi_j \end{array}} = - \boxed{\begin{array}{c} \vdots \\ \phi_j \\ \vdots \\ \phi_i \end{array}}$$

3) The orbitals occupying the first N-1 positions (of the SEF diagram) are coupled just as in the parent N-1 electron wavefunction. For example, the coupling between orbitals ϕ_i, ϕ_j and ϕ_k is the same in the two wavefunctions:

$$\begin{array}{|c|c|} \hline \phi_i & \phi_k \\ \cline{2-2} \phi_j & \multicolumn{1}{c}{} \\ \cline{1-1} \phi_l & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} \quad \text{and} \quad \begin{array}{|c|c|} \hline \phi_i & \phi_k \\ \cline{2-2} \phi_j & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array}$$

Hence, the 3-electron doublet wavefunction in which orbitals ϕ_1 and ϕ_2 are singlet coupled is:

$$\begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 \\ \cline{1-1}\end{array} = \frac{1}{\sqrt{2}}\mathcal{A}\,\phi_1\phi_2\phi_3(\alpha\beta-\beta\alpha)\alpha = \frac{1}{\sqrt{2}}\mathcal{A}\,(\phi_1\phi_2+\phi_2\phi_1)\phi_3\,\alpha\beta\alpha$$

Notice that this is distinctly different from:

$$\begin{array}{|c|c|}\hline \phi_2 & \phi_3 \\ \hline \phi_1 \\ \cline{1-1}\end{array} = \frac{1}{\sqrt{2}}\mathcal{A}\,\phi_2\phi_3\phi_1(\alpha\beta-\beta\alpha)\alpha = \frac{1}{\sqrt{2}}\mathcal{A}\,\phi_1\phi_2\phi_3\,\alpha(\alpha\beta-\beta\alpha)$$

in which orbitals ϕ_2 and ϕ_3 are singlet coupled rather than ϕ_1 and ϕ_2.

Using these SECs, a GVB wavefunction can be written in a very concise form. For example, the 3-electron doublet wavefunction can be written as:

$$\Psi = \varepsilon_1 \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 \\ \cline{1-1}\end{array} + \varepsilon_2 \begin{array}{|c|c|}\hline \phi_1 & \phi_3 \\ \hline \phi_2 \\ \cline{1-1}\end{array}$$

While it is computationally convenient to express a GVB wavefunction in terms of the orthogonal SEFs and a specific orbital sequence (standard SECs) as above, any linearly independent set of SECs will do. In fact, it is often the case that alternative sets lead to simpler and more physical interpretations of systems under investigation. To illustrate this and show kinds of circumstances in which spin coupling optimization is important, a few examples will now be presented.

D. The $H_2 + D \rightleftarrows H + HD$ Reaction

Consider the localized orbital description of the H_2 + D exchange reaction shown in Fig. 1. Initially the system consists of a hydrogen molecule and a deuterium atom infinitely separated. Therefore, the initial wavefunction must have orbitals H and H' singlet coupled. However, at the end of the reaction, orbitals H and D must be singlet paired in order to describe the HD molecule. Hence, the coupling between the orbitals must change significantly during the reaction. The wavefunction which allows for the required orbital recoupling and at the same time shows clearly the extent to which either singlet pair is present is

$$\Psi = \epsilon_i \begin{array}{|c|c|}\hline H & H' \\ \hline D & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \epsilon_f \begin{array}{|c|c|}\hline H & D \\ \hline H' & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

where ϵ_i decreases from 1 to 0 while ϵ_f increases in magnitude from 0 to 1 as the reaction proceeds.

This analysis of the reaction in terms of localized orbitals has been given mainly for pedagogical reasons. In actual GVB calculations[5] the orbitals delocalize drastically as shown in Fig. 2 . Only ϕ_H remains localized at all times. $\phi_{H'}$ gradually delocalizes over the entire system and finally relocalizes about the deuterium center. Simultaneously, ϕ_D delocalizes so as to remain orthogonal to the other two orbitals and finally becomes associated with the exiting hydrogen center. Upon looking only at these orbitals it is tempting to think that spin-coupling optimization is of no qualitative importance and that the reaction can be adequately described by a PPGVB wavefunction in which a fixed singlet pair simply moves from one region of space to another via orbital optimization. That this is not the case is shown in Fig. 3 in which the dominant coupling coefficient is plotted along the reaction coordinate. Also shown are the localized orbital and PPGVB curves.

At large molecule-atom separations, where the orbitals are still localized, the coupling change is as expected for localized orbitals. At shorter distances, the curve deviates from the localized plot owing to orbital delocalization. After reaching a minimum at the saddle point, the coefficient increases as expected as the orbitals relocalize. Clearly, the qualitative description of the reaction still involves orbital recoupling rather than just a movement of a fixed singlet pair. Moreover, at the saddle point, where the orbitals are completely delocalized, the PPGVB energy is about 0.6 ev higher than the GVB energy of -1.624 hartrees. Optimizing the coupling between the PPGVB orbitals gives an energy which is still 0.2 ev higher since these orbitals are inappropriate for the correct coupling.

Hence, as this example has served to demonstrate, spin coupling optimization is usually required in order to correctly describe chemical reactions in even a qualitative sense. Additional examples of this will be given in a later section.

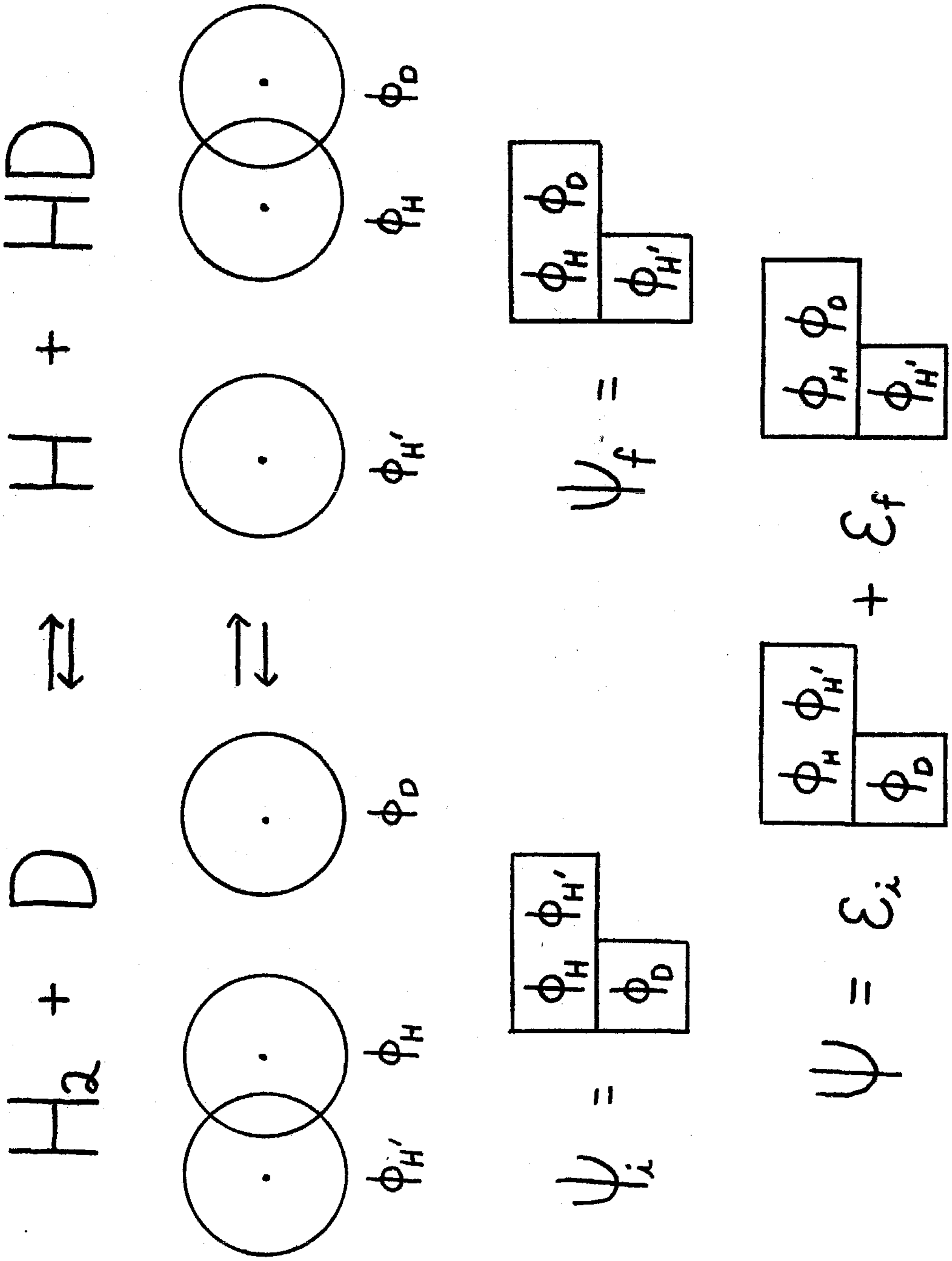

$H_2 + D \rightleftarrows H + HD$
$\phi_{H'}$
ϕ_H
ϕ_D
$\phi_{H'}$
ϕ_H
ϕ_D
$\psi_i =$
$\psi_f =$
$\psi = \varepsilon_i$
$+ \varepsilon_f$

FIG. 1

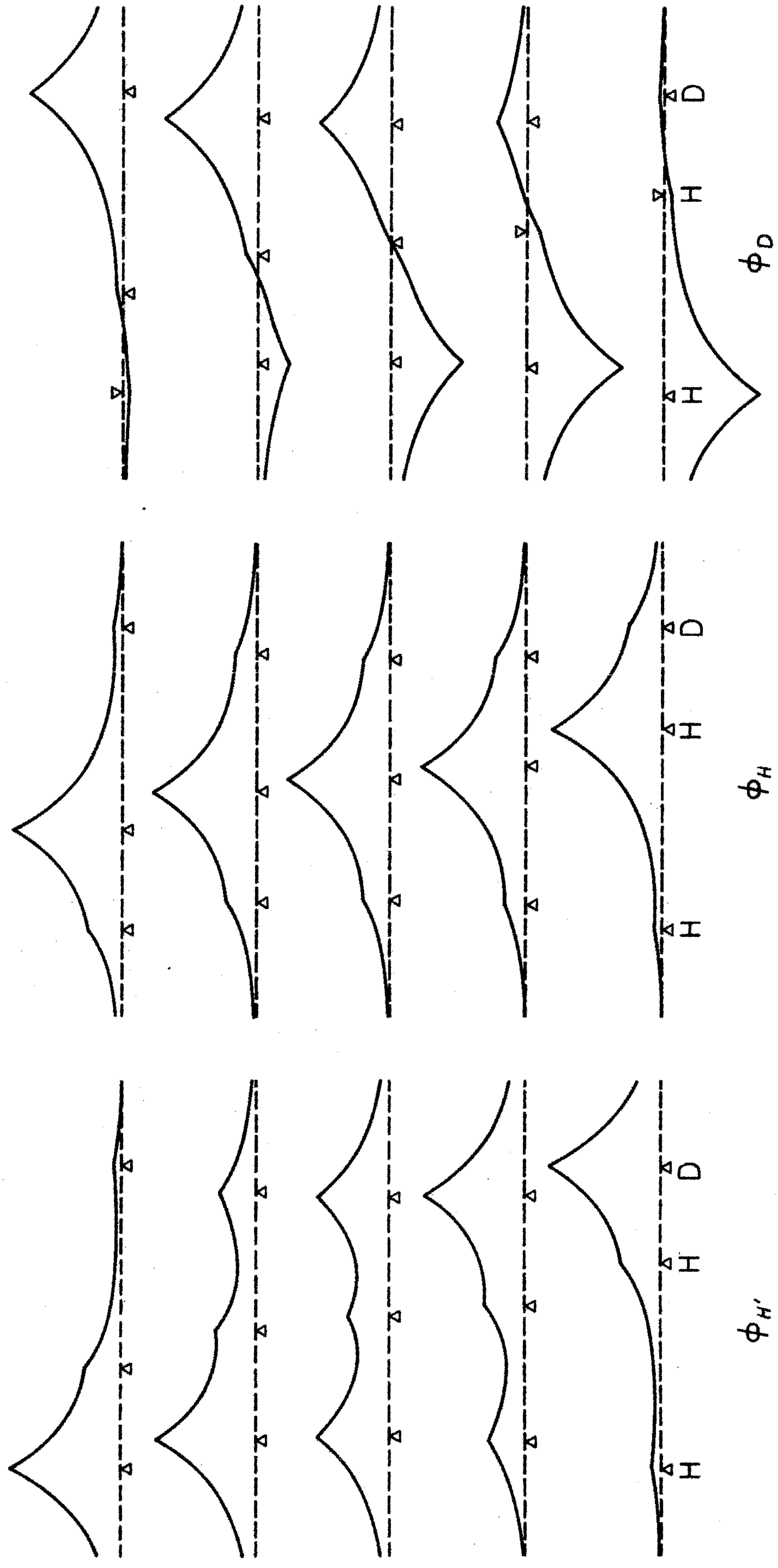


FIG. 2

H_2 + D SPIN COUPLING ϵ_{max} PLOT

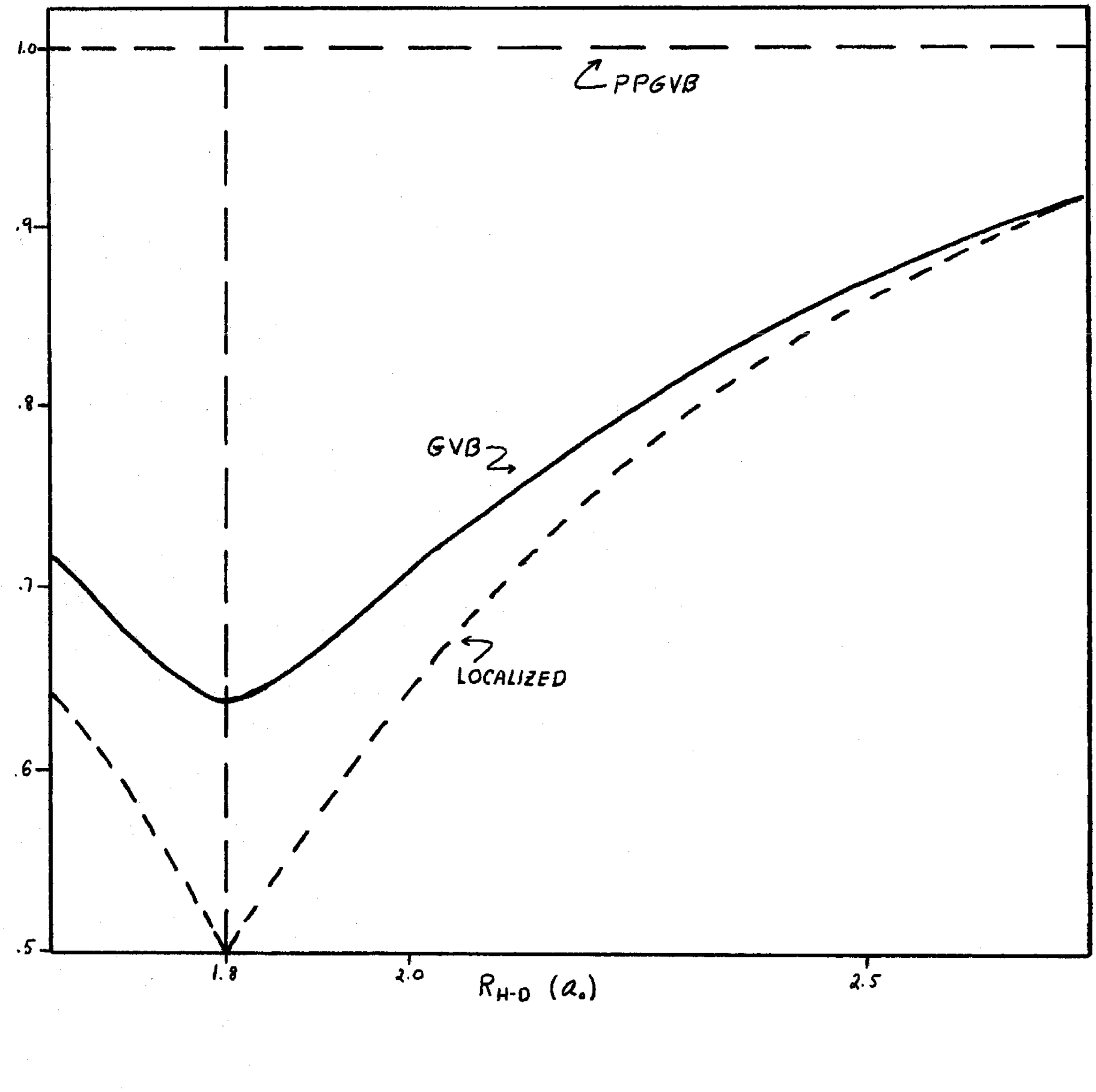
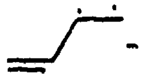


FIG. 3

E. Conjugated Systems

Spin coupling optimization can also be used to describe resonating systems. For example, the GVB wavefunction for the ground triplet state of trans-butadiene[6] quantifies this molecule in terms of the usual resonance structures:

$\Psi =$ 0.32  $- 0.36$  $+ 0.32$ 

where the double bond indicates which two essentially localized pi-orbitals are singlet paired. The energy of this wavefunction is over 0.3 ev lower than a Perfect-Pairing description. Likewise, the GVB wavefunction for the ground state of allyl radical can also be written in terms of the textbook resonance structures:[7]

$\Psi =$  $-$ 

III. THE SOGVB METHOD

As the above examples have illustrated, many chemically interesting systems require a more general spin coupling than is allowed for in PPGVB. In the SOGVB Method this situation is remedied by optimizing this coupling. However, the orbitals are still required to be strongly orthogonal just as in PPGVB. Thus, the first 2 x NP orbitals are grouped into nonorthogonal pairs:

$$\Psi = \mathcal{A} \left[\prod_{m}^{NP} \phi'_{m_1} \phi'_{m_2} \right] \Phi X_{SN}$$

$$X_{SN} = \sum_{i}^{f} \varepsilon_i X_i$$

where the spin function X_{SN} is now a general linear combination of the standard SEFs for N electrons having the desired spin multiplicity. Upon expressing the paired orbitals in terms of their orthogonal natural orbitals

$$\phi'_{m_1} = \eta \left(\phi_{m_1} + \lambda_m \phi_{m_2} \right) \; ; \; \phi'_{m_2} = \eta \left(\phi_{m_1} - \lambda_m \phi_{m_2} \right) \qquad \text{where } \langle \phi_{m_1} | \phi_{m_2} \rangle = 0$$

the wavefunction can be written in terms of orthonormal orbitals:

$$\Psi = \mathcal{A} \prod_{m}^{NP} \left[\phi_{m_1}^2 - \lambda_m^2 \phi_{m_2}^2 + \lambda_m \left(\phi_{m_2} \phi_{m_1} - \phi_{m_1} \phi_{m_2} \right) \right] \Phi X_{SN}$$

Pauli's Principle requires that the wavefunction be antisymmetric with respect to the interchange of any two electrons. Therefore, if two electrons occupy the same orbital (symmetric spatial coupling), they must be antisymmetrically (singlet) spin coupled. Likewise, if two orbitals are spatially antisymmetrically coupled ($\phi_1\phi_2 - \phi_2\phi_1$), they must be symmetrically (triplet) spin coupled. The antisymmetrizer, which embodies Pauli's Principle, projects away any disallowed combinations. Therefore, the SOGVB wavefunction can be written in terms of a set of SEF configurations involving orthonormal orbitals such that each configuration either contains only one orbital of a pair, with that orbital being doubly occupied or it contains both orbitals of a pair triplet coupled. The exact form of an SOGVB wavefunction written in this manner depends upon the number of electrons involved and the spin multiplicity. For example, the 3-electron doublet wavefunction is:

$$\Psi = A_1 \begin{array}{|c|c|}\hline \phi_{11} & \phi_{11} \\ \hline \phi_3 \\ \cline{1-1} \end{array} + A_2 \begin{array}{|c|c|}\hline \phi_{21} & \phi_{21} \\ \hline \phi_3 \\ \cline{1-1} \end{array} + A_3 \begin{array}{|c|c|}\hline \phi_{11} & \phi_3 \\ \hline \phi_{21} \\ \cline{1-1} \end{array}$$

whereas the 4-electron triplet wavefunction is:

$$\Psi = A_1 \begin{array}{|c|c|}\hline \phi_{11} & \phi_{11} \\ \hline \phi_{12} \\ \cline{1-1} \phi_{22} \\ \cline{1-1} \end{array} + A_2 \begin{array}{|c|c|}\hline \phi_{21} & \phi_{21} \\ \hline \phi_{12} \\ \cline{1-1} \phi_{22} \\ \cline{1-1} \end{array} + A_3 \begin{array}{|c|c|}\hline \phi_{12} & \phi_{12} \\ \hline \phi_{11} \\ \cline{1-1} \phi_{21} \\ \cline{1-1} \end{array} + A_4 \begin{array}{|c|c|}\hline \phi_{22} & \phi_{22} \\ \hline \phi_{11} \\ \cline{1-1} \phi_{21} \\ \cline{1-1} \end{array} + A_5 \left\{ \sqrt{\frac{2}{3}} \begin{array}{|c|c|}\hline \phi_{11} & \phi_{12} \\ \hline \phi_{21} \\ \cline{1-1} \phi_{22} \\ \cline{1-1} \end{array} + \frac{1}{\sqrt{3}} \begin{array}{|c|c|}\hline \phi_{11} & \phi_{22} \\ \hline \phi_{21} \\ \cline{1-1} \phi_{12} \\ \cline{1-1} \end{array} \right\}$$

where the last term corresponds to having the orbitals of both pairs simultaneously triplet coupled. Since the coefficients $\{A\}$ are functions of the pair coefficients $\{\lambda\}$ and the spin coupling coefficients $\{\varepsilon\}$, they are called spin-pair coefficients.

Because the configurations are occupied in this manner, the SOGVB energy expression has a relatively simple form:

$$E = 2\sum_{i}^{N} f_i h_{ii} + \sum_{i,j}^{N} \left[a_{ij} J_{ij} + b_{ij} K_{ij} \right] + \sum_{m}^{NP} \sum_{i \neq m_1, m_2}^{N} c_{mi} \langle \phi_{m_1} | K_i | \phi_{m_2} \rangle$$

$$+\sum_{m>n}^{NP}\left[d_{mn}(\phi_{m_1}\phi_{n_1}|\phi_{m_2}\phi_{n_2})+e_{mn}(\phi_{m_1}\phi_{n_2}|\phi_{m_2}\phi_{n_1})\right]$$

where {a, b, c, d, e, f} are functions of the spin-pair coefficients. Applying the Variational Principle to this equation, the variational condition for the optimum (real) orbitals is:

$$0=\sum_{i}^{N}\left[\langle\delta_i|H_i|\phi_i\rangle+\langle\delta_i|R_i\rangle\right]$$

subject to the constraint that the orbital variations $\{\delta\}$ preserve orbital orthogonality at least through first order. The field terms H and R have the general form:

$$H_i=f_i h+\sum_{j}^{N}\left[a_{ji}J_j+b_{ji}K_j\right]+\frac{1}{4}\sum_{n}^{NP}c_{ni}K_{n_1+n_2}$$

If $i>2{\times}NP$, $R_i=0$. If $i=m_j$:

$$R_{m_j}=\frac{1}{4}\left[\sum_{\nu\neq m_1,m_2}^{N}c'_{m\nu}K_\nu+\sum_{n\neq m}^{NP}c_{mn}K_{n_1+n_2}\right]|\phi_{m_{3-j}}\rangle$$
$$+\frac{1}{4}\sum_{n\neq m}^{NP}d'_{mn}\left(\int\frac{\phi_{n_{3-j}}\phi_{m_{3-j}}}{r_{12}}\right)|\phi_{n_j}\rangle\qquad j=1,2$$

H_i requires the same kinds of operators needed to construct PPGVB hamiltonians. The difference is that now there is a new exchange operator for each pair ($K_{n_1+n_2}$; n=1, NP). If ϕ_W is an unpaired orbital, $R_W=0$. For paired orbitals, R uses the same exchange operators as H. In addition, the new operators:

$$\int\frac{\phi_{m_i}\phi_{n_i}}{r_{12}}\qquad i=1,2\qquad NP\geq m>n$$

are required. However, since only a relatively few of these new operators are needed and since they are quite easy to construct, matrices over these terms are almost as easy to construct as in PPGVB once the spin-pair coefficients have been found by diagonalizing small CI matrices. If we symbolically define the one-particle hamiltonian:

$$\mathcal{H}_i = H_i + R_i \langle \phi_i |$$

the variational condition can be cast in its usual form:

$$0 = \sum_{i}^{N} \langle \delta_i | \mathcal{H}_i | \phi_i \rangle$$

and the energy can be written as:

$$E = \sum_{i}^{N} \langle \phi_i | f_i h + \mathcal{H}_i | \phi_i \rangle$$

These equations can easily be extended to include NSG strongly orthogonal singlet pairs as well. The hamiltonians for the orbitals involved in spin-coupling optimization need only be revised by including a (2J-K)-type core:

$$\mathcal{H}_i \Rightarrow \mathcal{H}_i + f_i \sum_{c=N+1}^{N+2NSG} f_c \left(2 J_c - K_c \right)$$

The hamiltonians for the singlet paired (core) orbitals are defined just as in PPGVB:

$$\mathcal{H}_c = f_c h + \sum_{j}^{N+2NSG} \left[a_{jc} J_j + b_{jc} K_j \right]$$

Since inclusion of closed-shell orbitals and singlet pairs does not require any new types of operators, SOGVB is formally defined to include these as well so that the wavefunction in terms of strongly orthogonal orbitals is:

$$\Psi = \mathcal{A}\left[\prod_{i}^{NDB}\bar{\phi}_i^2\alpha\beta\right]\left[\prod_{m}^{NSG}\phi''_{m_1}\phi''_{m_2}(\alpha\beta-\beta\alpha)\right]\left[\prod_{m}^{NP}\phi'_{m_1}\phi'_{m_2}\right]\left[\prod_{i}^{N-2NP}\phi_i\right]\chi_{SN}$$

Therefore, just as for PPGVB, SOGVB can handle relatively large numbers of electrons. This is done by partitioning the orbitals into closed, singlet paired, and spin coupling optimized shells. Since many chemical systems can be partitioned in this way with relatively few orbitals being involved in spin coupling optimization, SOGVB represents a practical approach toward treating large systems self-consistently without missing out on any important independent-particle effects.

If the strong orthogonality restriction of SOGVB is removed, the result is GVB. Obviously, a GVB wavefunction is inherently superior. However, the energy of a GVB wavefunction involves all one and two electron integrals. In addition, the associated density matrices are functions of orbital overlap. As a consequence, the one-particle hamiltonians are very complicated and, for this reason, GVB calculations are practical only for small numbers of electrons using relatively small basis sets. In systems where strong orthogonality is not a restriction owing to orbital symmetries, the computationally simpler SOGVB wavefunction gives the same results. Moreover, as was seen for the H_2+D reaction, orbitals tend to remain strongly orthogonal even when not so required. This is a consequnce of Pauli's Principle and, hence, is expected to be rather general. Therefore, in many cases SOGVB is essentially equivalent to GVB.

IV. COMPUTATIONAL DETAILS

A. SOGVB Energy and Variational Equations

The GVB wavefunction for N electrons is:

$$\psi = \mathcal{A}[\prod_{i=1}^{N} \phi_i]\chi_{SN}$$

where the spin term χ_{SN} is required to be an eigenfunction of spin but is otherwise unrestricted. The spatial orbitals $\{\phi\}$ are also unrestricted.

In the SOGVB approximation to GVB, the orbitals are grouped into NP nonorthogonal pairs, with ϕ'_{M_1} and ϕ'_{M_2} comprising the mth pair. All orbitals other than the two within a given pair are taken to be orthogonal (Strong Orthogonality Restriction)

$$\langle \phi'_{M_i} | \phi'_{L_j} \rangle = 0 \qquad M < L \leqslant NP;\ i,j = 1,2$$

$$\langle \phi'_{M_i} | \phi_k \rangle = 0 \qquad M \leqslant NP \text{ and } i = 1,2;\ k > 2NP$$

$$\langle \phi_k | \phi_\ell \rangle = 0 \qquad 2NP < k < \ell$$

where we also allow for N - 2NP additional orbitals that are not in any pair. These will be referred to as the unpaired orbitals. The SOGVB wavefunction thus has the form:

$$\Psi = \mathcal{A}[\prod_{M=1}^{NP} \phi'_{M_1}\phi'_{M_2}][\prod_{k>2NP}^{N} \phi_k]\,\chi_{SN}$$

The SOGVB wavefunction can be reexpressed in terms of orthogonal orbitals by reexpressing the orbitals of each pair as:

$$\phi'_{M_1} = \lambda_{m_1}\phi_{m_1} + \lambda_{m_2}\phi_{m_2} ; \phi'_{M_2} = \lambda_{m_1}\phi_{m_1} - \lambda_{m_2}\phi_{m_2}$$

where λ_{m_1} and λ_{m_2} are chosen so that $\langle\phi_{m_1}|\phi_{m_2}\rangle = 0$. In terms of these orthogonal orbitals, the SOGVB wavefunction becomes:

$$\Psi = \mathcal{A}\left\{\prod_{m=1}^{NP}\left[\lambda_{m_1}^2\phi_{m_1}^2 - \lambda_{m_2}^2\phi_{m_2}^2 - \lambda_{m_1}\lambda_{m_2}(\phi_{m_1}\phi_{m_2} - \phi_{m_2}\phi_{m_1})\right]\right\}\left\{\prod_{i>2\cdot NP}^{N}\phi_i\right\}\chi_{SN}$$

The orthogonal orbitals of each pair will be referred to as <u>natural</u> orbitals. In order to help keep it clear which set of orbitals is being discussed, we will use ϕ with lower case subscripts when referring to the orthogonal orbitals (e.g., ϕ_{m_i} and ϕ_k are orthogonal to all orbitals) and ϕ' with upper case subscripts when referring to the SOGVB orbitals (e.g., ϕ'_{M_1} and ϕ'_{M_2} can be nonorthogonal, but are orthogonal to all other orbitals).

A general energy expression for this wavefunction will be derived by starting with the energy of the corresponding GVB wavefunction. From the result, the variational equations needed to obtain the optimum orbitals will be derived. Finally, these equations will be modified to allow for inclusion of a core consisting of NDB closed shell orbitals and NSG strongly orthogonal singlet pairs as well:

$$\Psi = \mathcal{A}\{\text{CORE}\}\left\{\prod_{m}^{NP}\left[\lambda_{m_1}^2\phi_{m_1}^2 - \lambda_{m_2}^2\phi_{m_2}^2 - \lambda_{m_1}\lambda_{m_2}(\phi_{m_1}\phi_{m_2} - \phi_{m_2}\phi_{m_1})\right]\right\}\left\{\prod_{i>2\cdot NP}^{N}\phi_i\right\}\chi_{SN}$$

$$\text{CORE} = \left[\prod_{i=1}^{NDB}\bar{\phi}^2\alpha\beta\right]\prod_{i}^{NSG}\left[\gamma_{i_1}\bar{\phi}_{i_1}^2 - \gamma_{i_2}\bar{\phi}_{i_2}^2\right]\alpha\beta \quad , \quad \gamma_{i_1}^2 + \gamma_{i_2}^2 = 1$$

The wavefunction in terms of strongly orthogonal orbitals is then:

$$\Psi = \mathcal{A} \left\{ \prod_{i}^{NDB} \bar{\phi}_i^2 \alpha\beta \right\} \left\{ \prod_{I}^{NSG} \bar{\phi}'_{I_1} \bar{\phi}'_{I_2} (\alpha\beta - \beta\alpha) \right\} \left\{ \prod_{m}^{NP} \phi'_{M_1} \phi'_{M_2} \right\} \left\{ \prod_{i > 2 * NP}^{N} \phi_i \right\} X_{SN}$$

where:

$$\bar{\Phi}'_{I_1} = \gamma_{i_1}^{\frac{1}{2}} \bar{\Phi}_{i_1} + \gamma_{i_2}^{\frac{1}{2}} \bar{\Phi}_{i_2}$$

$$\bar{\Phi}'_{I_2} = \gamma_{i_1}^{\frac{1}{2}} \bar{\Phi}_{i_1} - \gamma_{i_2}^{\frac{1}{2}} \bar{\Phi}_{i_2}$$

$$\phi'_{M_1} = \lambda_{m_1} \phi_{m_1} + \lambda_{m_2} \phi_{m_2}$$

$$\phi'_{M_2} = \lambda_{m_1} \phi_{m_1} - \lambda_{m_2} \phi_{m_2}$$

1. SOGVB Energy Expression

Since an SOGVB wavefunction differs from a GVB wavefunction only by strong orthogonality, the most rigorous derivation of the SOGVB energy expression is obtained by starting with the general GVB energy expression. Strong orthogonality is imposed by grouping the first 2 × NP orbitals into nonorthogonal pairs. All orbitals other than the two within a given pair are then taken to be orthogonal. Finally, these pairs are reexpressed in terms of their corresponding orthogonal natural orbitals so that the final energy expression is for an SOGVB wavefunction written in terms of N orthogonal orbitals. In the following, the nonorthogonal orbitals of the m^{th} pair will be denoted as ϕ'_{M_1} and ϕ'_{M_2} or simply as M_1 and M_2 (upper case) whereas the natural orbitals for that pair will be denoted by ϕ_{m_1} and ϕ_{m_2} or simply m_1 and m_2 (lower case). For convenience, only real wavefunctions will be considered (extension to complex orbitals is trivial).

The GVB wavefunction for N electrons can be written as:

$$\psi = \mathcal{A}(O^L \Phi)X$$

where

$$\Phi = \prod_{i=1}^{N} \phi_i(i), \quad X = \alpha\beta\alpha\beta\cdots$$

and

$$O^L = \sum_{\tau \in \mathcal{S}_N} U^L(\tau)\, \tau$$

O^L is a Wigner projection operator which guarantees that ψ is an eigenfunction of spin.[8] $\mathcal{A}$ is the usual antisymmetrizer. The energy of this wavefunction is:

$$E = \Big[\sum_{i,j}^{N} \langle i|h|j\rangle D_j^i + \sum_{\substack{i,j,k,l\\ i\neq j,\, k\neq l}}^{N} (ik|jl)\, D_{kl}^{ij} \Big] / \langle \Phi | O^L \Phi \rangle$$

$$= [E_1 + E_2] / \langle \Phi | O^L \Phi \rangle$$

where:

$\langle i|h|j\rangle = h_{ij}$ = the usual 1-electron integral involving ϕ_i and ϕ_j

$(ik|j\ell)$ = a 2-electron integral involving ϕ_i, ϕ_j, ϕ_k, and ϕ_ℓ written in $(11|22)$ form.

$D_j^{\,i}$ = coefficient of $\phi_i^*(i)\phi_j(i)$ in $\int \Phi^* O^L \Phi \, dx_i'$

$D_{k\ell}^{ij}$ = coefficient of $\phi_i^*(i)\phi_j^*(j)\phi_k(i)\phi_\ell(\ell)$ in $\int \Phi^* O^L \Phi \, dx_{ij}''$

a. Evaluation of E_1:

Since $D_j^i = D_i^j$:

$$E_1 = 2 \sum_{i>j}^{N} \langle i|h|j\rangle D_j^i + \sum_{i}^{N} \langle i|h|i\rangle D_i^i$$

Because of the strong orthogonality restriction, $D_j^i = 0$ unless i and j refer to orbitals of the same pair (ϕ_{M_1} and ϕ_{M_2}) and $D_{M_1}^{M_1} = D_{M_2}^{M_2}$. Thus:

$$E_1 = \sum_{M=1}^{NP} [(h_{M_1M_1} + h_{M_2M_2}) D_{M_1}^{M_1} + 2\, h_{M_1M_2} D_{M_1}^{M_2}] + \sum_{\nu > 2\mathrm{xNP}}^{N} h_{\nu\nu} D_\nu^\nu$$

Expressing the pairs in terms of their corresponding orthogonal natural orbitals:

$$\phi'_{M_1} = \lambda_{m_1} \phi_{m_1} + \lambda_{m_2} \phi_{m_2} \;;\quad \phi'_{M_2} + \lambda_{m_1} \phi_{m_1} - \lambda_{m_2} \phi_{m_2} \tag{1}$$

where $\langle m_1 | m_2 \rangle = 0$ and $\lambda^2_{m_1} + \lambda^2_{m_2} = 1$:

$$h_{M_1M_1} = \lambda^2_{m_1} h_{m_1m_1} + \lambda^2_{m_2} h_{m_2m_2} + 2\,\lambda_{m_1}\lambda_{m_2} h_{m_1m_2}$$

$$h_{M_2M_2} = \lambda^2_{m_1} h_{m_1m_1} + \lambda^2_{m_2} h_{m_2m_2} - 2\,\lambda_{m_1}\lambda_{m_2} h_{m_1m_2}$$

$$h_{M_1M_2} = \lambda^2_{m_1} h_{m_1m_1} - \lambda^2_{m_2} h_{m_2m_2}$$

Thus:

$$E_1 = 2 \sum_{m=1}^{NP} \left[\lambda^2_{m_1} \left(D^{m_1}_{m_1} + D^{m_2}_{m_1} \right) h_{m_1m_1} + \lambda^2_{m_2} \left(D^{m_1}_{m_1} - D^{m_2}_{m_1} \right) h_{m_2m_2} \right] + 2 \sum_{\nu > 2 \cdot NP}^{N} \tfrac{1}{2} D^{\nu}_{\nu} h_{\nu\nu}$$

$$= 2 \sum_{i=1}^{N} f_i h_{ii}$$

b. Evaluation of E_2:

$$E_2 = \sum_{\substack{i,j,k,l \\ i \neq j,\, k \neq l}}^{N} (ik|jl)\, D^{ij}_{kl}$$

Since $D^{ij}_{k\ell} = D^{ji}_{\ell k} = D^{k\ell}_{ij}$ we have:

$$E_2 = 4 \sum_{\substack{i>j,\, k>l \\ ij > kl}}^{N} \left[(ik|jl)\, D^{ij}_{kl} + (il|jk)\, D^{ij}_{lk} \right] + 2 \sum_{i>j}^{N} \left[J_{ij} D^{ij}_{ij} + K_{ij} D^{ij}_{ji} \right]$$

where $J_{ij} + K_{ij}$ are the usual coulomb and exchange integrals:

$$J_{ij} = (ii|jj) = \langle i|J_j|i\rangle$$
$$K_{ij} = (ij|ij) = \langle i|K_j|i\rangle$$

and ij is the pair index:

$$\begin{aligned} ij &= i(i-1)/2+j \text{ if } i \geqslant j \\ &= j(j-1)/2+i \text{ if } j > i \end{aligned}$$

Owing to strong orthogonality, if i or j refer to an orbital of a pair, k or ℓ must also refer to an orbital of that pair in order for $D^{ij}_{k\ell}$ and $D^{ij}_{\ell k}$ to be nonzero. Also, if i or j refer to an unpaired orbital either k or ℓ must refer to that orbital in order for $D^{ij}_{k\ell}$ and $D^{ij}_{\ell k}$ to be nonzero. Therefore:

$$\begin{aligned} E_2 = 4 \sum_{M>N}^{NP} \Big\{ & \langle M_2 | J_{N_1} D^{m_2 n_1}_{m_1 n_1} + J_{N_2} D^{m_2 n_2}_{m_1 n_2} + K_{N_1} D^{m_2 n_1}_{n_1 m_1} + K_{N_2} D^{m_2 n_2}_{n_2 m_1} | M_1 \rangle \\ & + \langle N_2 | J_{M_1} D^{m_1 n_2}_{m_1 n_1} + J_{M_2} D^{m_2 n_2}_{m_2 n_1} + K_{M_1} D^{n_2 m_1}_{m_1 n_1} + K_{M_2} D^{n_2 m_2}_{m_2 n_1} | N_1 \rangle \\ & + \left[D^{m_2 n_2}_{m_1 n_1} + D^{m_2 n_1}_{m_1 n_2} \right] (M_1 M_2 | N_1 N_2) \\ & + D^{m_2 n_2}_{n_1 m_1} (M_2 N_1 | M_1 N_2) + D^{m_2 n_1}_{n_2 m_1} (M_2 N_2 | M_1 N_1) \Big\} \\ & + 4 \sum_{M=1}^{NP} \sum_{\nu > 2NP}^{N} \langle M_2 | J_\nu D^{\nu m_2}_{\nu m_1} + K_\nu D^{\nu m_2}_{m_1 \nu} | M_1 \rangle \\ & + 2 \sum_{i>j}^{N} \left[J_{ij} D^{ij}_{ij} + K_{ij} D^{ij}_{ji} \right] \end{aligned}$$

Due to strong orthogonality:

$$D^{m_1 i}_{m_1 j} = D^{m_2 i}_{m_2 j} \quad ; \quad D^{m_2 n_2}_{m_1 n_1} = D^{m_2 n_1}_{m_1 n_2}$$

Hence:

$$\begin{aligned} E_2 = 4 \sum_{M>N}^{NP} \Big\{ & \langle M_2 | (J_{N_1} + J_{N_2}) D^{m_2 n_1}_{m_1 n_1} + K_{N_1} D^{m_2 n_1}_{n_1 m_1} + K_{N_2} D^{m_2 n_2}_{n_2 m_1} | M_1 \rangle \\ & + \langle N_2 | (J_{M_1} + J_{M_2}) D^{m_1 n_2}_{m_1 n_1} + K_{M_1} D^{m_1 n_2}_{n_1 m_1} + K_{M_2} D^{m_2 n_2}_{n_1 m_2} | N_1 \rangle \\ & + 2 D^{m_2 n_2}_{m_1 n_1} (M_1 M_2 | N_1 N_2) + D^{m_2 n_2}_{n_1 m_1} (M_2 N_1 | M_1 N_2) \\ & + D^{m_2 n_1}_{n_2 m_1} (M_2 N_2 | M_1 N_1) \Big\} \\ & + 4 \sum_{m}^{NP} \sum_{\nu > 2NP}^{N} \langle M_2 | J_\nu D^{\nu m_2}_{\nu m_1} + K_\nu D^{\nu m_2}_{m_1 \nu} | M_1 \rangle \\ & + 2 \sum_{i>j}^{N} \left[J_{ij} D^{ij}_{ij} + K_{ij} D^{ij}_{ji} \right] \end{aligned}$$

Converting to natural orbital pairs (1) :

$$\langle M_2 | \mathcal{O}_p | M_1 \rangle = \sum_{i=1}^{2} \lambda^2_{m_i} (-1)^{i-1} \langle m_i | \mathcal{O}_p | m_i \rangle$$

$$J_{M_j} = \sum_{i=1}^{2} \lambda^2_{m_i} J_{m_i} + (-1)^{j-1} 2 \lambda_{m_1} \lambda_{m_2} \int \frac{m_1 m_2}{r_{12}}$$

$$K_{M_j} = \sum_{i=1}^{2} \lambda^2_{m_i} K_{m_i} + (-1)^{j-1} \lambda_{m_1} \lambda_{m_2} \left[\int \frac{m_1 (12) m_2}{r_{12}} + \int \frac{m_2 (12) m_1}{r_{12}} \right]$$

$$(M_1 M_2 | N_1 N_2) = \sum_{i,j=1}^{2} \lambda^2_{m_i} \lambda^2_{n_j} (-1)^{i+j} J_{m_i n_j}$$

$$\begin{aligned} (M_2 N_1 | M_1 N_2) = \sum_{i,j=1}^{2} \lambda^2_{m_i} \lambda^2_{n_j} (-1)^{i+j} K_{m_i n_j} + 2 \lambda_{m_1} \lambda_{m_2} \lambda_{n_1} \lambda_{n_2} \big[& (m_1 n_2 | m_2 n_1) \\ & - (m_1 n_1 | m_2 n_2) \big] \end{aligned}$$

$$
\begin{aligned}
(M_2 N_2 | M_1 N_1) = {} & \sum_{i,j=1}^{2} \lambda_{m_i}^2 \lambda_{n_j}^2 (-1)^{i+j} K_{m_i n_j} \\
& - 2 \lambda_{m_1} \lambda_{m_2} \lambda_{n_1} \lambda_{n_2} \left[(m_1 n_2 | m_2 n_1) - (m_1 n_1 | m_2 n_2) \right]
\end{aligned}
$$

Therefore:

$$
\begin{aligned}
E_2 = 4 \sum_{m>n}^{NP} \{ & \sum_{i,j=1}^{2} \lambda_{m_i}^2 \lambda_{n_j}^2 [2 (D^{m_1 n_1}_{m_1 n_1} + (-1)^{i+1} D^{m_2 n_1}_{m_1 n_1} + (-1)^{j+1} D^{n_2 m_1}_{n_1 m_1} \\
& + (-1)^{i+j} D^{m_2 n_2}_{m_1 n_1}) J_{m_i n_j} + (\tfrac{1}{2} [D^{m_1 n_1}_{n_1 m_1} + D^{m_2 n_1}_{n_1 m_2} + D^{m_1 n_2}_{n_2 m_1} \\
& + D^{m_2 n_2}_{n_2 m_2}] + (-1)^{i+1} [D^{m_2 n_1}_{n_1 m_1} + D^{m_2 n_2}_{n_2 m_1}] + (-1)^{j+1} [D^{n_2 m_1}_{m_1 n_1} + D^{n_2 m_2}_{m_2 n_1}] \\
& + (-1)^{i+j} [D^{m_2 n_2}_{n_1 m_1} + D^{m_2 n_1}_{n_2 m_1}]) K_{m_i n_j}] \\
& + \sum_{i=1}^{2} [\lambda_{m_i}^2 \lambda_{n_1} \lambda_{n_2} (D^{m_1 n_1}_{n_1 m_1} + D^{m_2 n_1}_{n_1 m_2} - D^{m_1 n_2}_{n_2 m_1} - D^{m_2 n_2}_{n_2 m_2} \\
& + (-1)^{i+1} 2 [D^{m_2 n_1}_{n_1 m_1} - D^{m_2 n_2}_{n_2 m_1}]) \langle n_1 | K_{m_i} | n_2 \rangle + \lambda_{n_i}^2 \lambda_{m_1} \lambda_{m_2} (D^{m_1 n_1}_{n_1 m_1} \\
& + D^{m_1 n_2}_{n_2 m_1} - D^{m_2 n_1}_{n_1 m_2} - D^{m_2 n_2}_{n_2 m_2} + (-1)^{i+1} 2 [D^{n_2 m_1}_{m_1 n_1} - D^{n_2 m_2}_{m_2 n_1}]) \langle m_1 | K_{n_i} | m_2 \rangle] \\
& + \lambda_{m_1} \lambda_{m_2} \lambda_{n_1} \lambda_{n_2} [(D^{m_1 n_1}_{n_1 m_1} + D^{m_2 n_2}_{n_2 m_2} - D^{m_2 n_1}_{n_1 m_2} - D^{m_1 n_2}_{n_2 m_1} + 2 [D^{m_2 n_2}_{n_1 m_1} \\
& - D^{m_2 n_1}_{n_2 m_1}]) (m_1 n_2 | m_2 n_1) + (D^{m_1 n_1}_{n_1 m_2} + D^{m_2 n_2}_{n_2 m_2} - D^{m_2 n_1}_{n_1 m_2} - D^{m_1 n_2}_{n_2 m_1} \\
& - 2 [D^{m_2 n_2}_{n_1 m_1} - D^{m_2 n_1}_{n_2 m_1}]) (m_1 n_1 | m_2 n_2) \} \\
+ 4 \sum_{\nu > 2NP}^{N} \sum_{m=1}^{NP} \{ & \sum_{i=1}^{2} \lambda_{m_i}^2 [(D^{m_1 \nu}_{m_1 \nu} + (-1)^{i+1} D^{\nu m_2}_{\nu m_1}) J_{m_i \nu} + \tfrac{1}{2} (D^{m_1 \nu}_{\nu m_1} \\
& + D^{m_2 \nu}_{\nu m_2} + (-1)^{i+1} 2 D^{\nu m_2}_{m_1 \nu}) K_{m_i \nu}] + \lambda_{m_1} \lambda_{m_2} (D^{m_1 \nu}_{\nu m_1} \\
& - D^{m_2 \nu}_{\nu m_2}) \langle m_1 | K_\nu | m_2 \rangle \}
\end{aligned}
$$

$$+ 2 \sum_{m}^{NP} \left\{ \sum_{i,j=1}^{2} \lambda_{m_i}^2 \lambda_{m_j}^2 \left(D_{m_1 m_2}^{m_1 m_2} + (-1)^{i+j} D_{m_2 m_1}^{m_1 m_2} \right) J_{m_i m_j} - 4 \lambda_{m_1}^2 \lambda_{m_2}^2 D_{m_1 m_2}^{m_1 m_2} K_{m_1 m_2} \right\}$$

$$+ 2 \sum_{i > j > 2NP}^{N} \left[J_{ij} D_{ij}^{ij} + K_{ij} D_{ji}^{ij} \right]$$

Thus, E_2 has the general form:

$$E_2 = \sum_{i,j=1}^{N} \left[a_{ij} J_{ij} + b_{ij} K_{ij} \right] + \sum_{m}^{NP} \sum_{\nu \neq m_1, m_2}^{N} c_{m\nu} \langle m_1 | K_\nu | m_2 \rangle + \sum_{m > n}^{NP} \left[d_{mn} (m_1 n_1 | m_2 n_2) + e_{mn} (m_1 n_2 | m_2 n_2) \right]$$

Hence, the total energy expression is:

$$E = (E_1 + E_2) / \langle \Phi | O^L \Phi \rangle$$

$$= 2 \sum_{i}^{N} f_i h_{ii} + \sum_{i,j}^{N} \left[a_{ij} J_{ij} + b_{ij} K_{ij} \right] + \sum_{m}^{NP} \sum_{\nu \neq m_1, m_2}^{N} c_{m\nu} \langle m_1 | K_\nu | m_2 \rangle + \sum_{n > m}^{NP} \left[d_{mn} (m_1 n_1 | m_2 n_2) + e_{mn} (m_1 n_2 | m_2 n_1) \right]$$

where $1/\langle \Phi | O^L \Phi \rangle$ has been absorbed into $\{f, a, b, c, d, e\}$. Also note that $a_{wv} = a_{vw}$, $b_{wv} = b_{vw}$, $d_{mn} = d_{nm}$ and $e_{mn} = e_{nm}$. Since

$$(m_1 n_1 | m_2 n_2) + (m_1 n_2 | m_2 n_1) = \langle m_1 | K_{n_1 + n_2} - K_{n_1} - K_{n_2} | m_2 \rangle$$

the energy can also be written as:

$$E = 2 \sum_{i}^{N} f_i h_{ii} + \sum_{i,j}^{N} \left[a_{ij} J_{ij} + b_{ij} K_{ij} \right] + \sum_{m}^{NP} \sum_{\nu \neq m_1, m_2}^{N} c'_{m\nu} \langle m_1 | K_\nu | m_2 \rangle + \sum_{m > n}^{NP} e_{mn} \langle m_1 | K_{n_1 + n_2} | m_2 \rangle + \sum_{m > n}^{NP} d'_{mn} (m_1 n_1 | m_2 n_2)$$

2. Evaluation of SOGVB Energy Coefficients

The preceding derivation of the SOGVB energy expression has served to give a general equation and to enumerate the kinds of 1- and 2-electron integrals required. However, the definitions of the coefficients {f, a, b, c, d, e} given there are of little practical value. In actual practice, these coefficients can be defined most efficiently by starting with the wavefunction itself:

$$\psi = \mathcal{A}\{ \prod_{m=1}^{NP} [(\lambda_{m_1}^2 \phi_{m_1}^2 - \lambda_{m_2}^2 \phi_{m_2}^2) - \lambda_{m_1}\lambda_{m_2}(\phi_{m_1}\phi_{m_2} - \phi_{m_2}\phi_{m_1})]\}\{ \prod_{\nu > 2xNP}^{N} \phi_\nu \} X_{SN} \tag{1}$$

$$X_{SN} = \sum_{i=1}^{F} \varepsilon_i \chi_i$$

where {x} are the standard orthogonal spin-eigenfunctions (SEFs) for N electrons having the desired spin multiplicity. The spin coupling coefficients {ε} are adjustable parameters. This wavefunction can be rewritten in terms of a set of orthogonal SEF configurations {θ} involving orthonormal orbitals:

$$\psi = \sum_{j=1} A_j \theta_j \tag{2}$$

where each configuration in (2) either contains only one orbital of a pair, with that orbital being doubly occupied, or it contains both orbitals of a pair triplet coupled. This is due to Pauli's Principle and the fact that in (1) the orbitals of a pair are either doubly-occupied or are spatially antisymmetrically coupled ($\phi_{m_1}\phi_{m_2} - \phi_{m_2}\phi_{m_1}$). The number and form of these configurations $\{\theta\}$ depends upon the number of electrons involved (N), the number of pairs (NP) and the spin multiplicity. The spin-pair coefficients $\{A\}$ are functions of the spin coupling coefficients $\{\varepsilon\}$ and the pair coefficients $\{\lambda\}$. In general, this set of coefficients is <u>not</u> linearly independent.

The energy expression:

$$E = \frac{\sum\limits_{i,j} A_i A_j \langle \theta_i | H | \theta_j \rangle}{\sum\limits_{i} A_i^2}$$

can be expanded directly into the desired form:

$$E = 2\sum_{i}^{N} f_i h_{ii} + \sum_{i,j}^{N} \left[a_{ij} J_{ij} + b_{ij} K_{ij} \right]$$
$$+ \sum_{m}^{NP} \sum_{\nu \neq m_1, m_2}^{N} c_{m\nu} \langle m_1 | K_\nu | m_2 \rangle + \sum_{m>n}^{NP} \left[d_{mn} (m_1 n_1 | m_2 n_2) + e_{mn} (m_1 n_2 | m_2 n_1) \right]$$

with $\{f, a, b, c, d, e\}$ as functions of $\{A\}$. The exact functional dependence of these parameters on $\{A\}$ depends upon N, NP and the spin multiplicity.

3. SOGVB Variational Equations

The energy of an SOGVB wavefunction can be written as:

$$E = \sum_{i}^{N} \left[2f_i h_{ii} + a_{ii} J_{ii} \right] + 2 \sum_{i>j} \left[a_{ij} J_{ij} + b_{ij} K_{ij} \right]$$
$$+ \sum_{m}^{NP} \sum_{\nu \neq m_1, m_2}^{N} C_{m\nu} \langle m_1 | K_\nu | m_2 \rangle + \sum_{m>n}^{NP} \left[d_{mn} (m_1 n_1 | m_2 n_2) + e_{mn} (m_1 n_2 | m_2 n_1) \right]$$

where there are N orthogonal orbitals. The first 2xNP of them are paired, with ϕ_{m_1} and ϕ_{m_2} comprising the m$^{\text{th}}$ pair. The remaining orbitals are unpaired. Starting with this equation, the variational equations for the optimum orbitals will be derived. For convenience, the orbitals will be taken to be real.

Allowing the orbitals to vary in an orthogonal manner:

$$\Phi_\nu = \frac{1}{N_\nu} (\phi_\nu + \delta_\nu) \text{ where } \langle \Phi_\nu | \Phi_\mu \rangle = \delta_{\mu\nu}$$

so that the above equation remains valid for the new orbitals $\{\Phi\}$, we obtain the usual expression for the first-order change in energy:

$$\delta E = \sum_{\nu=1}^{N} \langle \delta_\nu | H_\nu \phi_\nu + R_\nu \rangle$$

Letting $\delta E = 0$ then gives the variational condition for the optimum orbitals subject to maintenance of orbital orthonormality:

$$0 = \sum_{\nu=1}^{N} \langle \delta_\nu | H_\nu \phi_\nu + R_\nu \rangle$$

We must now evaluate the field terms H_ν and R_ν.

a. Paired Orbitals:

Isolating the terms in E which depend on orbital ϕ_{m_i} (paired with $\phi_{m_{3-i}}$):

$$
\begin{aligned}
E_{m_i} = {} & 2f_{m_i} h_{m_i m_i} + a_{m_i m_i} J_{m_i m_i} + 2\sum_{\nu \neq m_i}^{N} \left[a_{\nu m_i} J_{\nu m_i} + b_{\nu m_i} K_{\nu m_i} \right] \\
& + \sum_{\nu \neq m_1, m_2}^{N} \langle m_i | K_\nu | m_{3-i} \rangle + \sum_{n \neq m}^{NP} c_{n m_i} \langle n_1 | K_{m_i} | n_2 \rangle \\
& + \sum_{n \neq m}^{NP} \left[d_{mn} (m_i n_i | m_{3-i} n_{3-i}) + e_{mn} (m_i n_{3-i} | m_{3-i} n_i) \right]
\end{aligned}
$$

The first-order change in E_{m_i} for a change in ϕ_{m_i} is:

$$
\begin{aligned}
\delta E_{m_i} = {} & 4 f_{m_i} \langle \delta_{m_i} | h | m_i \rangle + 4 a_{m_i m_i} \langle \delta_{m_i} | J_{m_i} | m_i \rangle \\
& + 4 \left\langle \delta_{m_i} \middle| \sum_{\nu \neq m_i}^{N} \left(a_{\nu m_i} J_\nu + b_{\nu m_i} K_\nu \right) \middle| m_i \right\rangle \\
& + \sum_{\nu \neq m_1, m_2}^{N} c_{m\nu} \langle \delta_{m_i} | K_\nu | m_{3-i} \rangle \\
& + \sum_{n \neq m}^{NP} c_{n m_i} \left[(\delta_{m_i} n_1 | m_i n_2) + (m_i n_1 | \delta_{m_i} n_2) \right] \\
& + \sum_{n \neq m}^{NP} \left[d_{mn} (\delta_{m_i} n_i | m_{3-i} n_{3-i}) + e_{mn} (\delta_{m_i} n_{3-i} | m_{3-i} n_i) \right]
\end{aligned}
$$

If ϕ_{m_i} is optimum, then $\delta E_{m_i} = 0$:

$$\begin{aligned} 0 = \Big\langle \delta_{m_i} \Big| & f_{m_i} h + a_{m_i m_i} J_{m_i} + \sum_{\nu \neq m_i}^{N} \left(a_{\nu m_i} J_\nu + b_{\nu m_i} K_\nu \right) \Big| m_i \Big\rangle \\ & + \frac{1}{4} \sum_{n \neq m}^{NP} c_{nm_i} \left[(\delta_{m_i} n_1 | m_i n_2) + (\delta_{m_i} n_2 | m_i n_1) \right] \\ & + \frac{1}{4} \sum_{\nu \neq m_1, m_2}^{N} c_{m\nu} \langle \delta_{m_i} | K_\nu | m_{3-i} \rangle \\ & + \frac{1}{4} \sum_{n \neq m}^{NP} \left[d_{mn} (\delta_{m_i} n_i | m_{3-i} n_{3-i}) + e_{mn} (\delta_{m_i} n_{3-i} | m_{3-i} n_i) \right] \end{aligned}$$

Since:

$$(\delta_{m_i} n_1 | m_i n_2) + (\delta_{m_i} n_2 | m_i n_1) = \langle \delta_{m_i} | K_{n_1+n_2} - K_{n_1} - K_{n_2} | m_i \rangle$$

$$(\delta_{m_i} n_i | m_{3-i} n_{3-i}) + (\delta_{m_i} n_{3-i} | m_{3-i} n_i) = \langle \delta_{m_i} | K_{n_1+n_2} - K_{n_1} - K_{n_2} | m_{3-i} \rangle \quad :$$

$$\begin{aligned} 0 = \Big\langle \delta_{m_i} \Big| & f_{m_i} h + a_{m_i m_i} J_{m_i} + \sum_{\nu \neq m_i}^{N} \left(a_{\nu m_i} J_\nu + b_{\nu m_i} K_\nu \right) \\ & + \frac{1}{4} \sum_{n \neq m}^{NP} c_{nm_i} \left(K_{n_1+n_2} - K_{n_1} - K_{n_2} \right) \Big| m_i \Big\rangle \\ & + \frac{1}{4} \sum_{\nu \neq m_1, m_2}^{N} c_{m\nu} \langle \delta_{m_i} | K_\nu | m_{3-i} \rangle + \frac{1}{4} \sum_{n \neq m} \Big[(d_{mn} - e_{mn}) (\delta_{m_i} n_i | m_{3-i} n_{3-i}) \\ & \qquad + e_{mn} \langle \delta_{m_i} | K_{n_1+n_2} - K_{n_1} - K_{n_2} | m_{3-i} \rangle \Big] \end{aligned}$$

Thus:

$$0 = \langle \delta_{m_i} | H_{m_i} m_i + R_{m_i} \rangle$$

where:

$$\begin{aligned} H_{m_i} = f_{m_i} h & + \sum_{\nu}^{N} a_{\nu m_i} J_\nu + \frac{1}{4} \sum_{n \neq m}^{NP} \Big[c_{nm_i} K_{n_1+n_2} \\ & + \sum_{j=1}^{2} \left(4 b_{n_j m_i} - c_{nm_i} \right) K_{n_j} \Big] + b_{m_1 m_2} K_{m_{3-i}} \\ & + \sum_{\nu > 2NP}^{N} b_{\nu m_i} K_\nu \end{aligned}$$

$$R_{m_i} = \frac{1}{4} \left\{ \sum_{n \neq m}^{NP} \left[e_{mn} K_{n_1+n_2} + \sum_{j=1}^{2} (c_{mn_j} - e_{mn}) K_{n_j} \right] + \sum_{\nu > 2NP}^{N} c_{m\nu} K_\nu \right\} | \phi_{m_{3-i}} \rangle + \frac{1}{4} \sum_{n \neq m}^{NP} (d_{mn} - e_{mn}) \int \left(\frac{m_{3-i} n_{3-i}}{r_{12}} \middle| \phi_{n_i} \right)$$

b. Unpaired Orbitals

Isolating terms in E which depend on unpaired orbital ϕ_μ:

$$E_\mu = 2 f_\mu h_{\mu\mu} + a_{\mu\mu} J_{\mu\mu} + 2 \sum_{\nu \neq \mu}^{N} (a_{\nu\mu} J_{\nu\mu} + b_{\nu\mu} K_{\nu\mu}) + \sum_{m}^{NP} c_{m\mu} \langle m_1 | K_\mu | m_2 \rangle$$

The first-order change in E_μ for a change in ϕ_μ is:

$$\delta E_\mu = 4 f_\mu \langle \delta_\mu | h | \mu \rangle + 4 a_{\mu\mu} \langle \delta_\mu | J_\mu | \mu \rangle + 4 \sum_{\nu \neq \mu}^{N} \langle \delta_\mu | a_{\nu\mu} J_\nu + b_{\nu\mu} K_\nu | \mu \rangle + \sum_{m}^{NP} c_{m\mu} \left[(\delta_\mu m_1 | \mu m_2) + (\mu m_1 | \delta_\mu m_2) \right]$$

If ϕ_μ is optimum, $\delta E_\mu = 0$:

$$0 = \langle \delta_\mu | f_\mu h + a_{\mu\mu} J_\mu + \sum_{\nu \neq \mu}^{N} (a_{\nu\mu} J_\nu + b_{\nu\mu} K_\nu) + \frac{1}{4} \sum_{m=1}^{NP} c_{m\mu} (K_{m_1+m_2} - K_{m_1} - K_{m_2}) | \mu \rangle$$

Thus:

$$0 = \langle \delta_\mu | H_\mu | \mu \rangle$$

where:

$$H_{\omega} = f_{\omega} h + \sum_{\nu}^{N} a_{\nu\omega} J_{\nu} + \frac{1}{4} \sum_{m}^{NP} \left[c_{m\omega} K_{m_1+m_2} + \sum_{j=1}^{2} (4 b_{m_j \omega} - c_{m\omega}) K_{m_j} \right] + \sum_{\nu > 2NP}^{N} b_{\nu\omega} K_{\nu}$$

In summary, the variational condition for the optimum orbitals is:

$$0 = \sum_{\nu=1}^{N} \langle \delta_{\nu} | H_{\nu}\, \nu + R_{\nu} \rangle$$

where the orbital variations $\{\delta_{\nu}\}$ are constrained so as to maintain orbital orthogonality.

If $\nu \leqslant$ 2xNP so that $\phi_{\nu} = \phi_{m_i}$:

$$H_{m_i} = f_{m_i} h + \sum_{\omega}^{N} a_{\omega m_i} J_{\omega} + \frac{1}{4} \sum_{n \neq m} \Big[c_{nm_i} K_{n_1+n_2} + \sum_{j=1}^{2} (4 b_{n_j m_i} - c_{nm_i}) K_{n_j} \Big] + b_{m_1 m_2} K_{m_{3-i}} + \sum_{\omega > 2NP}^{N} b_{\omega m_i} K_{\omega}$$

$$R_{m_i} = \frac{1}{4} \Big\{ \sum_{n \neq m}^{NP} \Big[e_{mn} K_{n_1+n_2} + \sum_{j=1}^{2} (c_{mn_j} - e_{mn}) K_{n_j} \Big] + \sum_{\omega > 2NP}^{N} c_{m\omega} K_{\omega} \Big\} | \phi_{m_{3-i}} \rangle + \frac{1}{4} \sum_{n \neq m}^{NP} (d_{mn} - e_{mn}) \int \frac{m_{3-i}\, n_{3-i}}{r_{12}} | \phi_{n_i} \rangle$$

If $\nu >$ 2xNP:

$$H_{\nu} = f_{\nu} h + \sum_{\omega}^{N} a_{\omega\nu} J_{\omega} + \frac{1}{4} \sum_{m=1}^{NP} \left[c_{m\nu} K_{m_1+m_2} + \sum_{j=1}^{2} (4 b_{m_j \nu} - c_{m\nu}) K_{m_j} \right] + \sum_{\omega > 2NP}^{N} b_{\omega\nu} K_{\omega}$$

$R_\nu = 0$

N.B.

As is usual, the total energy can be written as:

$$E = \sum_{\nu=1}^{N} \left[f_\nu h_{\nu\nu} + \langle\nu|H_\nu|\nu\rangle + \langle\nu|R_\nu\rangle \right]$$

4. Inclusion of Core Orbitals In SOGVB

The SOGVB energy and variational equations derived previously consider only those N orbitals involved in spin coupling optimization (henceforth referred to as noncore orbitals). If the wavefunction is defined to also include a set of NC orthogonal core orbitals partitioned into NSP separated pairs such that:

$$\mathrm{Core} = \prod_{i}^{NSP} \Big[\sum_{j} \gamma_{ji}\, \phi_{ji}^{2} \Big] \alpha\beta \qquad ; \quad \sum_{j} \gamma_{ji}^{2} = 1$$

these equations require only minor modification. Since each core orbital is doubly-occupied and is orthogonal to all other orbitals, the contribution of these orbitals to the total energy is:

$$\begin{aligned} E_c = {} & \sum_{i=1}^{NSP} \sum_{j} \gamma_{ji}^{2} \left(2 h_{ji,ji} + J_{ji,ji} \right) + 2 \sum_{i>k}^{NSP} \sum_{j} \sum_{l} \gamma_{ji}^{2} \gamma_{kl}^{2} \big(2 J_{ji,kl} \\ & - K_{ji,kl} \big) + 2 \sum_{i}^{NSP} \sum_{j>k} \gamma_{ji} \gamma_{ki} K_{ji,ki} + 2 \sum_{i}^{NSP} \sum_{j} \sum_{\nu=1}^{N} \gamma_{ji}^{2} f_{\nu} \big(2 J_{ji,\nu} \\ & - K_{ji,\nu} \big) \end{aligned}$$

Thus, the total energy is obtained by adding E_c to the previously derived energy expression to give the general equation:

$$\begin{aligned} E = {} & 2 \sum_{i}^{N'} f_i h_{ii} + \sum_{i,j}^{N'} \left[a_{ij} J_{ij} + b_{ij} K_{ij} \right] \\ & + \sum_{m}^{NP} \sum_{\nu \neq m_1, m_2}^{N} c'_{m\nu} \langle m_1 | K_{\nu} | m_2 \rangle + \sum_{m>n}^{NP} \Big[e_{mn} \langle m_1 | K_{n_1+n_2} | m_2 \rangle \\ & \qquad + d'_{mn} \left(m_1 n_1 | m_2 n_2 \right) \Big] \end{aligned}$$

where there are N′ orbitals. The first N of them are the noncore orbitals. The remaining NC = N′-N are core orbitals. Of the noncore orbitals, the first 2 x NP of them are paired, with orbitals ϕ_{m_1} and ϕ_{m_2} comprising the m^th pair.

The variational condition for the optimum orbitals is as usual:

$$0 = \sum_{\omega}^{N'} \langle \delta_\omega | H_\omega \omega + R_\omega \rangle$$

where the orbital variations $\{\delta_w\}$ are constrained so as to maintain orbital orthogonality. For the various types of orbitals, H_w and R_w are as follows:

a. Paired Orbitals

If $w \leqslant 2 \times NP$ so that $\phi_w = \phi_{m_i}$ $(i = 1, 2)$:

$$H_{m_i} = f_{m_i} h + \sum_{\nu=1}^{N'} a_{\nu m_i} J_\nu + \frac{1}{4} \sum_{n \neq m}^{NP} \Big[c_{nm_i} K_{n_1+n_2} + \sum_{j=1}^{2} (4 b_{n_j m_i} - c_{nm_i}) K_{n_j} \Big] + b_{m_1 m_2} K_{m_{3-i}} + \sum_{\nu > 2NP}^{N'} b_{\nu m_i} K_\nu$$

$$R_{m_i} = \frac{1}{4} \Big\{ \sum_{n \neq m}^{NP} \Big[e_{mn} K_{n_1+n_2} + \sum_{j=1}^{2} (c_{mn_j} - e_{mn}) K_{n_j} \Big] + \sum_{\nu > 2NP}^{N'} c_{m\nu} K_\nu \Big\} | \phi_{m_{3-i}} \rangle + \frac{1}{4} \sum_{n \neq m}^{NP} (d_{mn} - e_{mn}) \int \frac{m_{3-i}\, n_{3-i}}{r_{12}} | \phi_{n_i} \rangle$$

b. Unpaired Orbitals

If $N \geqslant w > 2 \times NP$:

$$H_\omega = f_\omega h + \sum_{\nu}^{N'} a_{\nu\omega} J_\nu + \frac{1}{4} \sum_{m}^{NP} \Big[c_{m\omega} K_{m_1+m_2} + \sum_{j=1}^{2} (4 b_{m_j \omega} - c_{m\omega}) K_{m_j} \Big] + \sum_{\nu > 2NP}^{N'} b_{\nu\omega} K_\nu$$

$$R_\omega = 0$$

c. Core Orbitals

If w > N:

$$H_\omega = f_\omega h + \sum_\nu^{N'} \left[a_{\nu\omega} J_\nu + b_{\nu\omega} K_\nu \right]$$

$$R_\omega = 0$$

N.B.

1) The total energy can be written as:

$$E = \sum_\nu^{N'} \left[f_\nu h_{\nu\nu} + \langle \phi_\nu | H_\nu | \phi_\nu \rangle + \langle \phi_\nu | R_\nu \rangle \right]$$

2) The definitions of $\{f, a, b, c, d, e\}_{\text{noncore}}$ are unaffected by the presence of core orbitals.

3) In practice, the core is restricted to be:

$$\text{Core} = \left[\prod_i^{NDB} \phi_i^2 \alpha\beta \right] \prod^{NSG} \left[\gamma_{i_1} \phi_{i_1}^2 - \gamma_{i_2} \phi_{i_2}^2 \right] \alpha\beta$$

so as to describe a set of NDB closed shell orbitals (γ=1) and a set of NSG strongly orthogonal singlet pairs.

4) If ϕ_w is a core orbital

$f_w = \gamma_w^2$

$a_{ww} = 2f_w$ or $a_{ww} = f_w$

$b_{ww} = -f_w$ or $b_{ww} = 0$

If ϕ_ν is not in the same pair as ϕ_w:

$a_{w\nu} = 2f_w f_\nu$

$b_{w\nu} = -f_w f_\nu$

If ϕ_ν is in the same pair as ϕ_w:

$$a_{w\nu} = 0$$

$$b_{w\nu} = -\gamma_w \gamma_\nu$$

B. Optimization Procedure

An SOGVB wavefunction can be written as:

$$\Psi = \mathcal{A}\,[\mathrm{Core}] \sum_{j}^{F} A_j \Theta_j$$

$$\mathrm{Core} = \left[\prod_{i}^{NDB} \phi_i^2 \alpha\beta\right] \prod_{i}^{NSG} \left[\gamma_{i_1} \phi_{i_1}^2 - \gamma_{i_2} \phi_{i_2}^2\right] \alpha\beta$$

As explained previously, $\{\theta\}$ are orthogonal SEF configurations involving the N orthonormal noncore orbitals. The first 2 x NP noncore orbitals are grouped into pairs. Aside from the common property that each configuration either contains only one orbital of a pair (doubly occupied) or it contains both orbitals of a pair triplet coupled, the form and number of these configurations depends upon the number of electrons, the number of pairs and the spin multiplicity. The spin-pair coefficients $\{A\}$, which are usually not linearly independent, are used to define the energy coefficients needed to construct the field terms $\{H, R\}$ appearing in the orbital variational equations derived previously. The pair coefficients $\{\lambda\}$ and spin-coupling coefficient $\{\varepsilon\}$ needed to express ψ in terms of strongly orthogonal orbitals and standard spin-couplings are also functions of $\{A\}$. The functional relationships between all these coefficients also depend upon the number of noncore electrons, the number of pairs and the spin multiplicity.

Thus, solving for an SOGVB wavefunction involves an iterative process in which the spin-pair coefficient $\{A\}$, the core pair coefficients $\{\gamma\}$ and the orbitals $\{\phi\}$ are solved for self-consistency. As is usual, the orbitals are expressed in terms of a finite basis set :

$$\phi_\nu = \sum_i C_{i\nu} \chi_i$$

Therefore, orbital optimization is accomplished by self-consistently determining $\{C\}$. In practice, the iterative cycle is divided into four main sections:

1. MBSSEQ: The optimum spin-pair coefficients and optimum (orthogonal) mixing of the noncore orbitals with each other are determined.

2. OCBSE: The orbitals are sequentially optimized with respect to the space orthogonal to the current orbitals.

3. PAIRCI: The core orbital pair coefficients are optimized.

4. MIXORB: The core orbitals are optimally mixed with each other and with the noncore orbitals in an orthogonal manner. (Mixing of noncore orbitals with each other is accomplished in I).

In each of these sections, parameters not being optimized are frozen at their current values. This cycle is repeated as many times as necessary until self-consistency is achieved. Detailed general descriptions of each of these sections will now be given.

1. MBSSEQ

Ignoring the presence of a core, the SOGVB wavefunction in terms of orthogonal SEF configurations $\{\theta\}$ involving N orthonormal orbitals is:

$$\psi = \sum_{j} A_j \theta_j$$

In this section the equations for determining the optimum spin-pair coefficients $\{A\}$ are derived. In addition, the orbitals are optimized with respect to each other such that:

$$\phi_\nu = \sum_{i}^{N} C_{i\nu} \phi_i^\circ \qquad i = 1, N \quad ; \quad \langle \phi_i | \phi_j \rangle = \delta_{ij}$$

where $\{\phi^\circ\}$ are the initial guesses for the orbitals and $\{C\}$ are the adjustable mixing coefficients. This is all done using iterative configuration interaction techniques. Since the number and form of the configurations involved, as well as the nature of the dependencies within $\{A\}$, depend upon the number of electrons, the number of orbital pairs, and the spin multiplicity, only a general outline of the method used will be presented here. Specific details for cases already programmed are given in the Appendix.

The General Method

The wavefunction can always be written in terms of independent parameters $\{a\}$ such that:

$$\Psi = \mathcal{A} \prod_{i}^{F'} \Big[\sum_{j} a_{ji}\, \theta_{ji} \Big] + \sum_{k} a_k\, \theta_k$$

where F′ depends upon the number of orbital pairs and the spin multiplicity. If the two orbitals of a pair are allowed to mix orthogonally:

$$\phi_{m_1} = \mathcal{N} \left[\phi^{\circ}_{m_1} + C_{m_1 m_2}\, \phi^{\circ}_{m_2} \right] ; \quad \phi_{m_2} = \mathcal{N} \left[\phi^{\circ}_{m_2} - C_{m_1 m_2}\, \phi^{\circ}_{m_1} \right]$$

it can be shown that:

$$\Psi = \mathcal{A} \prod_{i}^{F} \Big[\sum_{j} b_{ji}\, \theta_{ji} \Big] + \sum_{k} b_k\, \theta_k \qquad (1)$$

where the coefficients $\{b\}$ are linearly independent. Hence, the optimum spin-pair coefficients and intrapair mixing coefficients can be found by solving for $\{b\}$ through a series of sequential configuration interaction calculations:

$$\psi_{w} = \sum_{\nu} b_{\nu w} \Big[\mathcal{A}\, \theta_{\nu w} \prod_{i+w}^{F} \Big(\sum_{j} b^{\circ}_{ji}\, \theta_{ji} \Big) \Big] + \sum_{k} b_k\, \theta_k$$

where b°_{ji} is a fixed (current value) parameter.

Keeping $\{b\}$ fixed, the remaining (interpair) mixing coefficients can be determined. In doing so, orbital orthogonality must be preserved. However, intrapair orthogonality need not be explicitly maintained since the energy of (1) is unaffected by reorthogonalization of these orbitals with subsequent redefinition of $\{b\}$. Thus, the orbitals of two pairs may be optimized with respect to each other by letting:

$$\phi_{m_1} = N_{m_1}[\phi^{\circ}_{m_1} + C_{n_1 m_1}\, \phi^{\circ}_{n_1} + C_{n_2 m_1} \phi^{\circ}_{n_2}]$$

$$\phi_{m_2} = N_{m_2}[\phi^{\circ}_{m_2} + C_{n_2 m_2}\, \phi^{\circ}_{n_1} + C_{n_2 m_2} \phi^{\circ}_{n_2}]$$

$$\phi_{n_1} = N_{n_1}[\phi^\circ_{n_1} - C_{n_1m_1}\phi^\circ_{m_1} - C_{n_1m_2}\phi^\circ_{m_2}]$$
$$\phi_{n_2} = N_{n_2}[\phi^\circ_{n_2} - C_{n_2m_1}\phi^\circ_{m_1} - C_{n_2m_2}\phi^\circ_{m_2}]$$

An unpaired orbital may be mixed with a pair by letting:

$$\phi_\nu = N_\nu[\phi^\circ_\nu + C_{m_1\nu}\phi^\circ_{m_1} + C_{m_2\nu}\phi^\circ_{m_2}]$$
$$\phi_{m_1} = N_{m_1}[\phi^\circ_{m_1} - C_{m_1\nu}\phi^\circ_\nu]$$
$$\phi_{m_2} = N_{m_2}[\phi^\circ_{m_2} - C_{m_2\nu}\phi^\circ_\nu]$$

whereas mixing of two unpaired orbitals is accomplished through a simple rotation:

$$\phi_\mu = N[\phi^\circ_\mu + C_{\nu\mu}\phi^\circ_\nu]$$
$$\phi_\nu = N[\phi^\circ_\nu - C_{\nu\mu}\phi^\circ_\mu]$$

By successively expanding the orbitals in terms of these three possibilities, one can express all the orbitals in terms of $\{\phi^\circ\}$ and $\{C\}$ while maintaining the required orthogonalities. Upon substituting $\{\phi\}$ in (1) and expanding, the wavefunction takes the general form:

$$\Psi = \psi_0 + \sum_i C_i \psi_i + \sum_{i \geq j} C_i C_j \psi_{(ij)} + \cdots$$

where it is assumed that $|C_i| \ll 1$. Since optimization is with respect to occupied space, a quadratically convergent solution for $\{C\}$ is required. This is accomplished by expressing the energy through second-order in $\{C\}$:

$$E = \frac{H_{oo} + 2\sum_{i} C_i H_{oi} + \sum_{i,j} C_i C_j \left[H_{ij} + H_{o(ij)} (1+\delta_{ij}) \right]}{S_{oo} + 2\sum_{i} C_i S_{oi} + \sum_{i,j} C_i C_j \left[S_{ij} + S_{o(ij)} (1+\delta_{ij}) \right]}$$

where $H_{ij} = \langle \psi_i | H | \psi_j \rangle$ and $S_{ij} = \langle \psi_i | \psi_j \rangle$. Letting :

$$\begin{array}{lll} \mathcal{H}_{oo} = H_{oo} & \mathcal{S}_{oo} = S_{oo} & \\ \mathcal{H}_{oi} = H_{oi} & \mathcal{S}_{oi} = S_{oi} & \\ \mathcal{H}_{ij} = H_{ij} + H_{o(ij)}(1+\delta_{ij}) & \mathcal{S}_{ij} = S_{ij} + S_{o(ij)}(1+\delta_{ij}) & i,j \neq 0 \end{array}$$

and $C'_i = C_i C'_o$:

$$E = \sum_{i,j=0} C'_i C'_j \mathcal{H}_{ij} \Big/ \sum_{i,j=0} C'_i C'_j \mathcal{S}_{ij}$$

Thus, $\{C\}$ is found by solving for the lowest energy root of (in matrix notation):

$$\underline{\mathcal{H}}\,\underline{C'} = \underline{E}\,\underline{\mathcal{S}}\,\underline{C'}$$

Paired orbitals can then be reorthogonalized with subsequent redefinition of $\{b\}$.

<u>N.B.</u>

1) Since the procedure described here is rapid compared to the initial construction of 1- and 2-electron integrals over $\{\phi^{\circ}\}$ from the primitive basis integrals, it is advantageous to iterate until $\{b\}$ and $\{C\}$ are self-consistent. In order to do this a CI matrix over the basic SEF configurations[9] must be generated using the new orbitals defined by the mixing coefficients. For cases already programmed, the most efficient way found to do this is to transform the current (full) CI matrix using a transformation matrix $\underline{D}$.

2) Since all core orbitals are doubly-occupied and each is orthogonal to all other orbitals, the presence of a fixed core can easily be taken into account by using a $\underline{h}_{\text{core}}$ integral matrix during CI matrix construction instead of the usual 1-electron integral $\underline{h}$ matrix:

$$\underline{h}_{core} = \underline{h} + \sum_{i}^{core} f_i \left[2\,\underline{J}_i - \underline{K}_i \right]$$

2. OCBSE[10]

In this section, the orbitals are sequentially optimized with respect to the space orthogonal to the current orbitals. If only orbital μ is optimized while keeping all other orbitals fixed, the variational condition is:

$$0 = \langle \delta_\mu | H_\mu | \mu \rangle + \langle \delta_\mu | R_\mu \rangle$$

where δ_μ must be orthogonal to all orbitals. For convenience, all orbitals are taken to be real.

If μ is expanded in terms of its current value (μ_0) and a set of NV orthonormal 'virtuals' $\{\chi\}$ which are orthogonal to all orbitals:

$$\mu = \frac{1}{N} \left[\mu_0 + \sum_i^{NV} c_i \chi_i \right] \qquad N = \left(1 + \sum_i c_i^2 \right)^{1/2}$$

then the linearly convergent solution for μ is obtained by solving:

$$\epsilon_\mu \langle \mu | \mu \rangle = \langle \mu | H_{\mu_0} | \mu \rangle + 2 \langle \mu | R_{\mu_0} \rangle$$

Therefore:

$$\epsilon_\mu \left(1 + \sum_i c_i^2 \right) = \langle \mu_0 + \sum_i c_i \chi_i | H_{\mu_0} | \mu_0 + \sum c_i \chi_i \rangle + 2N \langle \mu_0 + \sum c_i \chi_i | R_{\mu_0} \rangle$$

Assuming $\sum_i c_i^2 \ll 1$:

$$\begin{aligned} \epsilon_\mu \left(1 + \sum_i c_i^2 \right) = {} & \langle \mu_0 | H_{\mu_0} | \mu_0 \rangle + 2 \langle \mu_0 | R_{\mu_0} \rangle \\ & + 2 \sum_i c_i \left[\langle \chi_i | H_{\mu_0} | \mu_0 \rangle + \langle \chi_i | R_{\mu_0} \rangle \right] \\ & + \sum_{i,j} c_i c_j \left[\langle \chi_i | H_{\mu_0} | \chi_j \rangle + \delta_{ij} \langle \mu_0 | R_{\mu_0} \rangle \right] \end{aligned}$$

Therefore, if:

$$
\begin{aligned}
X_{00} &= \langle \mu_0 | H_{\mu_0} | \mu_0 \rangle + 2 \langle \mu_0 | R_{\mu_0} \rangle \\
X_{0i} &= \langle \chi_i | H_{\mu_0} | \mu_0 \rangle + \langle \chi_i | R_{\mu_0} \rangle & \qquad i > 0 \\
X_{ij} &= \langle \chi_i | H_{\mu_0} | \chi_j \rangle + \delta_{ij} \langle \mu_0 | R_{\mu_0} \rangle & \qquad i, j > 0 \\
C'_i &= C_i C'_0
\end{aligned}
$$

μ is obtained by solving (in matrix notation):

$$\underline{X}\,\underline{C}' = \underline{\epsilon}\,\underline{C}'$$

There are, of course, NV+1 solutions of this equation. The choice of which eigenvector to use for orbital μ is usually made in one of two ways. Orbital μ is either taken to be the eigenvector having the most negative eigenvalue or it is taken to be the eigenvector having the highest overlap with μ_0 (least change). Selection by eigenvalue is generally suitable for obtaining 'ground state' orbitals whereas selection by overlap is usually required to obtain 'excited state' orbitals. In many instances, both criteria lead to the same result. In the final analysis, the proper choice usually depends upon the particular problem at hand.

N.B.

Since the closed shell core orbitals all have the same H and R (R=0) terms, these orbitals can be simultaneously optimized by expanding each orbital in terms of each other and $\{\chi\}$. Mixing of these orbitals amongst themselves does not affect the energy. The eigenvectors obtained by diagonalization of $\underline{X}$ are, of course, orthogonal.

3. PAIRCI

In this section, the core pair coefficients $\{\gamma\}$ are optimized while keeping all other parameters fixed. Since:

$$Core = \left[\prod_{i}^{NDB} \phi_i^2 \alpha\beta \right] \prod_{i}^{NSG} \left(\gamma_{i_1} \phi_{i_1}^2 - \gamma_{i_2} \phi_{i_2}^2 \right) \alpha\beta \qquad ; \quad \gamma_{i_1}^2 + \gamma_{i_2}^2 = 1$$

these coefficients must be optimized iteratively one pair at a time.

The energy contribution of the nth core pair is:

$$E_n = \sum_{j=1}^{2} \gamma_{n_j}^2 \left[2 h_{n_j n_j} + J_{n_j n_j} + 2 \sum_{\nu \neq n_1 n_2} f_\nu \left(2 J_{\nu n_j} - K_{\nu n_j} \right) \right] - 2 \gamma_{n_1} \gamma_{n_2} K_{n_1 n_2}$$

Letting:

$$H_{jj} = h_{n_j n_j} + \tfrac{1}{2} J_{n_j n_j} + \sum_{\nu \neq n_1 n_2} f_\nu \left(2 J_{\nu n_j} - K_{\nu n_j} \right) \qquad j = 1,2$$

$$H_{12} = -\tfrac{1}{2} K_{n_1 n_2}$$

$$\epsilon_n = \tfrac{1}{2} E_n$$

$$\gamma_{n_1}^2 = 1 / (1 + \lambda^2)$$

$$\gamma_{n_2}^2 = \lambda^2 / (1 + \lambda^2)$$

$$\epsilon_n = \left[H_{11} + 2\lambda H_{12} + \lambda^2 H_{22} \right] / (1 + \lambda^2)$$

Requiring ϵ_n to be stationary with respect to λ ($\frac{\partial \epsilon_n}{\partial \lambda} = 0$) gives:

$$0 = \lambda^2 H_{12} - \lambda (H_{22} - H_{11}) - H_{12}$$

Therefore:

$$\lambda = \frac{H_{22} - H_{11}}{2 H_{12}} \pm \left[1 + \left(\frac{H_{22} - H_{11}}{2 H_{12}} \right)^2 \right]^{1/2} \qquad ; \quad H_{12} = 0 \Rightarrow \lambda = 0$$

where the root corresponding to the most negative ϵ_n is the desired one (since $K_{n_1, n_2} \geq 0$, this root always gives $\lambda \geq 0$).

Before solving for the coefficients of the next pair, f_{n_1} and f_{n_2} are redefined:

$$f_{n_1} = \gamma_{n_1}^{\ 2};\ f_{n_2} = \gamma_{n_2}^2$$

This process is continued until the $\{\gamma\}$ are self-consistent. Once this is achieved, the $\{f, a, b\}$ coefficients involving the core pairs are redefined:

$$f_\nu = \gamma_\nu^2$$

$$a_{\nu\nu} = f_\nu$$

$$\left.\begin{aligned} a_{\mu\nu} &= 2 f_\mu f_\nu \\ b_{\mu\nu} &= - f_\mu f_\nu \end{aligned}\right\} \quad \mu, \nu \text{ not in same core pair}$$

$$b_{n_1 n_2} = - \gamma_{n_1} \gamma_{n_2} \qquad n = 1, NSG$$

4. MIXORB

So far, we have considered optimizing the orbitals with respect to the space orthogonal to the orbitals and optimizing the noncore orbitals with respect to each other. There now remains the task of optimally mixing the core orbitals with each other and with the noncore orbitals. This, of course, must be done while maintaining orbital orthogonality. Moreover, since optimization is with respect to occupied space, a quadratically convergent solution is required." Both of these requirements can be most easily met by considering only two orbitals at a time. As usual, all orbitals will be taken to be real.

If orbitals μ and ν are allowed to change simultaneously, the variational condition is:

$$0 = \langle \delta_\mu | H_\mu | \mu \rangle + \langle \delta_\mu | R_\mu \rangle + \langle \delta_\nu | H_\nu | \nu \rangle + \langle \delta_\nu | R_\nu \rangle$$

subject to the constraint that $\langle \mu + \delta_\mu | \nu + \delta_\nu \rangle = 0$.

If:

$$\mu = \frac{1}{N}\left[\mu_0 + \Delta_\mu\right] \quad ; \quad \nu = \frac{1}{N}\left[\nu_0 + \Delta_\nu\right] \quad ; \quad N = (1+\Delta^2)^{1/2}$$

where μ_0 and ν_0 are the current guesses for orbitals μ and ν respectively, these orbitals can be obtained in a quadratically convergent manner by solving:

$$\begin{aligned}\epsilon_{\mu\nu} = {} & \langle \mu | H_{\mu_0} | \mu \rangle + 2\langle \mu | R_{\mu_0} \rangle + \langle \nu | H_{\nu_0} | \nu \rangle + 2\langle \nu | R_{\nu_0} \rangle \\ & + \langle \Delta_\mu | \Delta H_\mu | \mu_0 \rangle + \langle \Delta_\nu | \Delta H_\nu | \nu_0 \rangle + \langle \Delta_\mu | \Delta R_\mu \rangle + \langle \Delta_\nu | \Delta R_\nu \rangle\end{aligned}$$

provided $\Delta^2 \ll 1$. The first-order field time changes ΔH and ΔR are defined such that:

$$H_\mu = H_{\mu_0} + \Delta H_\mu + \cdots$$
$$R_\mu = R_{\mu_0} + \Delta R_\mu + \cdots$$

Choosing μ to always be a core orbital, $R_\mu = 0$. While R_ν may be nonzero, R_ν does not depend on μ or ν. Therefore:

$$\epsilon_{\mu\nu} = \langle \mu | H_{\mu_0} | \mu_0 \rangle + \langle \nu | H_{\nu_0} | \nu \rangle + 2 \langle \nu | R_{\nu_0} \rangle + \langle \Delta_\omega | \Delta H_\omega | \mu_0 \rangle + \langle \Delta_\nu | \Delta H_\nu | \nu_0 \rangle$$

Since μ_0 and ν_0 are being optimized only with respect to each other:

$$\Delta\mu = \lambda \nu_0 \text{ and } \Delta\nu = - \lambda \mu_0$$

where the rotation coefficient λ is an adjustable parameter which is assumed to be small. Therefore:

$$\epsilon_{\mu\nu} = \langle \mu | H_{\mu_0} | \mu_0 \rangle + \langle \nu | H_{\nu_0} | \nu \rangle + 2 \langle \nu | R_{\nu_0} \rangle + \lambda \langle \mu_0 | \Delta H_\mu - \Delta H_\nu | \nu_0 \rangle$$

Since:

$$\begin{aligned}\langle \mu_0 | \Delta H_\omega - \Delta H_\nu | \nu_0 \rangle &= \langle \mu_0 | (a_{\mu\mu} - a_{\mu\nu}) \Delta J_\mu + (b_{\mu\mu} - b_{\mu\nu}) \Delta K_\mu \\ &\quad + (a_{\nu\mu} - a_{\nu\nu}) \Delta J_\nu + (b_{\nu\mu} - b_{\nu\nu}) \Delta K_\nu | \nu_0 \rangle \\ &= \lambda \left[x K_{\mu_0\nu_0} + y J_{\mu_0\nu_0} \right]\end{aligned}$$

where:

$$y = b_{\mu\mu} + b_{\nu\nu} - b_{\mu\nu} - b_{\nu\mu}$$
$$x = 2 (a_{\mu\mu} + a_{\nu\nu} - a_{\mu\nu} - a_{\nu\omega}) +$$

Hence:

$$\epsilon_{\mu\nu} = \langle \mu | H_{\mu_0} | \mu \rangle + \langle \nu | H_{\nu_0} | \nu \rangle + 2 \langle \nu | R_{\nu_0} \rangle + \lambda^2 \left[x K_{\mu_0\nu_0} + y J_{\mu_0\nu_0} \right]$$

Expanding μ and ν and retaining terms through second order in λ:

$$\begin{aligned}\epsilon_{\mu\nu}(1+\lambda^2) = {} & \langle \mu_0 | H_{\mu_0} | \mu_0 \rangle + \langle \nu_0 | H_{\nu_0} | \nu_0 \rangle + 2 \langle \nu_0 | R_{\nu_0} \rangle \\ & + 2\lambda \left[\langle \mu_0 | H_{\mu_0} - H_{\nu_0} | \nu_0 \rangle - \langle \mu_0 | R_{\nu_0} \rangle \right] \\ & + \lambda^2 \left[\langle \mu_0 | H_{\nu_0} | \mu_0 \rangle + \langle \nu_0 | H_{\mu_0} | \nu_0 \rangle + \langle \nu_0 | R_{\nu_0} \rangle + x K_{\mu_0\nu_0} + y J_{\mu_0\nu_0} \right]\end{aligned}$$

Requiring $\epsilon_{\omega\nu}$ to be stationary with respect to λ $(\frac{\partial \epsilon_{\mu\nu}}{\partial \lambda} = 0)$ gives:

$$0 = C_0(1 - \lambda^2) + \lambda C_1$$

where:

$$C_0 = \langle \mu_0 | H_{\mu_0} - H_{\nu_0} | \nu_0 \rangle - \langle \mu_0 | R_{\nu_0} \rangle$$

$$C_1 = \langle \nu_0 | H_{\omega_0} - H_{\nu_0} | \nu_0 \rangle - \langle \mu_0 | H_{\mu_0} - H_{\nu_0} | \mu_0 \rangle - \langle \nu_0 | R_{\nu_0} \rangle + x K_{\mu_0\nu_0} + y J_{\mu_0\nu_0}$$

If $C_0 = 0$, $\lambda = 0$ as is required by the variational condition. If $C_0 \neq 0$:

$$\lambda = \frac{C_1}{2C_0} \pm \left[1 + \left(\frac{C_1}{2C_0} \right)^2 \right]^{1/2}$$

Since it was assumed that $\lambda^2 \ll 1$, only the smallest root is valid.

In theory, these rotations should be performed sequentially, using revised orbitals based on previous rotations. However, this is not practical. Instead, the orbitals are mixed through independent rotations. This, of course, can lead to nonorthogonalities which must be removed before continuing. The most satisfying way found to accomplish this is to orthogonalize sequentially based on increasing rotation coefficient magnitudes.

V. Illustrative Examples

Being only recently developed, the SOGVB method has been applied to only a few chemical systems. For the most part, the aim of these calculations has been to compare SOGVB results with previously obtained PPGVB and GVB solutions. As such, the following examples are presented simply to illustrate the general applicability of the SOGVB wavefunction.

A. CH Bond Formation[12]

1. The X $^2\pi$ State

Formation of the ground state of CH ($^2\pi$) provides a clear example of a reaction for which spin coupling optimization is essential. Ignoring the 1s carbon core electrons, the GVB orbitals for the ground ^3P state of carbon atom consist of two triplet coupled p-orbitals pointing along different axis and an sp hybridized singlet pair pointing in opposite directions along the remaining axes (Fig. 4). The $^2\pi$ state of CH can be envisioned to result when a ^2S hydrogen atom approaches a ^3P carbon atom along a p-orbital axis (Fig. 5). At infinite separation, the carbon orbitals must be coupled as in the atom. That is, orbitals p_y and p_z must be triplet coupled:

$$\Psi_{\infty} = \begin{array}{|c|c|} \hline \multicolumn{2}{|c|}{s_x \; s_{\bar{x}}} \\ \hline p_z & s_H \\ \cline{2-2} p_y & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} \qquad \text{(A)}$$

However, at equilibrium the C-H bond is expected to be described by singlet pairing between orbitals p_z and s_H (we retain atomic designations, realizing that orbitals do in fact change during molecular formation):

$$\Psi_e = \begin{array}{|cc|}\hline s_x & s_{\bar{x}} \\ \hline p_z & s_H \\ \hline \multicolumn{1}{|c|}{p_y} & \\ \cline{1-1}\end{array} \qquad \text{(B)}$$

Therefore, the simplest wavefunction capable of describing formation of this molecule from its constituent atoms is a linear combination of the atomic and molecular couplings:

$$\Psi = \varepsilon_\infty \begin{array}{|c|c|}\hline \multicolumn{2}{|c|}{s_x\ s_{\bar{x}}} \\ \hline p_z & s_H \\ \cline{2-2} p_y & \multicolumn{1}{|c}{} \\ \cline{1-1}\end{array} + \varepsilon_e \begin{array}{|cc|}\hline s_x & s_{\bar{x}} \\ \hline p_z & s_H \\ \hline \multicolumn{1}{|c|}{p_y} & \\ \cline{1-1}\end{array} \qquad |\varepsilon_\infty| + |\varepsilon_e| = 1$$

where ε_∞ is expected to decrease from unity as ε_e increases in magnitude from zero to approach unity as the internuclear distance decreases from infinity.

In going from infinite to equilibrium C-H separation the changes in the orbitals themselves are straightforward (Fig. 6). The carbon p_z orbital (ϕ_3) gradually hybridizes into the internuclear region. The hydrogen orbital (ϕ_6) polarizes somewhat toward carbon, but remains essentially atomiclike. The $\overline{s_x s_{\bar{x}}}$ singlet pair (only one of which is shown) gradually bends back away from the internuclear region, remaining orthogonal to the bonding pair. The carbon p_y orbital (not shown) remains virtually unchanged throughout.

The coupling between orbitals p_y, p_z, and s_H also changes as the internuclear separation is decreased. In Fig. 7 we see that, as expected, molecular coupling (B) becomes of increasing importance as the internuclear distance decreases and the overlap between orbitals ϕ_3 (p_z) and ϕ_5 (s_H) increases. At equilibrium, this coupling vastly dominates over residual atomic coupling (A).

The SOGVB and GVB descriptions for formation of this molecule are essentially identical since minimization of repulsive interactions favors keeping the $\overline{s_x s_{-x}}$ pair orthogonal to the bonding pair. Comparing this spin coupling optimized description to the PPGVB wavefunction (Fig, 8), we see that while the former behaves properly at all internuclear distances, the PPGVB wavefunction dissociates incorrectly to a carbon ^3P-^1D mixture.

2. The A $^2\Delta$ State

The GVB description of the ^1D state of carbon atom differs from that of the ^3P state only in that the singly-occupied p-orbitals are singlet paired. The low-lying $^2\Delta$ state of CH can be envisioned to result when a ^2S hydrogen atom approaches a ^1D carbon atom along the axis of hybridization (Fig. 9). At infinite separation, the carbon orbitals must be coupled as in the atom. That is, orbitals s_z and s_{-z} must be singlet paired as must orbitals p_x and p_y:

$$\psi_\infty = \begin{array}{|c|c|}\hline p_x & p_y \\ \hline s_z & s_{\bar{z}} \\ \hline s_H & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

Assuming orbitals remain localized, at equilibrium we can expect the C-H bond to be described by singlet pairing between orbitals s_z and s_H:

$$\psi_c = \begin{array}{|c|c|}\hline p_x & p_y \\ \hline s_z & s_H \\ \hline s_{\bar{z}} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

Therefore, the simplest localized orbital wavefunction capable of describing formation of this molecule is a linear combination of these atomic and molecular couplings:

$$\psi = \varepsilon_{12} \begin{array}{|c|c|}\hline p_x & p_y \\ \hline \phi_1 & \phi_2 \\ \hline \phi_3 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \varepsilon_{13} \begin{array}{|c|c|}\hline p_x & p_y \\ \hline \phi_1 & \phi_3 \\ \hline \phi_2 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

However, just as in the case of the H_2 + D exchange reaction, the sigma orbitals do not remain localized (Fig. 10). Only the carbon s_z orbital (ϕ_1) remains localized. The $s_{\bar{z}}$ orbital (ϕ_2) gradually delocalizes, while maintaining high overlap with ϕ_1, and finally relocalizes as the hydrogen centered bonding orbital. Simultaneously, orbital s_H (ϕ_3) also delocalizes so as to remain orthogonal to ϕ_1 and ϕ_2. This orbital finally relocalizes as the nonbonding sigma orbital. As expected, the singlet paired p_x and p_y orbitals (not shown) remain virtually unchanged throughout.

Orbital recoupling is also analogous to that observed for the H_2 + D reaction. As shown in Fig. 11, at large internuclear distances the atomiclike orbitals recouple as expected, with ε_{12} decreasing as ε_{13} increases in magnitude. However, owing to delocalization and subsequent relocalization of ϕ_2 and ϕ_3, this change deviates from the localized orbital idealization with $\mathcal{E}_{12}$ reaching its minimum value at full delocalization. As ϕ_2 and ϕ_3 relocalize, this trend reverses since singlet pairing between ϕ_1 and ϕ_2 now corresponds to molecular coupling.

Since orbitals ϕ_1 and ϕ_2 always remain highly overlapping while ϕ_3 always remains virtually orthogonal to these two orbitals even when strong orthogonality is not imposed, the SOGVB description for formation of this molecule is essentially the same as the GVB description. However, while the PPGVB wavefunction behaves correctly both near equilibrium and at large distances, it is discontinuous in intermediate regions (Fig. 12). Thus, even in cases where the PPGVB wavefunction adequately describes both the initial and final states, it can be incapable of continuously describing transition regions.

B. Formation of The Low-Lying $^1\pi$ and $^3\pi$ States of Boron Hydride [13, 14]

The GVB valence orbitals for the ground state of boron atom are analogous to those of carbon. That is, the valence shell consists of an sp hybridized singlet pair and a lone p-orbital (Fig. 12). Pi states can be envisioned to result when a hydrogen atom approaches a boron atom along the hybridization axis (Fig. 13). Considering a localized orbital description for formation of the $^1\pi$ and $^3\pi$ states, the initial boron $\overline{s_z s_{\bar{z}}}$ singlet pair must break in order for the $\overline{s_z s_H}$ bonding pair to form. Therefore, the wavefunctions for these molecules can be expected to be linear combinatons of the atomic and molecular couplings:

$$\Psi_{{}^3\pi} = \mathcal{E}_{12} \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \multicolumn{1}{|c}{} \\ \cline{1-1} p_x & \multicolumn{1}{|c}{} \\ \cline{1-1}\end{array} + \mathcal{E}_{13} \begin{array}{|c|c|}\hline \phi_1 & \phi_3 \\ \hline \phi_2 & \multicolumn{1}{|c}{} \\ \cline{1-1} p_x & \multicolumn{1}{|c}{} \\ \cline{1-1}\end{array}$$

$$\Psi_{{}^1\pi} = \mathcal{E}_{12} \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & p_x \\ \hline\end{array} + \mathcal{E}_{13} \begin{array}{|c|c|}\hline \phi_1 & \phi_3 \\ \hline \phi_2 & p_x \\ \hline\end{array}$$

where ϕ_1, ϕ_2, and ϕ_3 are initially orbitals s_z, $s_{\tilde{z}}$, and s_H respectively (for simplicity, we have omitted the $1s^2$ core orbital).

However, just as with formation of CH ($^2\Delta$), the sigma orbitals do not remain localized. As line plots for the $^3\pi$ state show (Fig. 15), only ϕ_1 remains localized. Orbitals ϕ_2 and ϕ_3 gradually delocalize and relocalize to effectively exchange initial identities. As in the H_2 + D reaction and CH ($^2\Delta$) formation, this occurs in such a way so as to maintain high overlap between ϕ_1 and ϕ_2 while ϕ_3 remains orthogonal to both of these orbitals.

Owing to these orbital changes, recoupling between them deviates from the localized orbital idealization in which $\mathcal{E}_{12}$ continually decreases from unity as $|\mathcal{E}_{13}|$ increases from zero to approach unity at equilibrium (Figs. 16 and 17). In addition, for the $^3\Pi$ state we see that a third allowed coupling in which orbitals ϕ_1 and p_x are singlet paired contributes at smaller internuclear distances. The net effect of this is to allow for favorable quartet coupling between orbitals ϕ_2 , ϕ_3 , and p_y. However, because of the simultaneously required unfavorable $\overline{\phi_1 \, p_x}$ singlet pairing, this coupling is always only of minor importance.

Comparing the SOGVB, GVB, and PPGVB results at 3.5 $a_\circ$, we find for the $^3\pi$ state that the SOGVB energy differs from the GVB energy of -3.8167 a. u. by only 10^{-5} a. u. . However, the PPGVB energy of -3.8042 a. u. is 0.3 ev higher. Optimizing the spin coupling between these PPGVB orbitals lowers this energy by less than 0.1 ev. For the $^1\pi$ state at 3.5 $a_\circ$, the SOGVB energy is 0.002 a. u. higher than the GVB energy of -3.8060 a. u.. This difference, which is due to strong orthogonality, is easily eliminated through a minimum basis set CI. As with the triplet state, the PPGVB energy is over a quarter of an ev higher and is little changed by optimization of the coupling between the PPGVB orbitals.

C. Formation of Oxygen Molecule [15]

Since GVB solutions can only be obtained for small numbers of electrons, GVB calculations of many chemically interesting systems cannot be obtained despite the fact the spin coupling optimization only involves a few orbitals. This is because changes in other orbitals which are not involved in orbital recoupling must also be taken into account. The SOGVB method overcomes this problem by allowing for inclusion of doubly-occupied and strongly orthogonal singlet paired orbitals as well. To demonstrate this, let's consider formation of the low-lying singlet and triplet states of O_2.

The GVB description of the ground state of oxygen atom (^3P) is essentially identical to the Hartree-Fock description. That is, aside from the $1s^2$ core orbital, the valence shell consists of a doubly-occupied 2s orbital, a doubly-occupied p-orbital and two singly-occupied p-orbitals which are triplet coupled (Fig. 18). Keeping orbital occupations fixed, the SOGVB wavefunctions for the low-lying states of O_2 consist of six doubly-occupied (core) orbitals and four singly-occupied orbitals.

The lowest triplet and singlet states of O_2 can be envisioned to result when two ^3P oxygen atoms approach each other along a singly-occupied p-orbital axis, with the remaining two singly occupied p-orbitals being in different molecular planes (Fig. 19). At infinite separation, these p-orbitals must be coupled as in the atoms. That is, each of the singly-occupied p-orbital pairs on each center must be triplet coupled:

$$\Psi^{(\infty)}_{^3\Sigma_g^-} \quad \sqrt{\tfrac{2}{3}} \begin{array}{|c|c|} \hline \multicolumn{2}{|c|}{\text{Core}} \\ \hline p_{z\ell} & p_{zr} \\ \cline{2-2} p_{y\ell} & \multicolumn{1}{|c}{} \\ \cline{1-1} p_{xr} & \multicolumn{1}{|c}{} \\ \cline{1-1} \end{array} + \sqrt{\tfrac{1}{3}} \begin{array}{|c|c|} \hline \multicolumn{2}{|c|}{\text{CORE}} \\ \hline p_{z\ell} & p_{xr} \\ \cline{2-2} p_{y\ell} & \multicolumn{1}{|c}{} \\ p_{zr} & \multicolumn{1}{|c}{} \\ \cline{1-1} \end{array} = \left[\boxed{\text{Core}} : \begin{array}{|c|} \hline p_{z\ell} \\ p_{y\ell} \\ \hline \end{array} : \begin{array}{|c|} \hline p_{zr} \\ p_{xr} \\ \hline \end{array} \right]_T$$

$$\Psi^{(\infty)}_{{}^1\Delta_g} = \begin{array}{|c|c|}\hline \multicolumn{2}{|c|}{\text{core}} \\ \hline p_{z_l} & p_{z_r} \\ p_{y_l} & p_{x_r} \\ \hline \end{array}$$

(where we have identified these as being the ${}^3\Sigma_g^-$ and ${}^1\Delta_g$ states even though the wavefunctions actually represent only one component of the proper symmetry functions).

However, at equilibrium, the O-O bond is expected to be described by singlet pairing between orbitals $p\,z_l$ and pz_r:

$$\Psi^{(e)}_{{}^3\Sigma_g^-} = \begin{array}{|c|c|}\hline \multicolumn{2}{|c|}{\text{core}} \\ \hline p_{z_l} & p_{z_r} \\ \hline \multicolumn{1}{|c|}{p_{y_l}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{p_{x_r}} & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array}$$

$$\Psi^{(e)}_{{}^1\Delta_g} = \begin{array}{|c|c|}\hline \multicolumn{2}{|c|}{\text{core}} \\ \hline p_{z_l} & p_{z_r} \\ \hline p_{y_l} & p_{y_r} \\ \hline \end{array}$$

Therefore, just as in the case of CH (${}^2\pi$) formation, the simplest wavefunctions capable of describing formation of these molecules from the constituent atoms is a linear combination of the atomic and molecular couplings:

$$\Psi_{{}^3\Sigma_g^-} = \mathcal{E}_e \begin{array}{|c|c|}\hline \multicolumn{2}{|c|}{\text{core}} \\ \hline p_{z_l} & p_{z_r} \\ \hline \multicolumn{1}{|c|}{p_{y_l}} & \multicolumn{1}{c}{} \\ \multicolumn{1}{|c|}{p_{x_r}} & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} + \mathcal{E}_\infty \left[\boxed{\text{core}} : \begin{array}{|c|}\hline p_{z_l} \\ p_{y_l} \\ \hline \end{array} : \begin{array}{|c|}\hline p_{z_r} \\ p_{x_r} \\ \hline \end{array} \right]_T$$

$$\psi_{{}^1\Delta_g} = \mathcal{E}_e \begin{array}{|c|}\hline \text{core} \\ \hline p_{zl}\,p_{zr} \\ \hline p_{yl}\,p_{xr} \\ \hline \end{array} + \mathcal{E}_\infty \begin{array}{|c|c|}\hline \multicolumn{2}{|c|}{\text{core}} \\ \hline p_{zl} & p_{zr} \\ p_{yl} & p_{xr} \\ \hline \end{array}$$

As seen from the potential energy curves in Fig. 20, the SOGVB wavefunctions for these states behave properly at all internuclear distances. This is in contrast to the PPGVB wavefunctions which, of course, cannot dissociate correctly. Moreover, at large distances the PPGVB wavefunctions actually order these states incorrectly. For example, at 4.0 a_0 the PPGVB energies of -149.5717 and -149.5712 for the triplet and singlet states, respectively, are not only too high, but also order the triplet lower than the singlet.

The orbital changes during molecule formation are straightforward. As would be expected, the 1s core orbitals remain essentially unchanged The 2s orbitals hybridize somewhat away from the internuclear region as the bonding orbitals hybridize somewhat into the internuclear region. The doubly-occupied p-orbitals delocalize onto the adjacent center while the singly-occupied p-orbitals do likewise. The final set of orbitals for the ${}^3\Sigma_g^-$ state are shown in Fig. 21. Thus, we see that there are significant changes in all of the oxygen atom valence orbitals during molecule formation and that this is why a wavefunction in which doubly-occupied orbitals are frozen as atomic orbitals (which is what would have to be done in GVB calculations) cannot adequately describe these molecules.

As the internuclear distance is decreased and the orbitals readjust, the coupling between these orbitals also changes. As expected, as the O-O separation decreases and the overlap between the bonding orbitals increases, molecular coupling becomes of increasing importance. At equilibrium, this coupling vastly dominates over residual atomic coupling. These changes are perfectly analogous to that observed during formation of the $^2\pi$ state of CH.

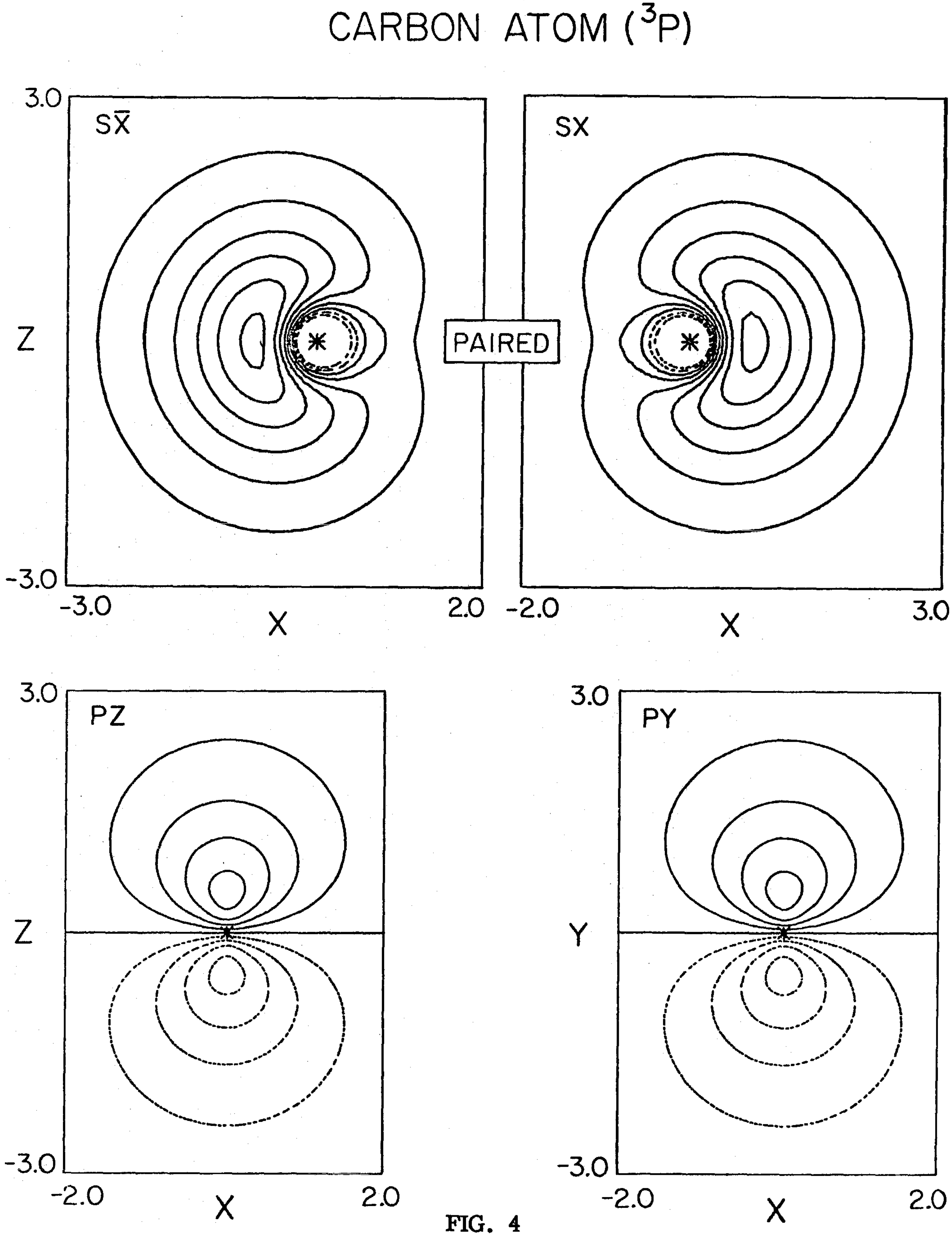
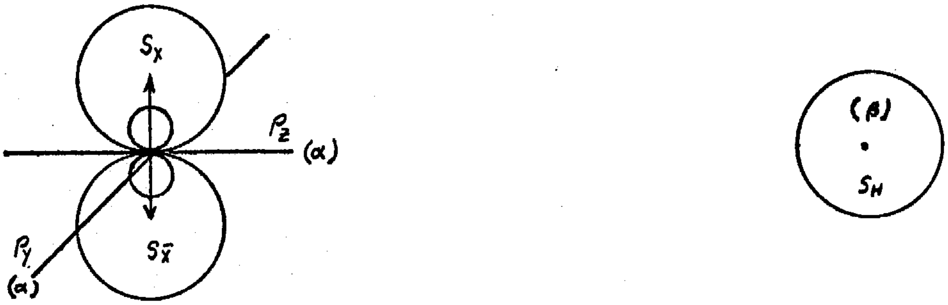
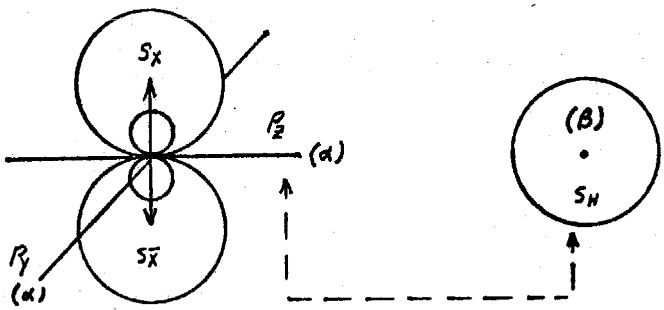

CARBON ATOM (^{3}P)
S$\bar{X}$
SX
PAIRED
3.0
-3.0
-3.0
2.0
-2.0
3.0
Z
X
X
PZ
PY
3.0
-3.0
-2.0
2.0
Z
X
3.0
-3.0
-2.0
2.0
Y
X

FIG. 4

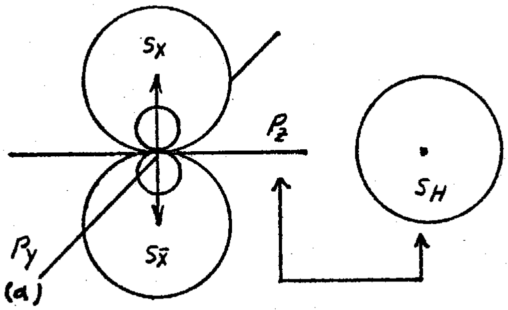
CH $^2\Pi$ FORMATION



a. Infinite Separation



b. Intermediate Separation



c. Equilibrium

FIG. 5

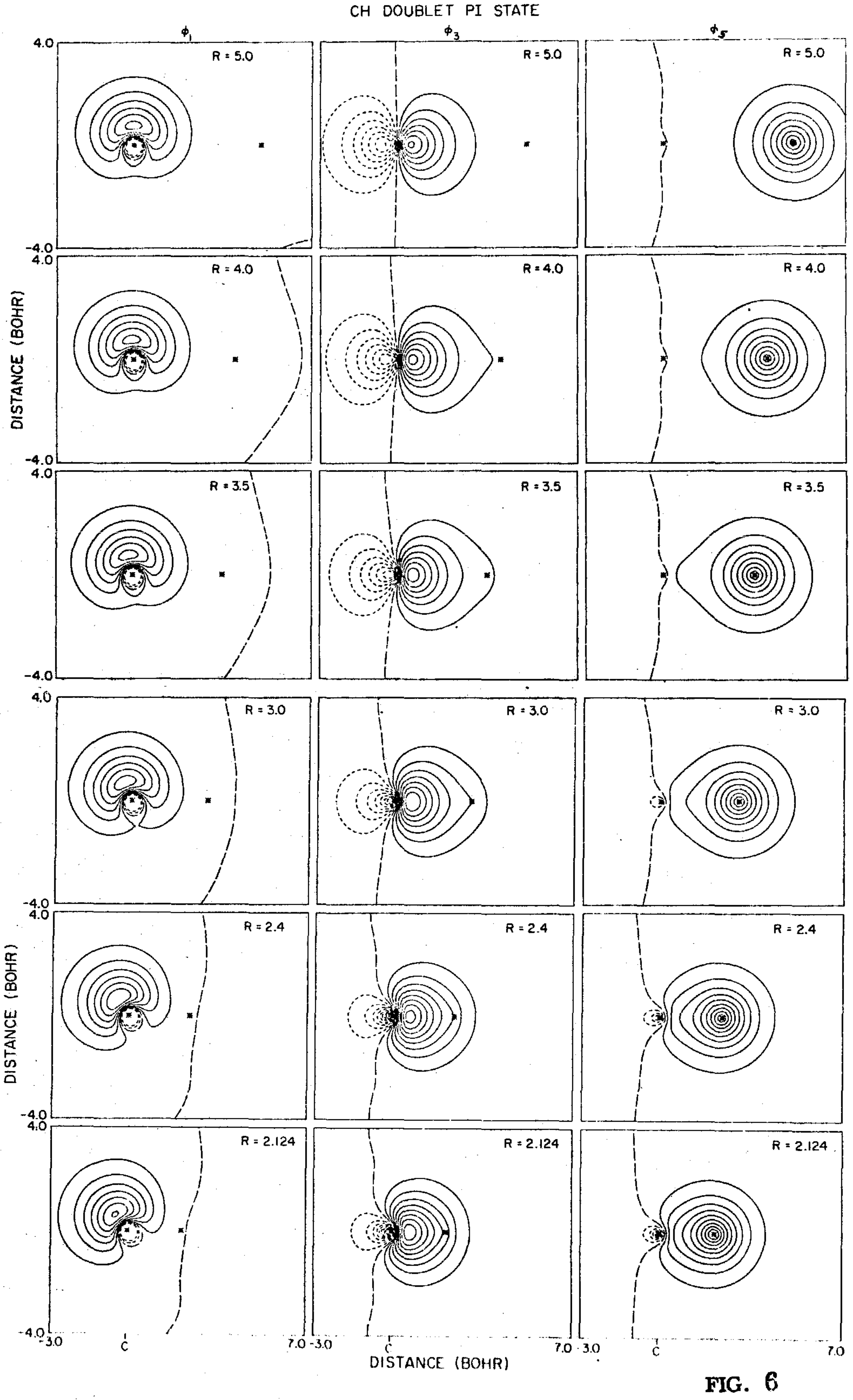

CH DOUBLET PI STATE
ϕ_1
ϕ_3
ϕ_5
R = 5.0
R = 4.0
R = 3.5
R = 3.0
R = 2.4
R = 2.124
4.0
-4.0
DISTANCE (BOHR)
-3.0
C
7.0
DISTANCE (BOHR)

FIG. 6

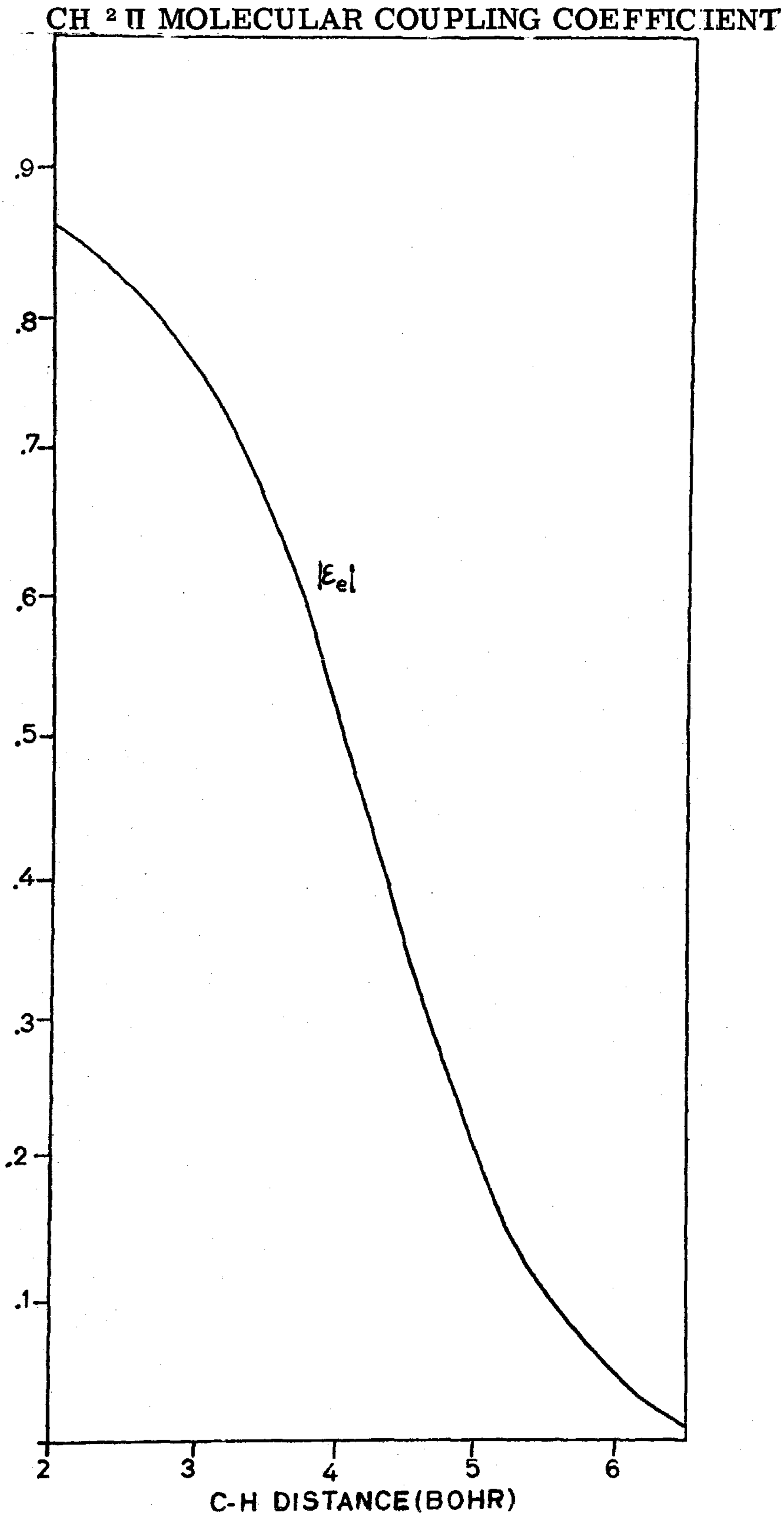

CH ²Π MOLECULAR COUPLING COEFFICIENT
.9
.8
.7
.6
.5
.4
.3
.2
.1
$|\varepsilon_e|$
2
3
4
5
6
C-H DISTANCE (BOHR)

FIG. 7

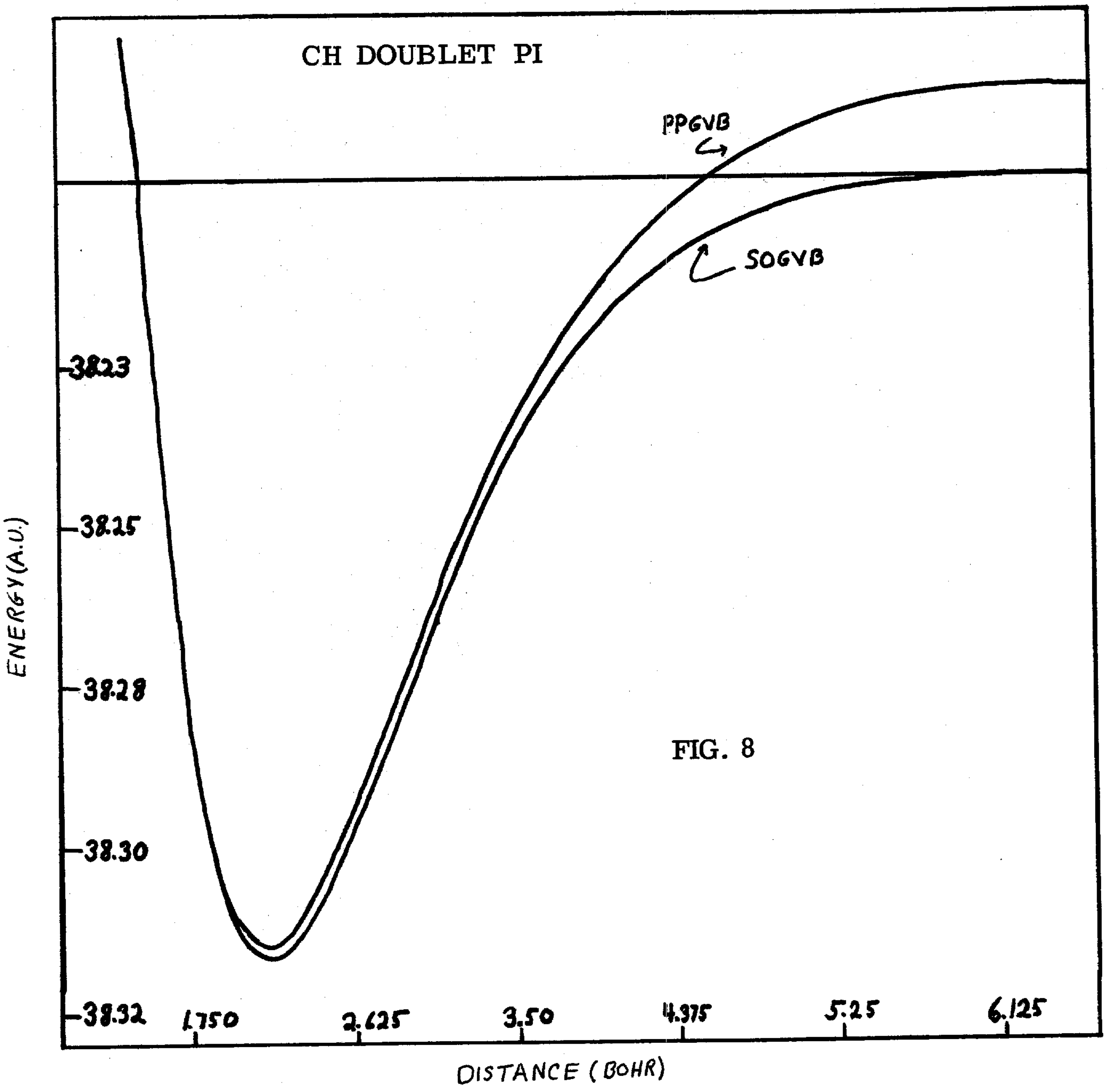
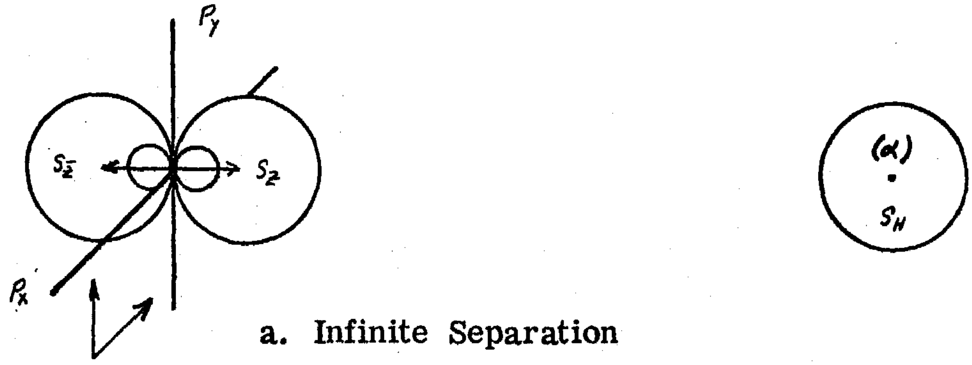
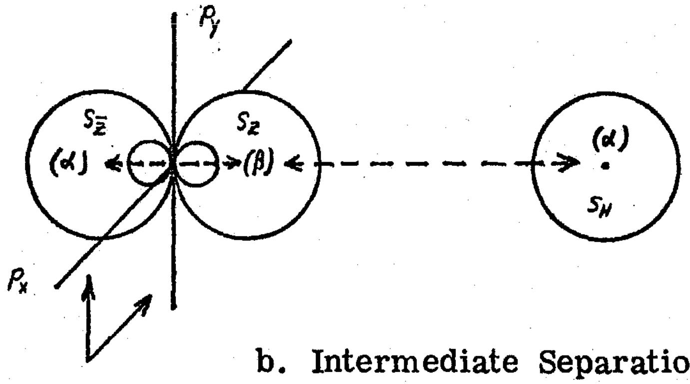

CH DOUBLET PI
PPGVB
SOGVB
-38.23
-38.25
-38.28
-38.30
-38.32
ENERGY (A.U.)
1.750
2.625
3.50
4.375
5.25
6.125
DISTANCE (BOHR)

FIG. 8

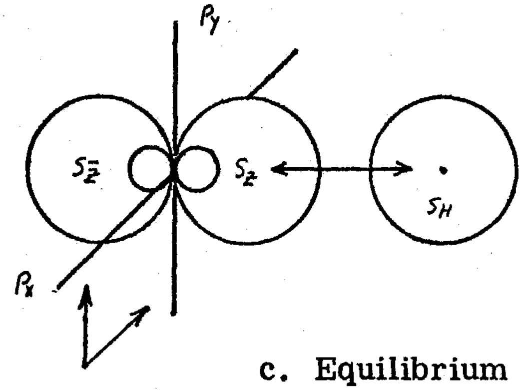
CH $^2\Delta$ FORMATION



a. Infinite Separation



b. Intermediate Separation



c. Equilibrium

FIG. 9

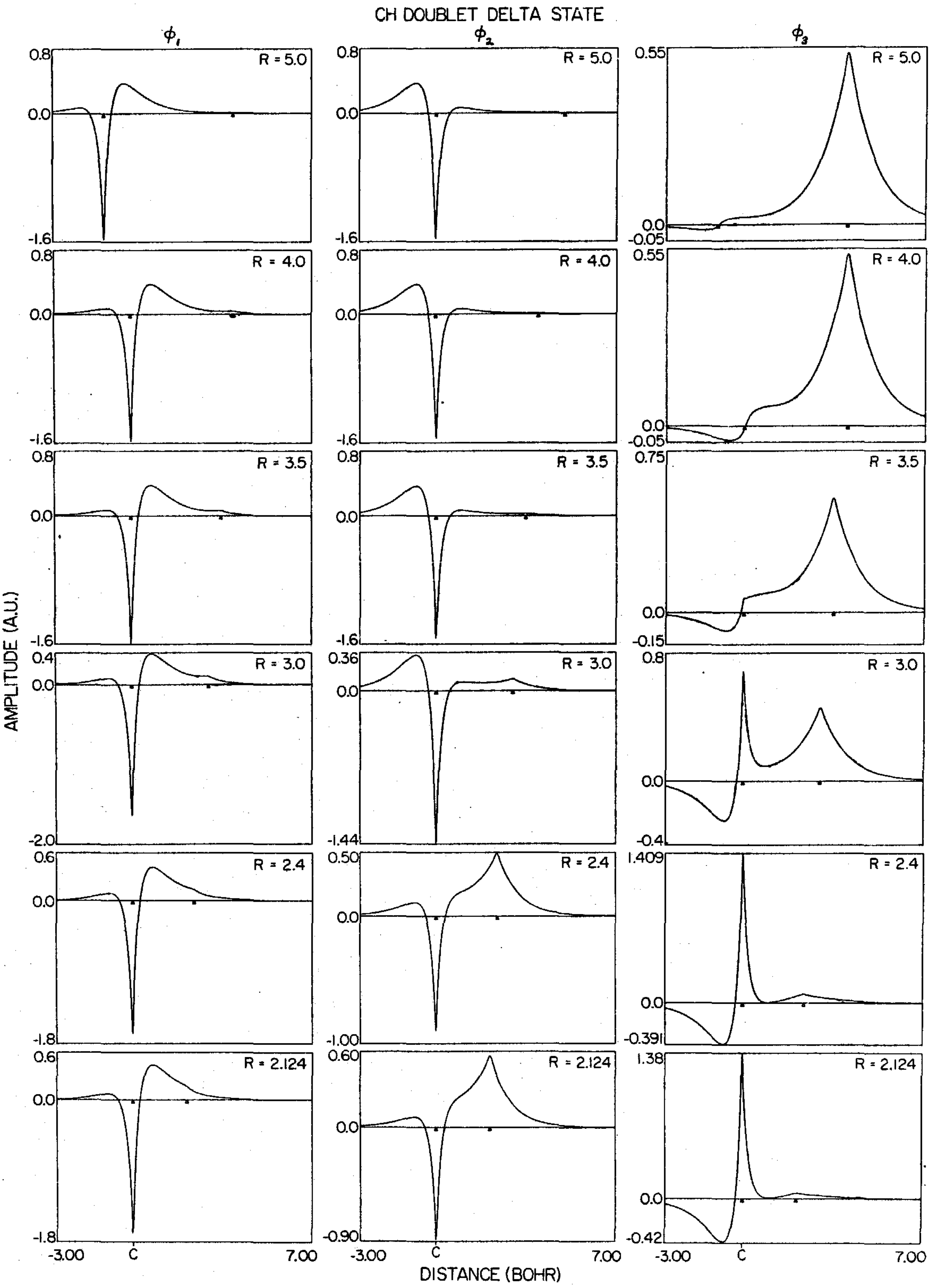
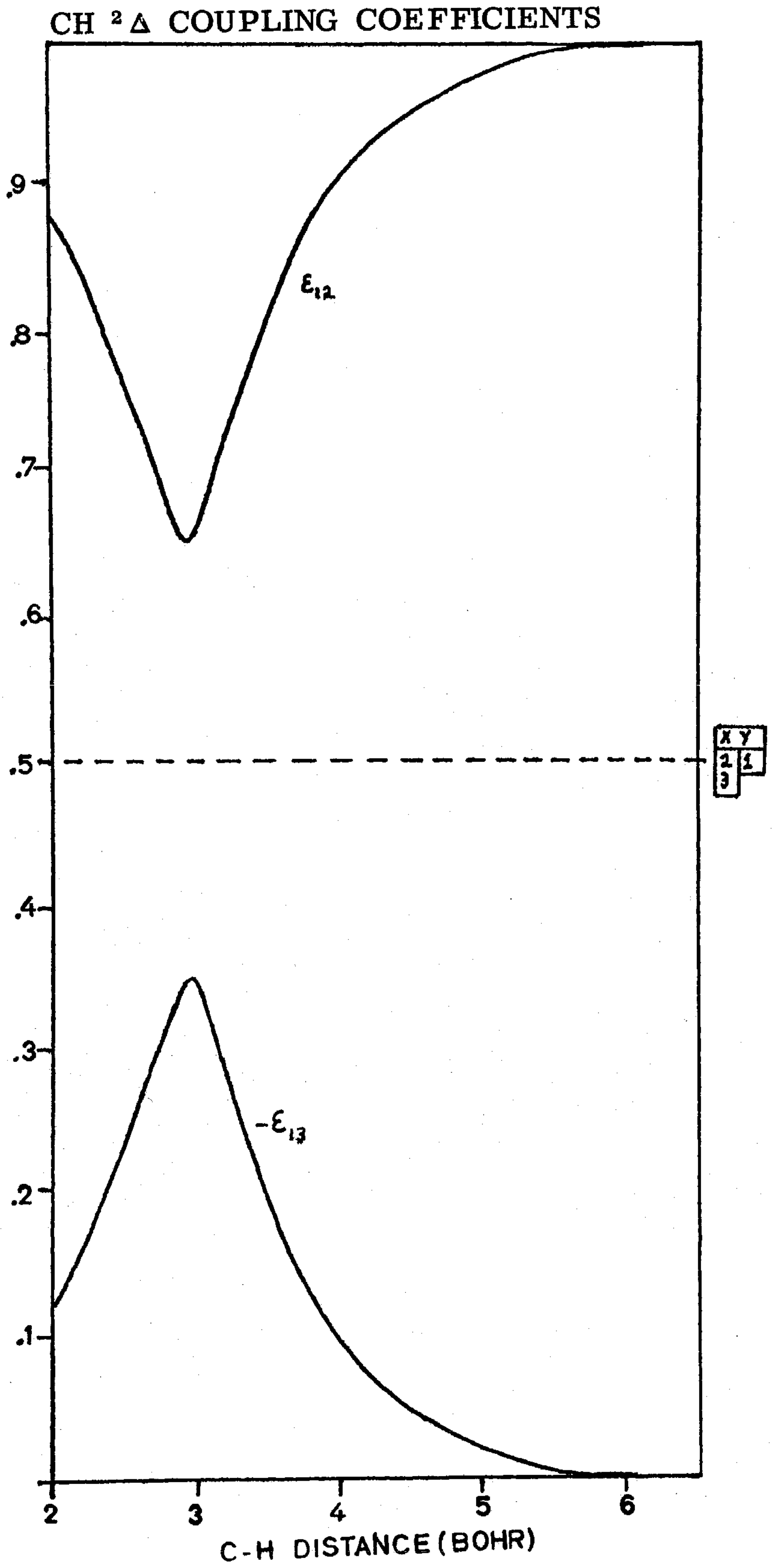

CH DOUBLET DELTA STATE
ϕ_1
ϕ_2
ϕ_3
R = 5.0
R = 4.0
R = 3.5
R = 3.0
R = 2.4
R = 2.124
0.8
0.0
-1.6
0.55
-0.05
0.75
-0.15
0.4
-2.0
0.36
-1.44
-0.4
0.6
-1.8
0.50
-1.00
1.409
-0.391
0.60
-0.90
1.38
-0.42
AMPLITUDE (A.U.)
-3.00
C
7.00
DISTANCE (BOHR)

FIG. 10



CH ²Δ COUPLING COEFFICIENTS

FIG. 11

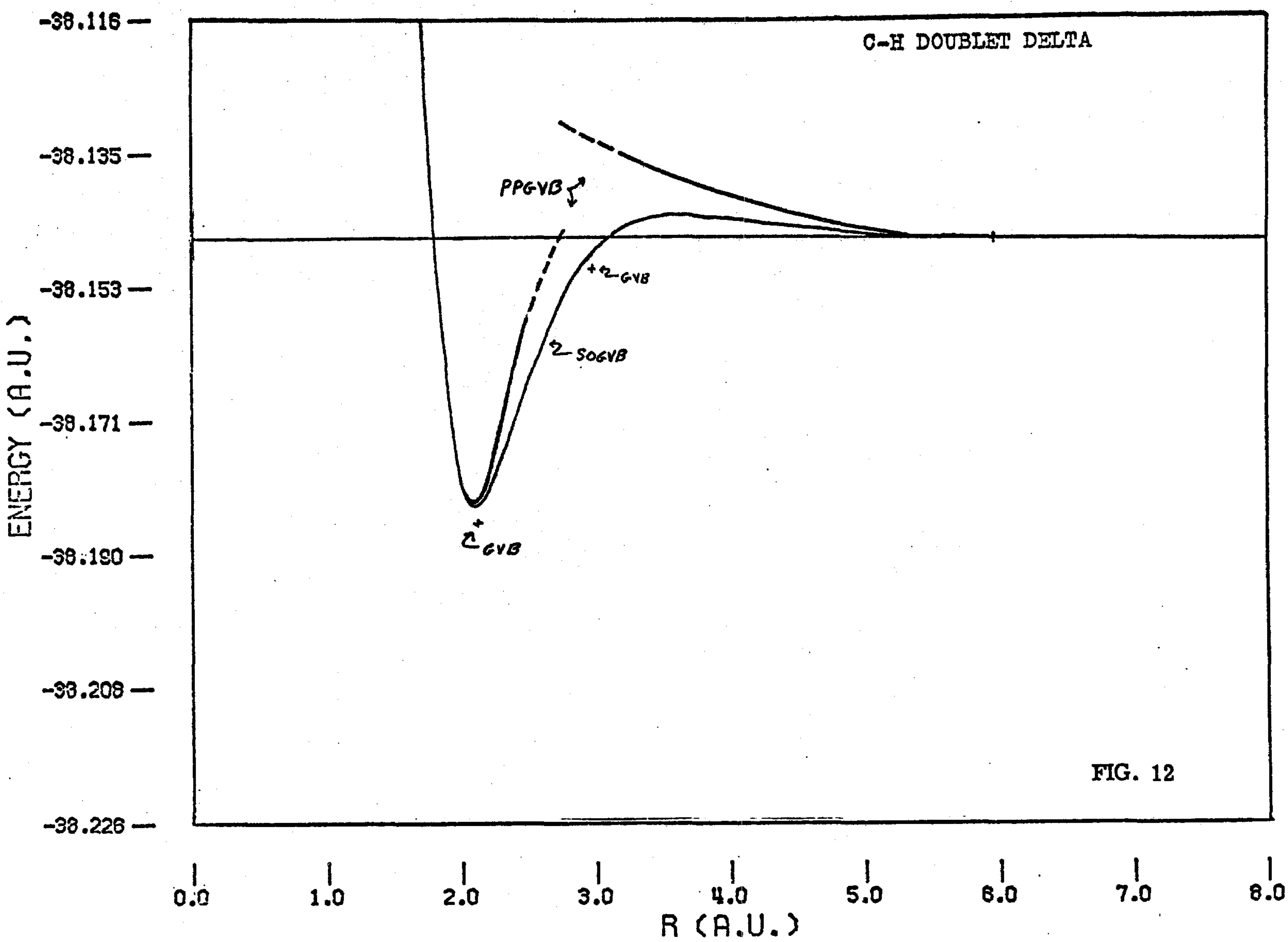

C-H DOUBLET DELTA
PPGVB
+ GVB
SOGVB
+ GVB
-38.116
-38.135
-38.153
-38.171
-38.190
-38.208
-38.226
ENERGY (A.U.)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
R (A.U.)

FIG. 12

BORON ATOM (^2P)

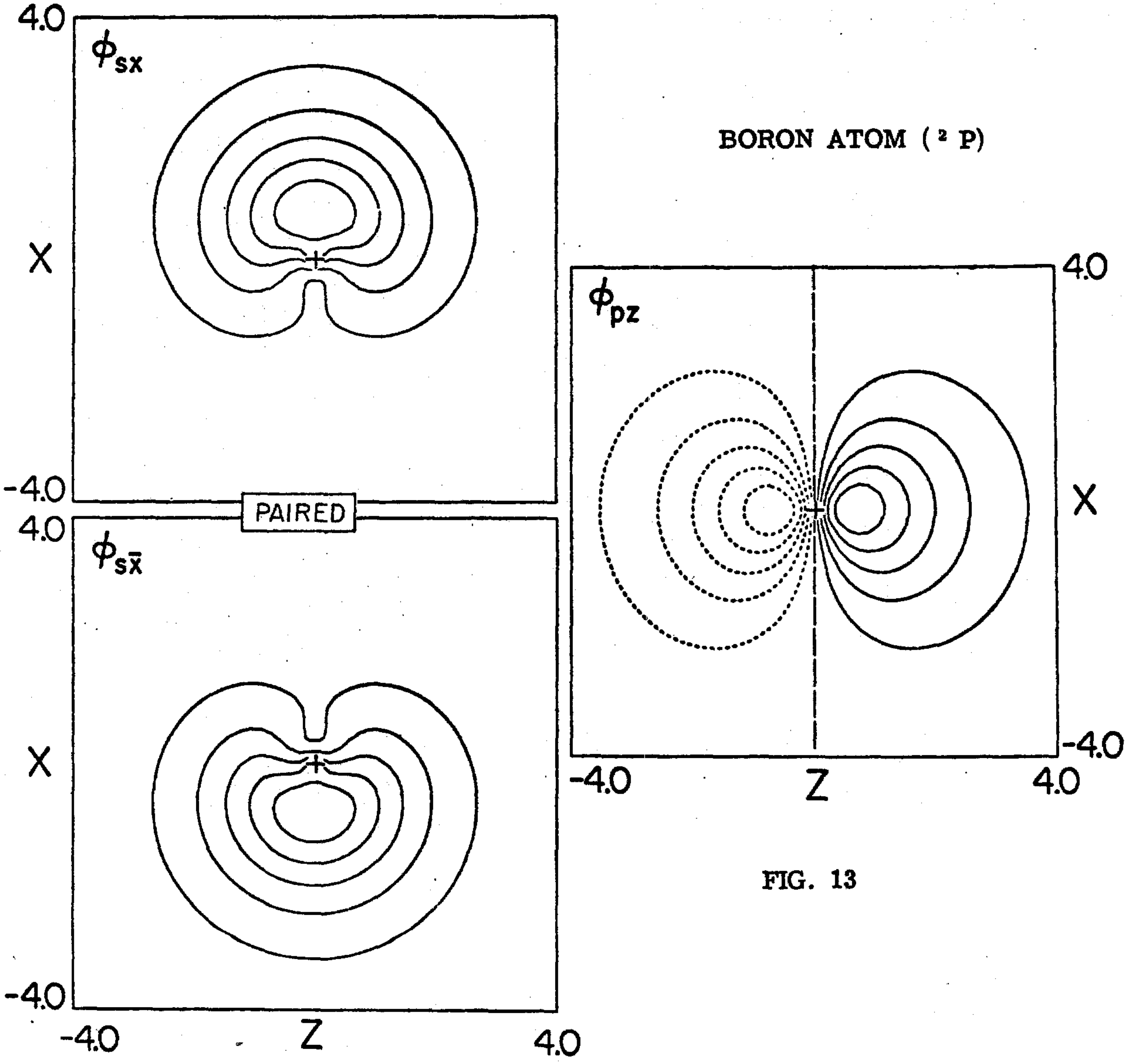
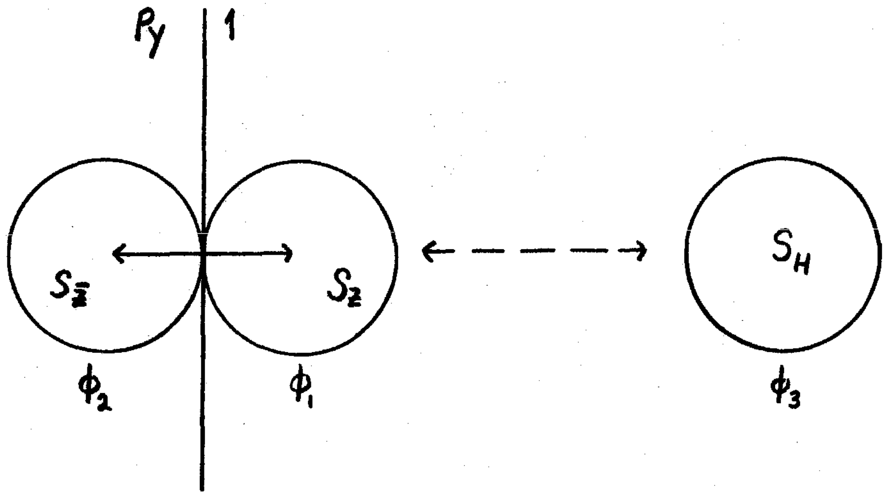


FIG. 13

BH PI FORMATION



$$\Psi_{^1\pi} = \varepsilon_{12} \begin{array}{|cc|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & P_y \\ \hline \end{array} + \varepsilon_{13} \begin{array}{|cc|}\hline \phi_1 & \phi_3 \\ \hline \phi_2 & P_y \\ \hline \end{array}$$

$$\Psi_{^3\pi} = \varepsilon_{12} \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \multicolumn{1}{c}{} \\ P_y & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} + \varepsilon_{13} \begin{array}{|c|c|}\hline \phi_1 & \phi_3 \\ \hline \phi_2 & \multicolumn{1}{c}{} \\ P_y & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array}$$

FIG. 14

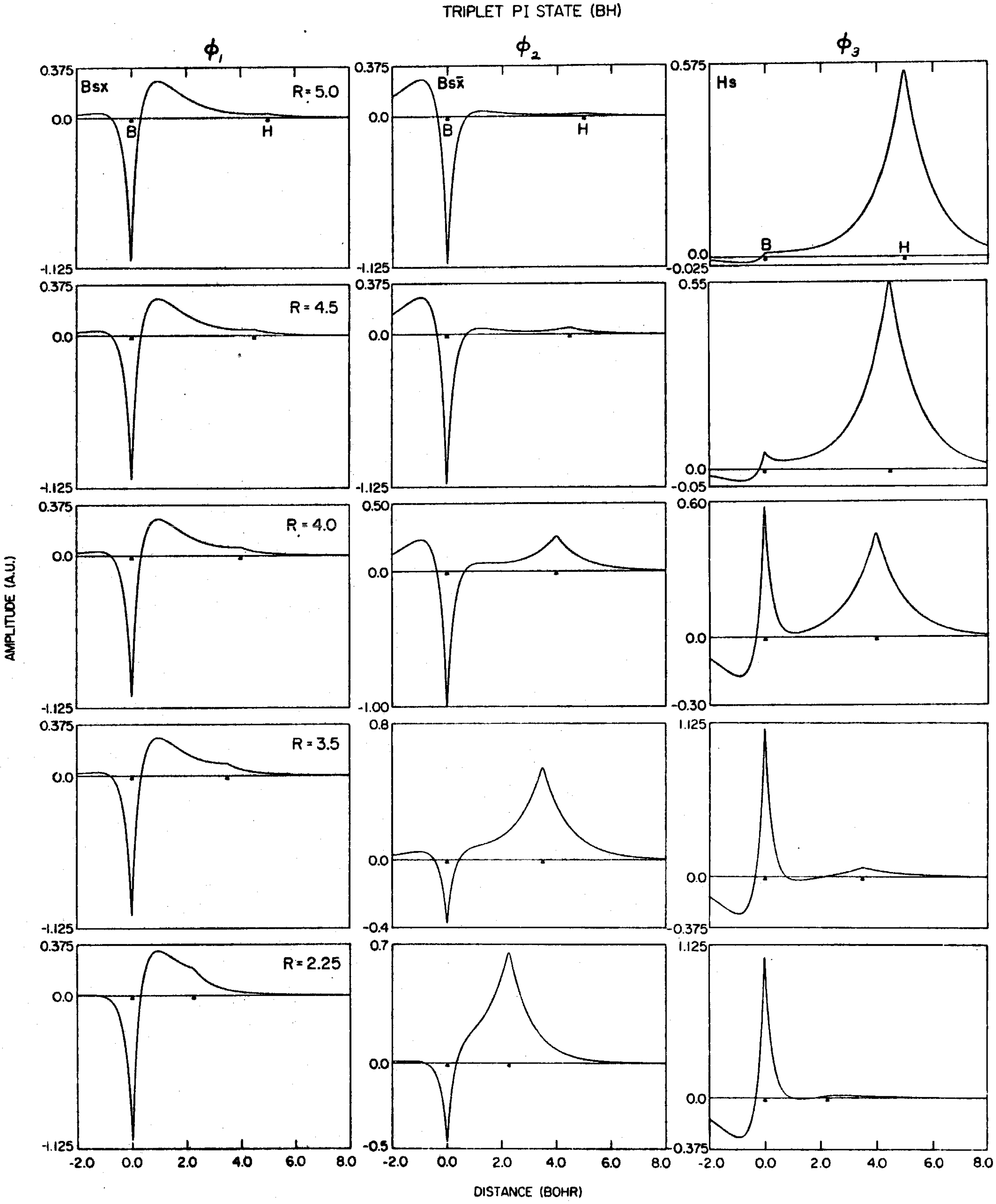

TRIPLET PI STATE (BH)
ϕ_1
ϕ_2
ϕ_3
Bsx
Bs$\bar{x}$
Hs
R = 5.0
R = 4.5
R = 4.0
R = 3.5
R = 2.25
B
H
0.375
0.0
-1.125
0.575
-0.025
0.55
-0.05
0.50
-1.00
0.60
-0.30
0.8
-0.4
1.125
-0.375
0.7
-0.5
AMPLITUDE (A.U.)
-2.0
0.0
2.0
4.0
6.0
8.0
DISTANCE (BOHR)

FIG. 15

BH $^3\Pi$ SPIN COUPLING COEFFICIENTS

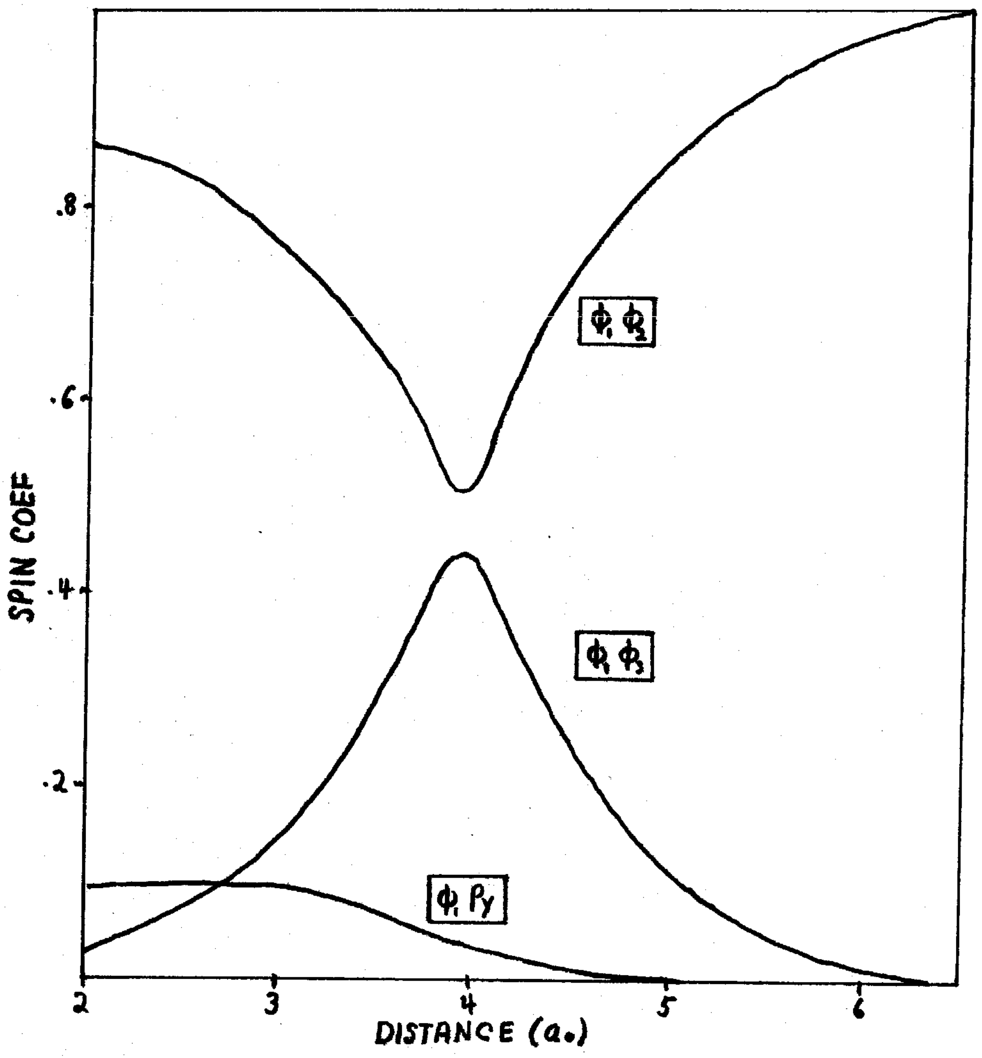


FIG. 16

BH $^1\Pi$ SPIN COUPLING COEFFICIENTS

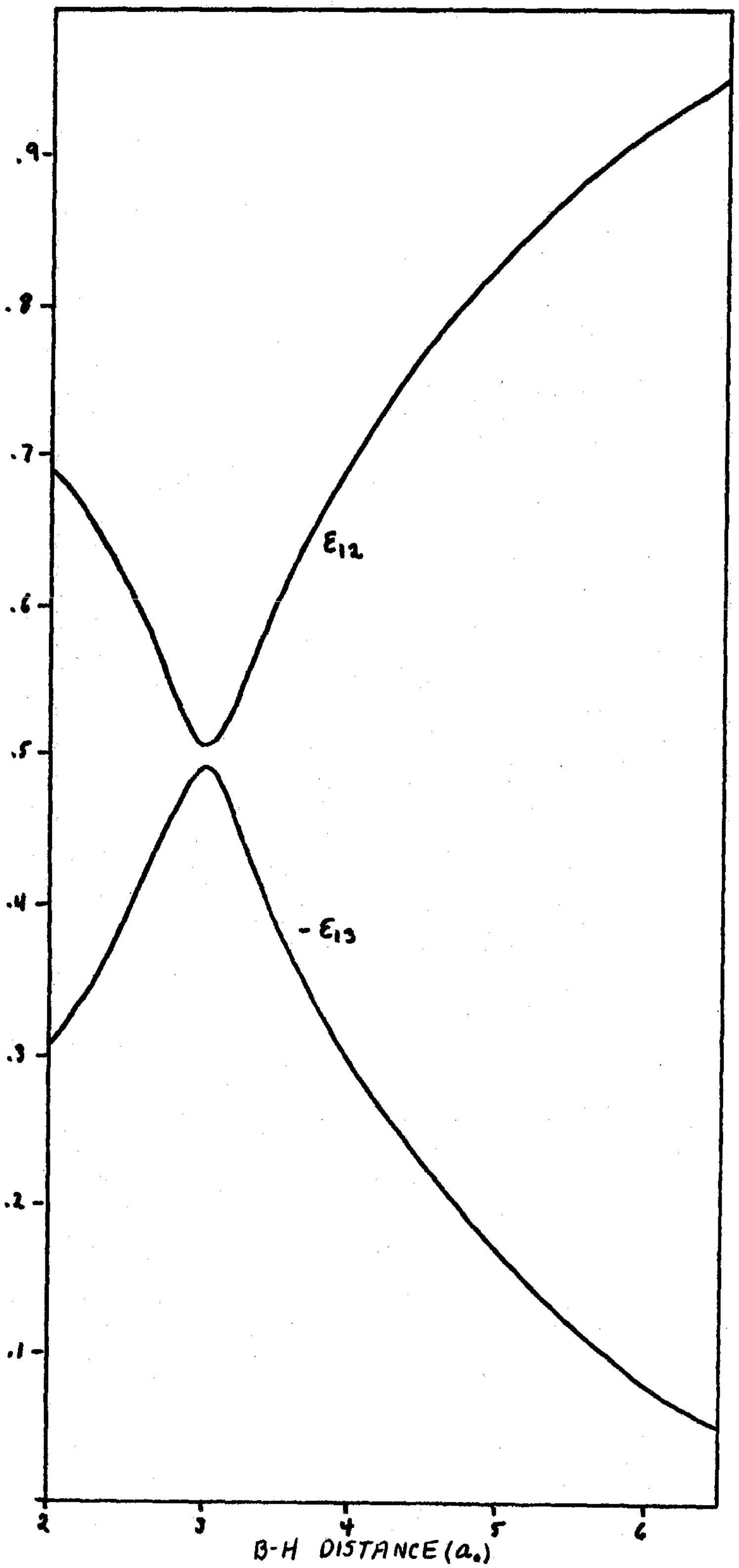


FIG. 17

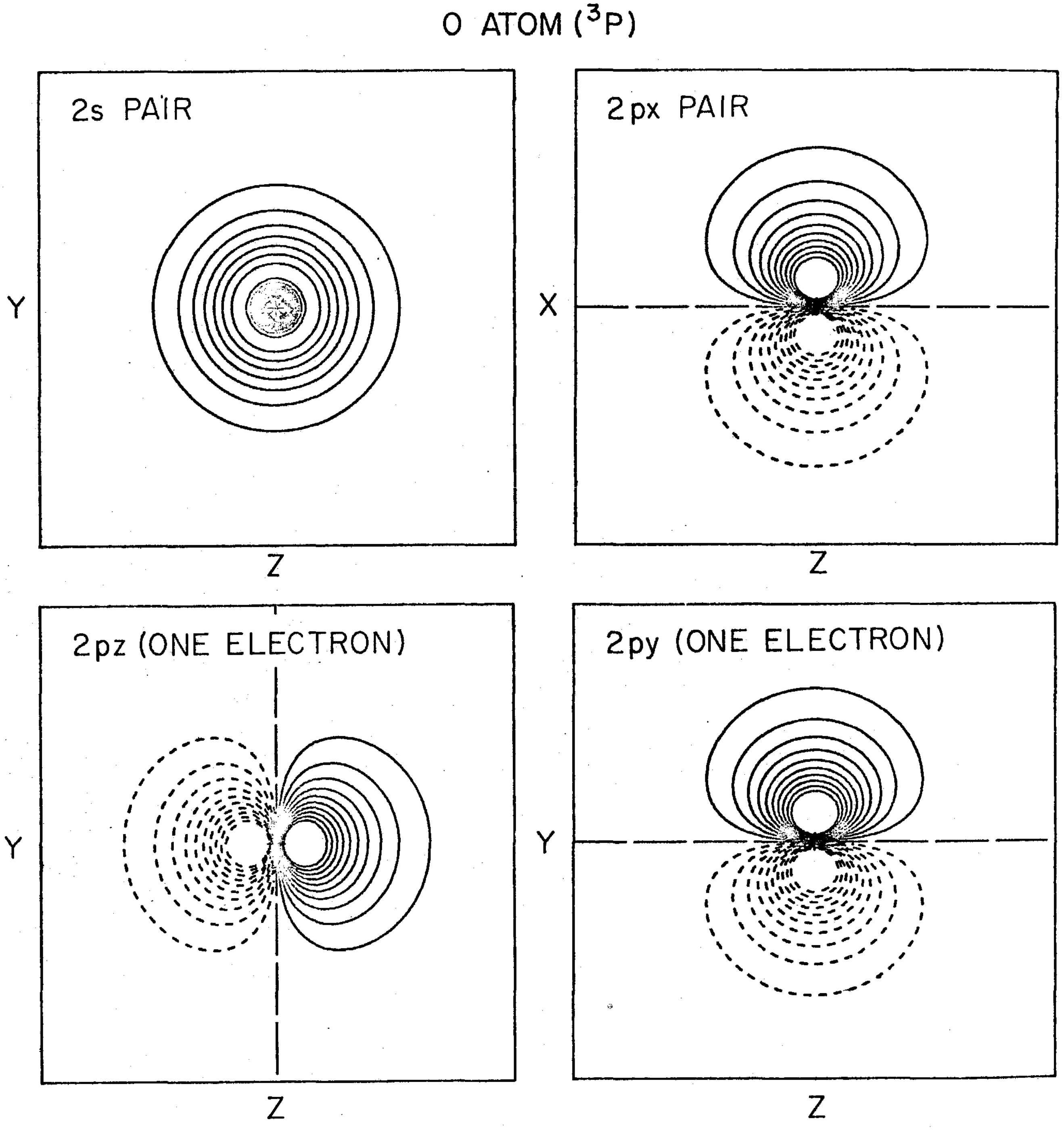
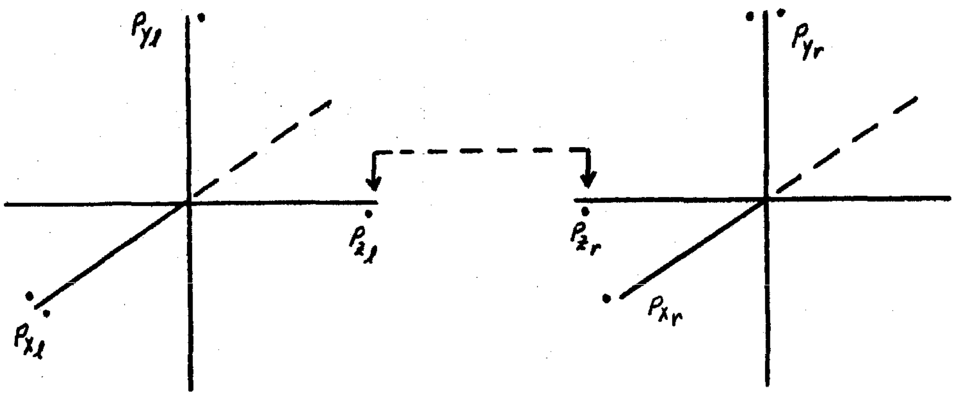

O ATOM (^{3}P)
2s PAIR
Y
Z
2px PAIR
X
Z
2pz (ONE ELECTRON)
Y
Z
2py (ONE ELECTRON)
Y
Z

FIG. 18

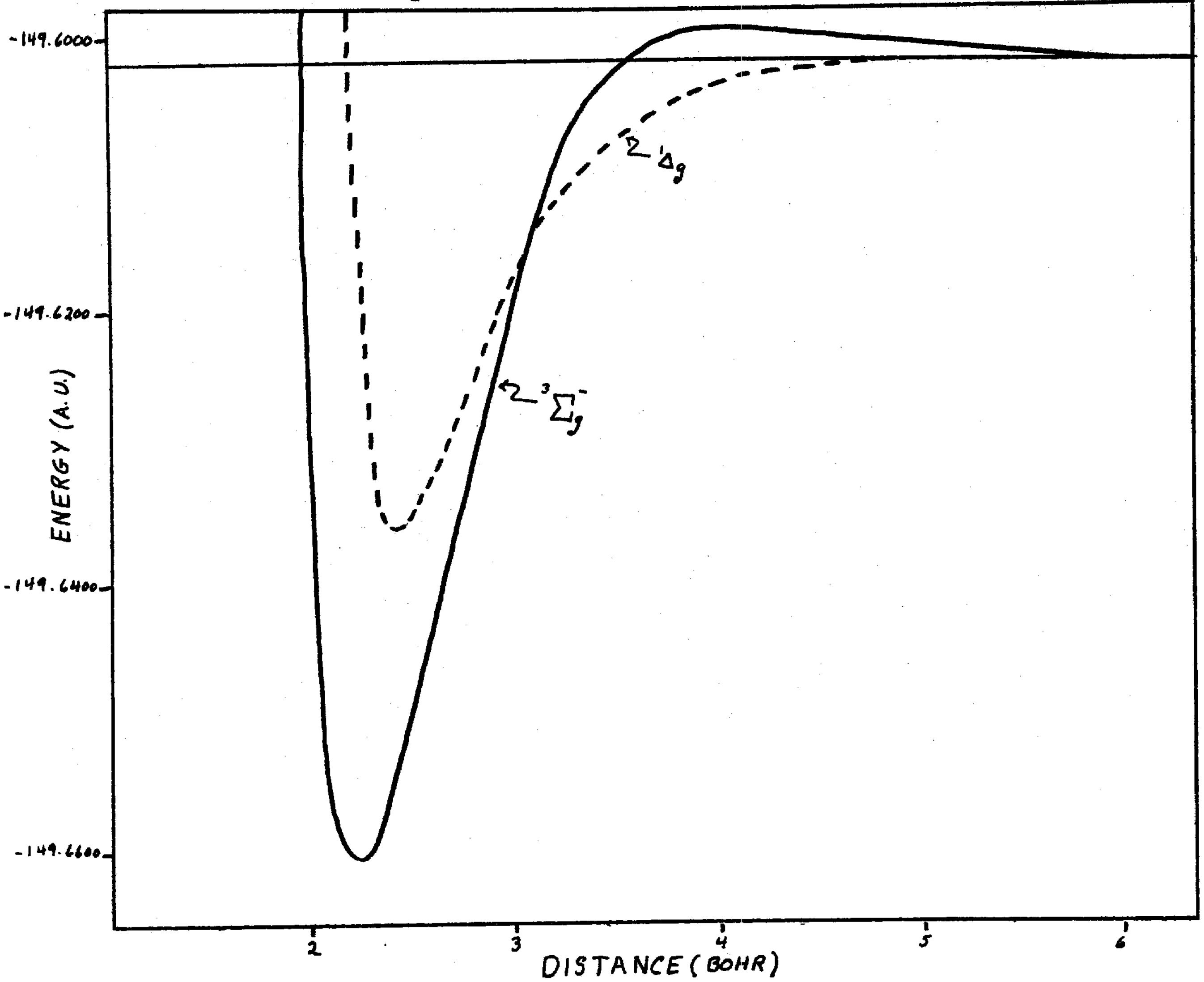
OXYGEN MOLECULE FORMATION



$$\psi_{{}^1\Delta_g} = \mathcal{E}_\infty \begin{array}{|c|c|}\hline p_{z_l} & p_{z_r} \\ p_{y_l} & p_{y_r} \\ \hline\end{array} + \mathcal{E}_e \begin{array}{|cc|}\hline p_{z_l} & p_{z_r} \\ \hline p_{y_l} & p_{x_r} \\ \hline\end{array}$$

$$\psi_{{}^3\Sigma_g^-} = \mathcal{E}_\infty \left[\begin{array}{|c|}\hline p_{z_l} \\ p_{y_l} \\ \hline\end{array} : \begin{array}{|c|}\hline p_{z_r} \\ p_{x_r} \\ \hline\end{array} \right]_T + \mathcal{E}_e \begin{array}{|c|c|}\hline p_{z_r} & p_{z_l} \\ \hline p_{y_l} & \multicolumn{1}{c}{} \\ \cline{1-1} p_{x_r} & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

FIG. 19



SOGVB O_2 POTENTIAL ENERGY CURVES

FIG. 20

GVB ORBITALS $O_2(X\,^3\Sigma_g^-)$

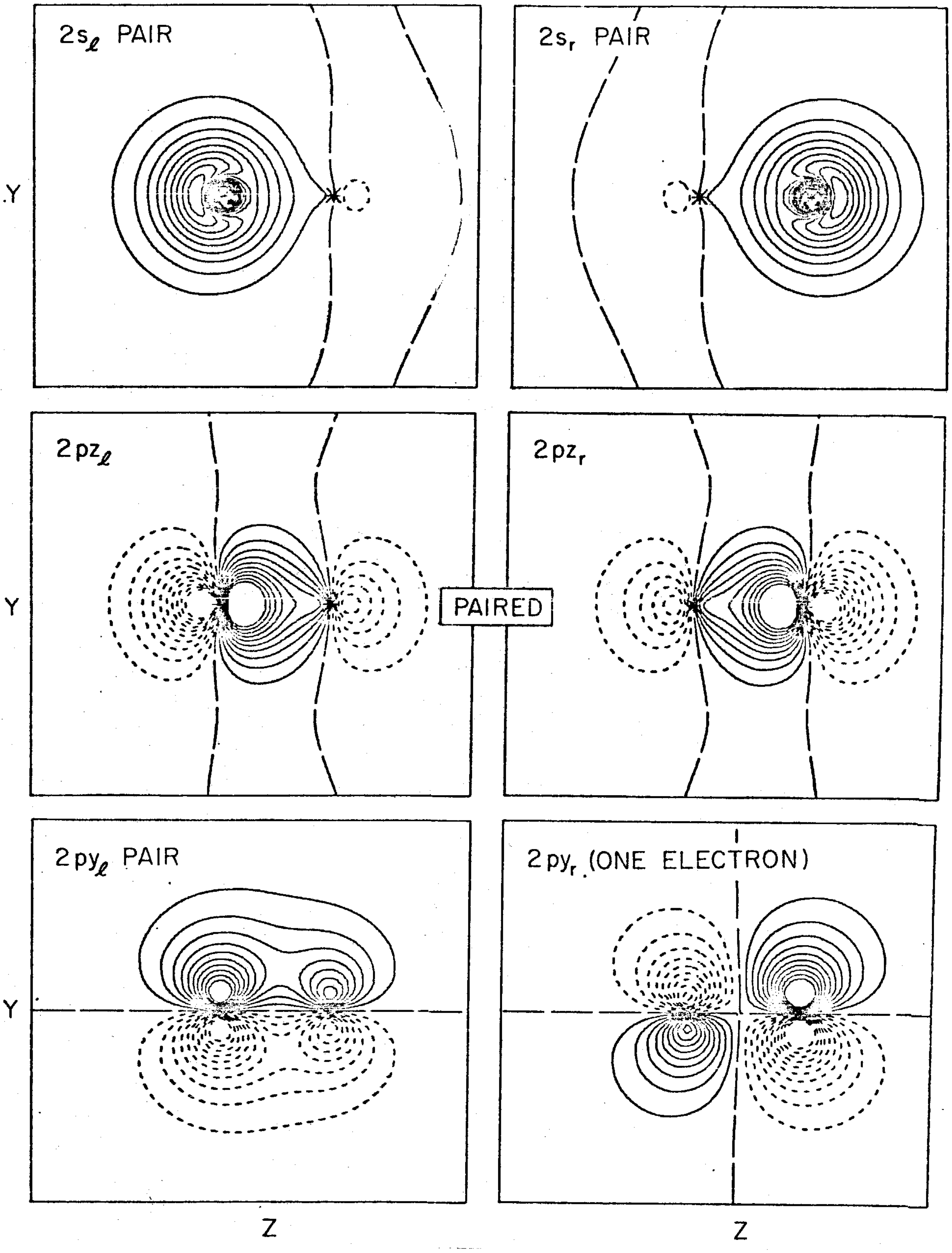


FIG. 21

VI. Conclusion

A detailed description of the SOGVB wavefunction has been presented. This method is intermediate between the GVB and PPGVB methods. It retains most of the simplifying features of the PPGVB approximation and is capable of correctly describing many chemical reactions. Since the Strong Orthogonality Restriction of SOGVB does not appear to affect the accuracy of the wavefunction to any great extent, this method represents a practical approach toward treating large systems self-consistently without missing out on any important independent-particle effects.

APPENDIX

Specific Case MBSSEQ

Details

Detailed MBSSEQ equations and energy coefficient definitions will now be presented for those cases already programmed. These are (excluding core orbitals) the three-electron doublet, the four-electron singlet and the four electron triplet. From the pattern set by these cases, extension to larger numbers of electrons will be obvious. In each case, equations are derived for a variable number of orbital pairs rather than just for the maximum number possible. In the abstract, this is of course not necessary. There are, however, two practical reasons for doing so. If two orbitals which would normally be reexpressed in terms of a pair, are orthogonal by symmetry, these symmetries would be destroyed in the natural orbital pair representation. Since imposition of symmetry constraints increases computational efficiency and can also permit calculation of excited states, this lack of symmetry is highly undesirable. Moreover, being able to control the number of pairs, and hence, the number of meaningful orthogonalities, represents yet another way of obtaining excited states which would normally collapse (computationally speaking) into ground states if these constraints were not imposed.

A. The Three-Electron Doublet

The wavefunction in terms of strongly orthogonal orbitals and the standard spin couplings is:

$$\psi = \mathcal{E}_1 \begin{array}{|c|c|}\hline \phi_1' & \phi_2' \\ \hline \phi_3 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \mathcal{E}_2 \begin{array}{|c|c|}\hline \phi_1' & \phi_3 \\ \hline \phi_2' & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

1. Basic SEF Configuration Definitions and Relationships

Definitions:

$$|(12)3| = \frac{1}{\sqrt{2}} \mathcal{A}\, \phi_1\phi_2\phi_3 (\alpha\beta-\beta\alpha)\alpha$$

$$|[12]3| = -\frac{1}{\sqrt{6}} \mathcal{A}\, \phi_1\phi_2\phi_3 (2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)$$

$$|112| = \mathcal{A}\, \phi_1\phi_1\phi_2\, \alpha\beta\alpha$$

Unique Relationships:

$$|(13)2| = -\frac{1}{2}|(12)3| + \frac{\sqrt{3}}{2}|[12]3|$$

$$|[13]2| = \frac{\sqrt{3}}{2}|(12)3| + \frac{1}{2}|[12]3|$$

$$|(11)2| = \sqrt{2}\,|112|$$

$$|(12)1| = -\frac{1}{\sqrt{2}}|112|$$

$$|[12]1| = \sqrt{\frac{3}{2}}\,|112|$$

2. The 0-Pair Wavefunction

Since all orbitals are taken to be orthogonal:

$${}^{\circ}\psi = A_1|(12)3| + A_2|[12]3| \quad ; \quad A_1 = \mathcal{E}_1 \text{ and } A_2 = -\mathcal{E}_2$$

Allowing ϕ_1 and ϕ_2 to mix orthogonally:

$$\phi_1 \Rightarrow N(\phi_1 + C_{12}\phi_2)$$
$$\phi_2 \Rightarrow N(\phi_2 - C_{12}\phi_1)$$

$$
\begin{aligned}
{}^{0}\psi &= A_1 \left[(1-C_{12}^2)\,|(12)3| - \sqrt{2}\,C_{12}\,(|113| - |223|) \right] + A_2 (1+C_{12}^2)\,|[12]3| \\
&= b_1 \left[|113| - |223| \right] + b_3\,|(12)3| + b_4\,|[12]3|
\end{aligned}
$$

Hence, C_{12} and $\{A\}$ are found by solving a 3 x 3 CI for $\{b\}$:

$$C_{12} = \frac{b_3}{2b_1} \pm \left[1 + \left(\frac{b_3}{2b_1}\right)^2 \right]^{1/2} \qquad b_1 = 0 \Rightarrow C_{12} = 0$$
$$A_1 = b_3 / (1 - C_{12}^2) \quad ; \quad A_2 = b_4 / (1 + C_{12}^2)$$

3. The 1-Pair Wavefunction

$${}^{1}\psi = \varepsilon_1\,|(1'2')3| - \varepsilon_2\,|[1'2']3|.$$

Since $\langle\phi_1'|\phi_2'\rangle \neq 0$, let:

$$\phi_1' = N(\phi_1 + \sqrt{\lambda}\,\phi_2)$$
$$\phi_2' = N(\phi_1 - \sqrt{\lambda}\,\phi_2)$$

where $\langle\phi_1|\phi_2\rangle = 0$. Thus:

$$
\begin{aligned}
{}^{1}\psi &= \sqrt{2}\,\varepsilon_1 \left[|113| - \lambda\,|223| \right] + 2\sqrt{\lambda}\,\varepsilon_2\,|[12]3| \\
&= A_1\,|113| + A_2\,|223| + A_3\,|[12]3|
\end{aligned}
$$

Allowing ϕ_1 and ϕ_2 to mix:

$$\phi_1 \Rightarrow N(\phi_1 + C_{12}\,\phi_2)$$
$$\phi_2 \Rightarrow N(\phi_2 - C_{12}\,\phi_1)$$

$$
{}^1\Psi = (A_1 + A_2 C_{12}^2)\,|113| + (A_2 + A_1 C_{12}^2)\,|223| + \sqrt{2}\,C_{12}(A_1 - A_2)\,|(12)3| + A_3(1 + C_{12}^2)\,|[12]3|
$$

$$
= b_1\,|113| + b_2\,|223| + b_3\,|(12)3| + b_4\,|[12]3|
$$

Hence, C_{12} and $\{A\}$ are found by solving a 4 x 4 CI for $\{b\}$:

$$
C_{12} = \frac{b_2 - b_1}{\sqrt{2}\,b_3} \pm \left[1 + \left(\frac{b_2 - b_1}{\sqrt{2}\,b_3}\right)^2\right]^{1/2} \quad ; \quad b_3 = 0 \Rightarrow C_{12} = 0
$$

$$
A_3 = b_4/(1 + C_{12}^2) \;;\; A_2 = (b_2 - b_1 C_{12}^2)/(1 - C_{12}^4) \;;\; A_1 = b_1 - A_2 C_{12}^2
$$

4. Determination of Interpair Mixing Coefficients

$$
\psi = b_1'\,|113| + b_2'\,|223| + b_3'\,|(12)3| + b_4'\,|[12]3|
$$

Substituting:

$\phi_1 \Rightarrow N_1^{-1}(\phi_1 + C_1\,\phi_3)$

$\phi_2 \Rightarrow N_2^{-1}(\phi_2 + C_2\,\phi_3)$

$\phi_3 \Rightarrow N_3^{-1}(\phi_3 - C_1\,\phi_1 - C_2\,\phi_2)$

where it is assumed $|C_i| < 1$

$b_1' = b_1 N_1^2 N_3$

$b_2' = b_2 N_2^2 N_3$

$b_3' = b_3 N_1 N_2 N_3$

$b_4' = b_4 N_1 N_2 N_3$

where $\{b\}$ are the current values of these parameters in ψ and expanding through second-order in $\{C\}$ gives:

$$
\psi = \theta_0 + \sum_{i=1}^{2} C_i\,\theta_i + \sum_{i \geq j}^{2} C_i C_j\,\theta_{ji}
$$

where:

$$\Theta_0 = b_1 \,|113| + b_2 \,|223| + b_3 \,|(12)3| + b_4 \,|[12]3|$$

$$\Theta_1 = -b_1 \,|331| - b_2 \,|221| + \tfrac{1}{\sqrt{2}} (\sqrt{3}\, b_4 - b_3) \left[\, |332| - |112| \,\right]$$

$$\Theta_2 = -b_1 \,|112| - b_2 \,|332| + \tfrac{1}{\sqrt{2}} (\sqrt{3}\, b_4 + b_3) \left[\, |221| - |331| \,\right]$$

$$\Theta_{11} = b_1 \,|113| + \tfrac{1}{2} (\sqrt{3}\, b_4 + b_3) \,|(12)3| + \tfrac{1}{2} (\sqrt{3}\, b_3 - b_4) \,|[12]3|$$

$$\Theta_{12} = \tfrac{1}{\sqrt{2}} (\sqrt{3}\, b_4 + b_3) \,|223| - \tfrac{1}{\sqrt{2}} (\sqrt{3}\, b_4 - b_3) \,|113| + \tfrac{1}{\sqrt{2}} (b_1 + b_2) \,|(12)3|$$
$$- \tfrac{\sqrt{3}}{2} (b_1 - b_2) \,|[12]\;|$$

$$\Theta_{22} = b_2 \,|223| - \tfrac{1}{2} (\sqrt{3}\, b_4 - b_3) \,|(12)3| - \tfrac{1}{2} (\sqrt{3}\, b_3 + b_4) \,|[12]3|$$

After solving for C_1 and C_2 quadratically to give the new orbitals, ϕ_2 is orthogonalized to ϕ_1. Assuming $\{b\}$ is to be optimized for these orbitals, there is no need to redefine these coefficients at this point. For the 0-pair wavefunction, orthogonalization introduces only a high-order error owing to the $b_2 = -b_1$ constraint.

5. The Basic SEF Configuration Transformation Matrix

If :

$$\phi_\omega = \sum_i c_{i\omega} \chi_i \quad :$$

$$|(\omega\nu)\gamma| = \sum_i c_{i\omega} \,|(i\nu)\gamma| = \sqrt{2} \sum_i c_{i\omega} c_{i\nu} \,|ii\gamma| + \sum_{i \neq j} c_{i\omega} c_{j\nu} \,|(ij)\gamma|$$

$$= \frac{1}{\sqrt{2}} \sum_{i \neq j} C_{ii}^{\omega\nu} c_{j\gamma} \,|iij| + \sum_{i>j} C_{ij}^{\omega\nu} \sum_k c_{k\gamma} \,|(ij)k|$$

$$= \frac{1}{\sqrt{2}} \sum_{i \neq j} \left[C_{ii}^{\omega\nu} c_{j\gamma} - C_{ij}^{\omega\nu} c_{i\gamma} \right] |iij| + \sum_{\substack{k,\, i>j \\ k \neq i,j}} C_{ij}^{\omega\nu} c_{k\gamma} \,|(ij)k|$$

where: $C_{ij}^{\omega\nu} = c_{i\omega} c_{j\nu} + c_{j\omega} c_{i\nu}$

Since: $$\sum_{\substack{k,\, i>j \\ k \neq i,j}}^{3} C_{ijk}^{\omega\nu\gamma} \,|(ij)k| = \frac{1}{2} \left[2\, C_{123}^{\omega\nu\gamma} - C_{132}^{\omega\nu\gamma} - C_{231}^{\omega\nu\gamma} \right] |(12)3|$$
$$+ \frac{\sqrt{3}}{2} \left[C_{132}^{\omega\nu\gamma} - C_{231}^{\omega\nu\gamma} \right] |[12]3|$$

$$|(\omega\nu)\gamma| = \sum_{i \neq j} D_{iij}^{(\omega\nu)\gamma} \,|iij| + \sum_{i>j>k} \left[D_{(ij)k}^{(\omega\nu)\gamma} \,|(ij)k| + D_{[ij]k}^{(\omega\nu)\gamma} \,|[ij]k| \right]$$

$$D^{(\mu\nu)\gamma}_{iij} = \frac{1}{\sqrt{2}}\left[C^{\mu\nu}_{ii}c_{j\gamma} - C^{\mu\nu}_{ij}c_{i\gamma}\right]$$
$$D^{(\mu\nu)\gamma}_{(ij)\gamma} = \frac{1}{2}\left[2C^{\mu\nu}_{ij}c_{k\gamma} - C^{\mu\nu}_{ik}c_{j\gamma} - C^{\mu\nu}_{jk}c_{i\gamma}\right]$$
$$D^{(\mu\nu)\gamma}_{[ij]k} = \frac{\sqrt{3}}{2}\left[C^{\mu\nu}_{ik}c_{j\gamma} - C^{\mu\nu}_{jk}c_{i\gamma}\right]$$

Thus:

$$\Theta = \sum_{i \neq j} D^{\Theta}_{iij}\,|iij| + \sum_{i<j<k}\left[D^{\Theta}_{(ij)k}\,|(ij)k| + D^{\Theta}_{[ij]k}\,|[ij]k|\right]$$

where:
$$D^{\mu\mu\gamma}_{\Theta} = \frac{1}{\sqrt{2}}D^{(\mu\mu)\gamma}_{\Theta} \;;\quad D^{[\mu\nu]\gamma}_{\Theta} = \frac{1}{\sqrt{5}}D^{(\mu\nu)\gamma}_{\Theta} + \frac{2}{\sqrt{3}}D^{(\mu\gamma)\nu}_{\Theta}$$

B. The Four-Electron Singlet

The wavefunction in terms of strongly orthogonal orbitals and standard spin couplings is:

$$\psi = \mathcal{E}_1 \begin{array}{|cc|}\hline \phi_1' & \phi_2' \\ \hline \phi_3' & \phi_4' \\ \hline \end{array} + \mathcal{E}_2 \begin{array}{|c|c|}\hline \phi_1' & \phi_3' \\ \phi_2' & \phi_4' \\ \hline \end{array}$$

1. Basic SEF Configuration Definitions and Relationships

Definitions:

$$|(12)(34)| = \frac{1}{2}\mathcal{A}\,\phi_1\phi_2\phi_3\phi_4\,(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)$$
$$|[12][34]| = -\frac{1}{\sqrt{12}}\mathcal{A}\,\phi_1\phi_2\phi_3\phi_4\left[2(\alpha\alpha\beta\beta+\beta\beta\alpha\alpha)-(\alpha\beta+\beta\alpha)(\alpha\beta+\beta\alpha)\right]$$
$$|11(23)| = \frac{1}{\sqrt{2}}\mathcal{A}\,\phi_1\phi_1\phi_2\phi_3\,\alpha\beta(\alpha\beta-\beta\alpha)$$
$$|1122| = \mathcal{A}\,\phi_1\phi_1\phi_2\phi_2\,\alpha\beta\alpha\beta$$

Relationships:

$$|(13)(24)| = -\tfrac{1}{2}\,|(12)(34)| + \tfrac{\sqrt{3}}{2}\,|[12][34]|$$

$$|[13][24]| = \tfrac{\sqrt{3}}{2}\,|(12)(34)| + \tfrac{1}{2}\,|[12][34]|$$

$$|(12)(13)| = -\tfrac{1}{\sqrt{2}}\,|1123|$$

$$|[12][13]| = \sqrt{\tfrac{3}{2}}\,|1123|$$

$$|(11)(23)| = \sqrt{2}\,|11(23)|$$

$$|(11)(22)| = 2\,|1122|$$

2. The 0-Pair Wavefunction

Since all orbitals are assumed to be orthogonal in the first place, $\{\phi'\} = \{\phi\}$:

$${}^{\circ}\psi = A_1\,|(12)(34)| + A_2\,|[12][34]| \quad ; \quad A_1 = \mathcal{E}_1 \text{ and } A_2 = -\mathcal{E}_2$$

Allowing for $\phi_1 \leftrightarrow \phi_2$ and $\phi_3 \leftrightarrow \phi_4$ mixing:

$$\phi_1 \Rightarrow N(\phi_1 + C_{12}\phi_2)$$

$$\phi_2 \Rightarrow N(\phi_2 - C_{12}\phi_1)$$

$$\phi_3 \Rightarrow N'(\phi_3 + C_{34}\phi_4)$$

$$\phi_4 \Rightarrow N'(\phi_4 - C_{34}\phi_3)$$

$$\begin{aligned}{}^{\circ}\psi = {} & \Big|\,[-\sqrt{2}\,C_{12}\,N_1\,|11-22| + (1-C_{12}^2)\,|(12)|\,]\,[-\sqrt{2}\,C_{34}\,N_2\,|33-44| + (1-C_{34}^2)\,|(34)|\,\Big| \\ & + A_2\,(1+C_{12}^2)(1+C_{34}^2)\,|[12][34]|\end{aligned}$$

where $A_1 = N_1N_2$. Thus:

$$\begin{aligned}{}^{\circ}\psi = {} & \Big|\,[\,b_{11}\,|11-22| + b_{31}\,|(12)|\,]\,[\,b_{12}\,|33-44| + b_{32}\,|(34)|\,\Big| \\ & + b_4\,|[12][34]|\end{aligned}$$

Hence, C_{12}, C_{34} and $\{A\}$ are obtained by solving for $\{b\}$ through two sequential 3 x 3 CIs:

$$\begin{aligned}
\Psi_1 = \; & b_{11} \left[b^{\circ}_{12} \left(|1133| - |1144| - |2233| + |2244| \right) + b^{\circ}_{32} \left(|11(34)| \right.\right. \\
& \left.\left. - |22(34)| \right) \right] + b_{31} \left[b^{\circ}_{12} \left(|33(12)| - |44(12)| \right) + b^{\circ}_{32} \, |(12)(34)| \right] \\
& + b_4 \, |[12][34]|
\end{aligned}$$

$$\begin{aligned}
\Psi_2 = \; & b_{12} \left[b^{\circ}_{11} \left(|1133| - |1144| - |2233| + |2244| \right) + b^{\circ}_{31} \left(|33(12)| - |44(12)| \right) \right] \\
& + b_{32} \left[b^{\circ}_{11} \left(|11(34)| - |22(34)| \right) + b^{\circ}_{31} \, |(12)(34)| \right] + b_4 \, |[12][34]|
\end{aligned}$$

where:

$$C_{12} = \frac{b_{31}}{\sqrt{2}\, b_{11}} \pm \left[1 + \left(\frac{b_{31}}{\sqrt{2}\, b_{11}} \right)^2 \right]^{1/2} \qquad ; \qquad b_{11} = 0 \Rightarrow C_{12} = 0$$

$$C_{34} = \frac{b_{32}}{\sqrt{2}\, b_{12}} \pm \left[1 + \left(\frac{b_{32}}{\sqrt{2}\, b_{12}} \right)^2 \right]^{1/2} \qquad ; \qquad b_{12} = 0 \Rightarrow C_{34} = 0$$

$$A_1 = b_{31}\, b_{32} \,/\, (1 - C_{12}^2)(1 - C_{34}^2)$$

$$A_2 = b_4 \,/\, (1 + C_{12}^2)(1 + C_{34}^2)$$

3. The 1-Pair Wavefunction

$${}^1\psi = \varepsilon_1 \,|(1'2')(34)| - \varepsilon_2 \,|[1'2'][34]|$$

Letting:

$$\phi_1' = \mathcal{N} \left[\phi_1 + \sqrt{\lambda}\, \phi_2 \right] \; ; \quad \phi_2' = \mathcal{N} \left[\phi_1 - \sqrt{\lambda}\, \phi_2 \right] \qquad \langle \phi_1 | \phi_2 \rangle = 0$$

$$\begin{aligned}
{}^1\Psi &= \sqrt{2}\, \varepsilon_1 \left[|11(34)| - \lambda \, |22(34)| \right] + 2 \sqrt{\lambda}\, \varepsilon_2 \, |[12][34]| \\
&= A_1 \, |11(34)| + A_2 \, |22(34)| + A_3 \, |[12][34]|
\end{aligned}$$

Allowing for $\phi_1 \leftrightarrow \phi_2$ and $\phi_3 \leftrightarrow \phi_4$ mixing:

$$\phi_1 \Rightarrow N(\phi_1 + C_{12}\phi_2)$$
$$\phi_2 \Rightarrow N(\phi_2 - C_{12}\phi_1)$$
$$\phi_3 \Rightarrow N'(\phi_3 + C_{34}\phi_4)$$
$$\phi_4 \Rightarrow N'(\phi_4 - C_{34}\phi_3)$$

$^1\psi = \big|[b_{11}|11| + b_{21}|22| + b_{31}|(12)][b_{12}|33\text{-}44| + b_{32}|(34)|]\big| +$ $b_4\big|[12][34]\big|$ where :

$$b_{11} = (A_1 + A_2C_{12}^2)/N''$$
$$b_{21} = (A_2 + A_1C_{12}^2)/N''$$
$$b_{31} = \sqrt{2}\, C_{12}(A_1 - A_2)/N''$$
$$b_{12} = -\sqrt{2}\, C_{34}N''$$
$$b_{32} = (1-C_{34}^2)N''$$
$$b_4 = A_3(1 + C_{12}^2)(1 + C_{34}^2)$$

Hence, $\{A\}$, C_{12} and C_{34} are obtained by solving for $\{b\}$ through two sequential CIs.

$$C_{12} = \left(\frac{b_{21}-b_{11}}{\sqrt{2}\, b_{31}}\right) \pm \left[1 + \left(\frac{b_{21}-b_{11}}{\sqrt{2}\, b_{31}}\right)^2\right]^{1/2} \quad ; \quad b_{31}=0 \Rightarrow C_{12}=0$$
$$C_{34} = \frac{b_{34}}{\sqrt{2}\, b_{12}} \pm \left[1 + \left(\frac{b_{34}}{\sqrt{2}\, b_{12}}\right)^2\right]^{1/2} \quad ; \quad b_{12}=0 \Rightarrow C_{34}=0$$
$$A_3 = b_4 / (1+C_{34}^2)(1+C_{12}^2)$$
$$A_2 = b_{32}\,(b_{21} - b_{11}C_{12}^2)/(1-C_{12}^4)(1-C_{34}^2)$$
$$A_3 = -A_2C_{12}^2 + b_{11}b_{32}/(1-C_{34}^2)$$

4. The 2-Pair Wavefunction

$$^2\psi = \varepsilon_1\big|(1'2')(3'4')\big| - \varepsilon_2\big|[12][34]\big|$$

Letting:

$$\phi_1' = \mathcal{N}\,(\phi_1 + \sqrt{\lambda_1}\,\phi_2)\ ;\quad \phi_2' = \mathcal{N}\,(\phi_1 - \sqrt{\lambda_1}\,\phi_2) \qquad \langle \phi_1 | \phi_2 \rangle = 0$$

$$\phi_3' = \mathcal{N}\,(\phi_3 + \sqrt{\lambda_2}\,\phi_4)\ ;\quad \phi_4' = \mathcal{N}\,(\phi_3 - \sqrt{\lambda_2}\,\phi_4) \qquad \langle \phi_3 | \phi_4 \rangle = 0$$

$$\begin{aligned} {}^2\psi &= \varepsilon_1 \left[\, |1133| - \lambda_2\, |1144| \,\right] - \lambda_1 \varepsilon_1 \left[\, |2233| - \lambda_2\, |2244| \,\right] \\ &\qquad - 2\sqrt{\lambda_1 \lambda_2}\ |[12][34]| \\ &= A_1\, |1133| + A_2\, |1144| + A_3\, |2233| + A_4\, |2244| + A_5\, |[12][34]| \end{aligned}$$

where $A_4A_1 = A_2A_3$. Thus :

$${}^2\psi = |(a_{11}|11| + a_{21}|22|)(a_{12}|33| + a_{22}|44|)| + a_3|[12][34]|$$

Allowing for $\phi_1 \leftrightarrow \phi_2$ and $\phi_3 \leftrightarrow \phi_4$ mixing:

$$\phi_1 \Rightarrow \mathcal{N}\,(\phi_1 + C_{12}\,\phi_2) \quad ; \quad \phi_2 \Rightarrow \mathcal{N}\,(\phi_2 - C_{12}\,\phi_1)$$

$$\phi_3 \Rightarrow \mathcal{N}'\,(\phi_3 + C_{34}\,\phi_4) \quad ; \quad \phi_4 \Rightarrow \mathcal{N}'\,(\phi_4 - C_{34}\,\phi_3)$$

$$\begin{aligned} {}^2\psi = \Big|\, &\left[b_{11}\, |11| + b_{21}\, |22| + b_{31}\, |(12)| \right] \left[b_{12}\, |33| + b_{22}\, |44| + b_{32}\, |(34)| \right] \Big| \\ &+ b_4\, |[12][34]| \end{aligned}$$

Thus, by solving for $\{b\}$ through two sequential CIs, $\{A\}$, C_{12} and C_{34} can be obtained:

$$C_{12} = \frac{b_{21} - b_{11}}{\sqrt{2}\, b_{31}} \pm \left[1 + \left(\frac{b_{21} - b_{11}}{\sqrt{2}\, b_{31}} \right)^2 \right]^{1/2} \qquad ; \quad b_{31} = 0 \Rightarrow C_{12} = 0$$

$$C_{34} = \frac{b_{22} - b_{12}}{\sqrt{2}\, b_{32}} \pm \left[1 + \left(\frac{b_{22} - b_{12}}{\sqrt{2}\, b_{32}} \right)^2 \right]^{1/2} \qquad ; \quad b_{32} = 0 \Rightarrow C_{34} = 0$$

$$\begin{aligned} A_5 &= b_4\, (1 - C_{12}^2)(1 - C_{34}^2) \\ A_1 &= (b_{11} - b_{21} C_{12}^2)(b_{12} - b_{22} C_{34}^2) \\ A_2 &= (b_{11} - b_{21} C_{12}^2)\,(b_{22} - b_{12} C_{34}^2) \\ A_3 &= (b_{12} - b_{22} C_{34}^2)\,(b_{21} - b_{11} C_{12}^2) \\ A_4 &= A_2 A_3 / A_1 \end{aligned}$$

5. Determination of Interpair Mixing Coefficients

$$\Psi = b'_{11} b'_{12} \,|1133| + b'_{11} b'_{22} \,|1144| + b'_{11} b_{32} \,|11(34)| + b'_{21} b'_{12} \,|2233| + b'_{21} b'_{22} \,|2244|$$
$$+ b'_{21} b'_{32} \,|22(34)| + b'_{31} b_{12} \,|33(12)| + b'_{31} b'_{22} \,|44(12)| + b'_{31} b'_{32} \,|(12)(34)| + b'_{4} \,|[12][34]|$$

Letting:

$$\phi_1 \Rightarrow N_1^{-\frac{1}{2}}(\phi_1 + C_1\phi_3 + C_2\phi_4)$$
$$\phi_2 \Rightarrow N_2^{-\frac{1}{2}}(\phi_2 + C_3\phi_3 + C_4\phi_4)$$
$$\phi_3 \Rightarrow N_3^{-\frac{1}{2}}(\phi_3 - C_1\phi_1 - C_3\phi_2)$$
$$\phi_4 \Rightarrow N_4^{-\frac{1}{2}}(\phi_4 - C_2\phi_1 - C_4\phi_2)$$

$b'_{11} = b_{11}N_1 \quad b'_{21} = b_{21}N_2 \quad b'_{31} = b_{31}(N_1N_2)^{\frac{1}{2}}$

$b'_{12} = b_{12}N_3 \quad b'_{22} = b_{22}N_4 \quad b'_{32} = b_{32}(N_3N_4)^{\frac{1}{2}} \quad b'_{11} = b_4(N_1N_2N_3N_4)^{\frac{1}{2}}$

$B_{ij} = b_{i1}b_{j2}$

and expanding ψ through second-order in $\{C\}$ gives:

$$\Psi = \theta_0 + \sum_{i}^{4} C_i\,\theta_i + \sum_{i \geq j}^{4} C_i C_j\,\theta_{ji}$$

where the definitions of the configuration $\{\theta\}$ are given in Table 1. After determining the new orbitals by solving quadratically for $\{C\}$, ϕ_2 is orthogonalized to ϕ_1 and ϕ_4 is orthogonalized to ϕ_3. If $\{b\}$ is to be reoptimized for these orbitals only b_{12}, b_{22} and b_{32} need be redefined at this point:

$$b_{12} \Rightarrow b_{12}N_3 + b_{22}N_4S_{34}^2 + \sqrt{2}\; b_{32}S_{34}(N_3N_4)^{\frac{1}{2}}$$
$$b_{22} \Rightarrow b_{22}N_4N_4'$$
$$b_{32} \Rightarrow [\,b_{32}N_3^{\frac{1}{2}} + \sqrt{2}\; S_{34}b_{22}N_4^{\frac{1}{2}}]\,(N_3N_4)^{\frac{1}{2}}$$

where:

$$N_3 = (1 + C_1^2 + C_3^2)$$
$$N_4 = (1 + C_2^2 + C_4^2)$$
$$S_{34} = (C_1C_2 + C_3C_4)/(N_3N_4)^{\frac{1}{2}}$$
$$N_4' = 1 - S_{34}^2$$

(If it is required that $b_{11} = - b_{21}$ and/or $b_{12} = - b_{22}$ reorthogonalization introduces only high order errors).

6. The Basic SEF Configuration Transformation Matrix

$$\text{If } \phi_\mu = \sum_i C_{i\mu} \chi_i$$

$$|(\mu\nu)(\gamma\varepsilon)| = \frac{1}{\sqrt{2}} \sum_i C^{\mu\nu}_{ii} \, |ii(\gamma\varepsilon)| + \sum_{i<j} C^{\mu\nu}_{ij} \, |(ij)(\gamma\varepsilon)|$$
$$= \frac{1}{2} \sum_{i\neq j} C^{\omega\nu\gamma\varepsilon}_{iijj} \, |iijj| + \frac{1}{\sqrt{2}} \sum_{\substack{i,\, k>l \\ i\neq k,l}} \left(C^{\omega\nu\gamma\varepsilon}_{iikl} + C^{\omega\nu\gamma\varepsilon}_{klii} \right) |ii(kl)|$$
$$+ \sum_{i<j,\, k<l} C^{\mu\nu\gamma\varepsilon}_{ijkl} \, |(ij)(kl)|$$

where:

$$C^{\mu\nu}_{ij} = C_{i\omega}C_{j\nu} + C_{j\omega}C_{i\nu} \quad ; \quad C^{\omega\nu\gamma\varepsilon}_{ijkl} = C^{\omega\nu}_{ij} C^{\gamma\varepsilon}_{kl}$$

Since:

$$\sum_{i<j,\, k<l} C^{\omega\nu\gamma\varepsilon}_{ijkl} \, |(ij)(kl)| = - \sum_{i<j} C^{\mu\nu\gamma\varepsilon}_{ijij} \, |iijj| + \sum_{\substack{i<j,\, k<l \\ i,j\neq k,l}} C^{\omega\nu\gamma\varepsilon}_{ijkl} \cdot |(ij)(kl)|$$
$$+ \frac{1}{\sqrt{2}} \sum_{\substack{i,\, j<l \\ i\neq j,l}} \left(C^{\omega\nu\gamma\varepsilon}_{ijil} + C^{\omega\nu\gamma\varepsilon}_{ilij} \right) |ii(jl)|$$

$$|(\omega\nu)(\gamma\varepsilon)| = \frac{1}{2}\sum_{i<j}\left(C^{\omega\nu\gamma\varepsilon}_{iijj} + C^{\omega\nu\gamma\varepsilon}_{jjii} - 2\,C^{\omega\nu\gamma\varepsilon}_{ijij}\right)|iijj|$$

$$+\frac{1}{\sqrt{2}}\sum_{\substack{i,j<l\\ i\neq j,l}}\left(C^{\omega\nu\gamma\varepsilon}_{iijl} + C^{\omega\nu\gamma\varepsilon}_{jlii} - C^{\omega\nu\gamma\varepsilon}_{ijil} - C^{\omega\nu\gamma\varepsilon}_{ilij}\right)|ii(jl)|$$

$$+\sum_{\substack{i<j,\,k<l\\ i,j\neq k,l\\ ij>kl}}\left(C^{\omega\nu\gamma\varepsilon}_{ijkl} + C^{\omega\nu\gamma\varepsilon}_{klij}\right)|(ij)(kl)|$$

Since:

$$|(13)(24)| = -\frac{1}{2}\,|(12)(34)| + \frac{\sqrt{3}}{2}\,|[12][34]|$$

$$|(23)(14)| = -\frac{1}{2}\,|(12)(34)| - \frac{\sqrt{3}}{2}\,|[12][34]|$$

$$\sum^{4}_{\substack{i<j,\,k<l\\ i,j\neq k,l\\ ij>kl}}\left(C^{\omega\nu\gamma\varepsilon}_{ijkl} + C^{\omega\nu\gamma\varepsilon}_{klij}\right)|(ij)(kl)| = \frac{1}{2}\Big[2\big(C^{\omega\nu\gamma\varepsilon}_{1234} + C^{\omega\nu\gamma\varepsilon}_{3412}\big) - C^{\omega\nu\gamma\varepsilon}_{1324}$$

$$- C^{\omega\nu\gamma\varepsilon}_{2413} - C^{\omega\nu\gamma\varepsilon}_{2314} - C^{\omega\nu\gamma\varepsilon}_{1423}\Big]\,|(12)(34)| + \frac{\sqrt{3}}{2}\Big[C^{\omega\nu\gamma\varepsilon}_{1324} + C^{\omega\nu\gamma\varepsilon}_{2413}$$

$$- C^{\omega\nu\gamma\varepsilon}_{2314} - C^{\omega\nu\gamma\varepsilon}_{1423}\Big]\,|[12][34]|$$

Hence:

$$\sum_{\substack{i<j,\,k<l\\ i,j\neq k,l\\ ij>kl}}\left(C^{\omega\nu\gamma\varepsilon}_{ijkl} + C^{\omega\nu\gamma\varepsilon}_{klij}\right)|(ij)(kl)| = \sum_{i<j<k<l}\Big[D^{(\omega\nu)\gamma\varepsilon}_{(ij)(kl)}\,|(ij)(kl)|$$

$$+ D^{(\omega\nu)(\gamma\varepsilon)}_{[ij][kl]}\,|[ij][kl]|\Big]$$

where:

$$D^{(\omega\nu)(\gamma\varepsilon)}_{(ij)(kl)} = \frac{1}{2}\Big[2\big(C^{\omega\nu\gamma\varepsilon}_{ijkl} + C^{\omega\nu\gamma\varepsilon}_{klij}\big) - C^{\omega\nu\gamma\varepsilon}_{ikjl} - C^{\omega\nu\gamma\varepsilon}_{jlik} - C^{\omega\nu\gamma\varepsilon}_{jkil} - C^{\omega\nu\gamma\varepsilon}_{iljk}\Big]$$

$$D^{(\omega\nu)(\gamma\varepsilon)}_{[ij][kl]} = \frac{\sqrt{3}}{2}\Big[C^{\omega\nu\gamma\varepsilon}_{jlik} + C^{\omega\nu\gamma\varepsilon}_{ikjl} - C^{\omega\nu\gamma\varepsilon}_{jkil} - C^{\omega\nu\gamma\varepsilon}_{iljk}\Big]$$

Therefore if:

$$D^{(\omega\nu)(\gamma\varepsilon)}_{iijj} = \frac{1}{2}\Big[C^{\omega\nu\gamma\varepsilon}_{iijj} + C^{\omega\nu\gamma\varepsilon}_{jjii} - 2\,C^{\omega\nu\gamma\varepsilon}_{ijij}\Big]$$

$$D^{(\omega\nu)(\gamma\varepsilon)}_{iijl} = \frac{1}{\sqrt{2}}\Big[C^{\omega\nu\gamma\varepsilon}_{iijl} + C^{\omega\nu\gamma\varepsilon}_{jlii} - C^{\omega\nu\gamma\varepsilon}_{ijil} - C^{\omega\nu\gamma\varepsilon}_{ilij}\Big]$$

$$|(\mu\nu)(\gamma\varepsilon)| = \sum_{i<j} D_{iijj}^{(\mu\nu)(\gamma\varepsilon)} \, |iijj| + \sum_{\substack{i,\, j<l \\ i\neq j,l}} D_{ii(jl)}^{(\mu\nu)(\gamma\varepsilon)} \, |ii(jl)|$$

$$+ \sum_{i<j<k<l} \left[D_{(ij)(kl)}^{(\mu\nu)(\gamma\varepsilon)} \, |(ij)(kl)| + D_{[ij][kl]}^{(\mu\nu)(\gamma\varepsilon)} \, |[ij][kl]| \right]$$

Since:

$$|\mu\mu(\gamma\varepsilon)| = \frac{1}{\sqrt{2}} \, |(\mu\mu)(\gamma\varepsilon)|$$

$$|\mu\mu\nu\nu| = \frac{1}{2} \, |(\mu\mu)(\nu\nu)|$$

$$|[\mu\nu][\gamma\varepsilon]| = \frac{1}{\sqrt{3}} \, |(\mu\nu)(\gamma\varepsilon)| + \frac{2}{\sqrt{3}} \, |(\mu\gamma)(\nu\varepsilon)|$$

$$D_{\Theta}^{\mu\mu(\gamma\varepsilon)} = \frac{1}{\sqrt{2}} D_{\Theta}^{(\mu\nu)(\gamma\varepsilon)}$$

$$D_{\Theta}^{\mu\mu\nu\nu} = \frac{1}{2} D_{\Theta}^{(\mu\mu)(\nu\nu)}$$

$$D_{\Theta}^{[\mu\nu][\gamma\varepsilon]} = \frac{1}{\sqrt{3}} D_{\Theta}^{(\mu\nu)(\gamma\varepsilon)} + \frac{2}{\sqrt{3}} D_{\Theta}^{(\mu\gamma)(\nu\varepsilon)}$$

$$\Theta = \sum_{i<j} D_{iijj}^{\Theta} \, |iijj| + \sum_{\substack{i,\, j<l \\ i\neq j,l}} D_{ii(jl)}^{\Theta} \, |iijl|$$

$$+ \sum_{i<j<k<l} \left[D_{(ij)(kl)}^{\Theta} \, |(ij)(kl)| + D_{[ij][kl]}^{\Theta} \, |[ij][kl]| \right]$$

Table 1 Four-Electron Singlet Interpair CI Configurations

Θ	0	1	2	3	4	11	12	13	14	22	23	24	33	34	44
$\vert 11(23)\vert$	0	B_{31}	$\frac{1}{\sqrt{2}}(B_{33}+\sqrt{3}b_4)$	$-\sqrt{2}B_{11}$	$-B_{13}$	0	0	0	0	0	0	0	0	0	0
$\vert 11(24)\vert$	0	$\frac{1}{\sqrt{2}}(B_{33}-\sqrt{3}b_4)$	B_{32}	$-B_{31}$	$-\sqrt{2}B_{12}$	0	0	0	0	0	0	0	0	0	0
$\vert 11(34)\vert$	B_{13}	0	0	0	0	B_{13}	$\sqrt{2}(B_{11}+B_{12})$	$\frac{1}{\sqrt{2}}(B_{33}-\sqrt{3}b_4)$	B_{31}	B_{13}	B_{32}	$\frac{1}{\sqrt{2}}(B_{33}+\sqrt{3}b_4)$	0	0	0
$\vert 1122\vert$	0	0	0	0	0	B_{21}	$\sqrt{2}B_{23}$	$-\sqrt{2}B_{31}$	$\sqrt{3}b_4-B_{33}$	B_{22}	$-B_{33}-\sqrt{3}b_4$	$-\sqrt{2}B_{32}$	B_{11}	$\sqrt{2}B_{13}$	B_{12}
$\vert 22(13)\vert$	0	$-\sqrt{2}B_{21}$	$-B_{23}$	B_{31}	$\frac{1}{\sqrt{2}}(B_{33}-\sqrt{3}b_4)$	0	0	0	0	0	0	0	0	0	0
$\vert 22(14)\vert$	0	$-B_{23}$	$-\sqrt{2}B_{22}$	$\frac{1}{\sqrt{2}}(B_{33}+\sqrt{3}b_4)$	B_{32}	0	0	0	0	0	0	0	0	0	0
$\vert 22(34)\vert$	B_{23}	0	0	0	0	0	0	$\frac{1}{\sqrt{2}}(B_{33}+\sqrt{3}b_4)$	B_{32}	0	B_{31}	$\frac{1}{\sqrt{2}}(B_{33}-\sqrt{3}b_4)$	B_{23}	$\sqrt{2}(B_{21}+B_{22})$	B_{23}
$\vert 1133\vert$	B_{11}	0	0	0	0	$2B_{11}$	$\sqrt{2}B_{13}$	$\sqrt{2}B_{31}$	0	0	$B_{33}+\sqrt{3}b_4$	0	0	0	0
$\vert 33(12)\vert$	B_{31}	0	0	0	0	B_{31}	$\frac{1}{\sqrt{2}}(B_{33}-\sqrt{3}b_4)$	$\sqrt{2}(B_{11}+B_{21})$	B_{13}	0	B_{23}	0	B_{31}	$\frac{1}{\sqrt{2}}(B_{33}+\sqrt{3}b_4)$	0
$\vert 33(14)\vert$	0	$-B_{13}$	$\sqrt{2}B_{11}$	$-\frac{1}{\sqrt{2}}(B_{33}+\sqrt{3}b_4)$	B_{31}	0	0	0	0	0	0	0	0	0	0
$\vert 2233\vert$	B_{21}	0	0	0	0	0	0	$\sqrt{2}B_{31}$	$B_{33}-\sqrt{3}b_4$	0	0	0	$2B_{21}$	$\sqrt{2}B_{23}$	0
$\vert 33(24)\vert$	0	$\frac{1}{\sqrt{3}}(\sqrt{3}b_4-B_{33})$	B_{31}	$-B_{23}$	$\sqrt{2}B_{21}$	0	0	0	0	0	0	0	0	0	0
$\vert 1144\vert$	B_{12}	0	0	0	0	0	$\sqrt{2}B_{13}$	0	$B_{33}-\sqrt{3}b_4$	$2B_{12}$	0	$\sqrt{2}B_{32}$	0	0	0
$\vert 44(12)\vert$	B_{32}	0	0	0	0	0	$\frac{1}{\sqrt{2}}(B_{33}+\sqrt{3}b_4)$	0	B_{23}	B_{32}	B_{13}	$\sqrt{2}(B_{12}+B_{22})$	0	$\frac{1}{\sqrt{2}}(B_{33}-\sqrt{3}b_4)$	B_{32}
$\vert 44(13)\vert$	0	$\sqrt{2}B_{12}$	$-B_{31}$	B_{32}	$\frac{1}{\sqrt{3}}(\sqrt{3}b_4-B_{33})$	0	0	0	0	0	0	0	0	0	0
$\vert 2244\vert$	B_{22}	0	0	0	0	0	0	0	0	0	$B_{33}+\sqrt{3}b_4$	$\sqrt{2}B_{32}$	0	$\sqrt{2}B_{23}$	$2B_{22}$
$\vert 44(23)\vert$	0	B_{32}	$-\frac{1}{\sqrt{2}}(B_{33}+\sqrt{3}b_4)$	$\sqrt{2}B_{22}$	$-B_{23}$	0	0	0	0	0	0	0	0	0	0
$\vert 3344\vert$	0	0	0	0	0	B_{12}	$-\sqrt{2}B_{13}$	$\sqrt{2}B_{32}$	$\sqrt{3}b_4-B_{33}$	B_{11}	$-B_{33}-\sqrt{3}b_4$	$\sqrt{2}B_{31}$	B_{22}	$-\sqrt{2}B_{23}$	B_{21}
$\vert(12)(34)\vert$	B_{33}	0	0	0	0	$\frac{1}{2}(B_{33}+\sqrt{3}b_4)$	$\frac{1}{\sqrt{2}}(B_{31}+B_{32})$	$\frac{1}{\sqrt{2}}(B_{13}+B_{23})$	$B_{21}+B_{12}$	$\frac{1}{2}(B_{33}-\sqrt{3}b_4)$	$B_{11}+B_{22}$	$\frac{1}{\sqrt{2}}(B_{13}+B_{23})$	$\frac{1}{2}(B_{33}-\sqrt{3}b_4)$	$\frac{1}{\sqrt{2}}(B_{31}+B_{32})$	$\frac{1}{2}(B_{33}+\sqrt{3}b_4)$
$\vert[12][34]\vert$	b_4	0	0	0	0	$\frac{1}{2}(\sqrt{3}B_{33}-b_4)$	$\sqrt{\frac{3}{2}}(B_{32}-B_{31})$	$\sqrt{\frac{3}{2}}(B_{23}-B_{13})$	$-\sqrt{3}(B_{12}+B_{21})$	$-\frac{1}{2}(b_4+\sqrt{3}B_{33})$	$\sqrt{3}(B_{11}+B_{22})$	$\sqrt{\frac{3}{2}}(B_{13}-B_{23})$	$-\frac{1}{2}(\sqrt{3}B_{33}+b_4)$	$\sqrt{\frac{3}{2}}(B_{31}-B_{32})$	$\frac{1}{2}(\sqrt{3}B_{33}-b_4)$

C. The Four-Electron Triplet

The wavefunction in terms of strongly orthogonal orbitals and standard spin couplings is:

$$\psi = \mathcal{E}_1 \begin{array}{|c|c|}\hline \phi_1' & \phi_2' \\ \hline \phi_3' & \multicolumn{1}{c}{} \\ \cline{1-1} \phi_4' & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \mathcal{E}_2 \begin{array}{|c|c|}\hline \phi_1' & \phi_3' \\ \hline \phi_2' & \multicolumn{1}{c}{} \\ \cline{1-1} \phi_4' & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \mathcal{E}_3 \begin{array}{|c|c|}\hline \phi_1' & \phi_4' \\ \hline \phi_2' & \multicolumn{1}{c}{} \\ \cline{1-1} \phi_3' & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

1. Basic SEF Configuration Definitions and Relationships

Definitions:

$$|(12)[34]| = \frac{1}{\sqrt{2}}\mathcal{A}\,\phi_1\phi_2\phi_3\phi_4(\alpha\beta-\beta\alpha)\alpha\alpha = G_1$$
$$|[12]34| = -\frac{1}{\sqrt{6}}\mathcal{A}\,\phi_1\phi_2\phi_3\phi_4(2\alpha\alpha\beta\alpha-\beta\alpha\alpha\alpha-\alpha\beta\alpha\alpha) = -G_2$$
$$|[123]4| = -\frac{1}{\sqrt{12}}\mathcal{A}\,\phi_1\phi_2\phi_3\phi_4(3\alpha\alpha\alpha\beta-\alpha\alpha\beta\alpha-\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha) = -G_3$$
$$|11[34]| = \mathcal{A}\,\phi_1\phi_1\phi_3\phi_4\,\alpha\beta\alpha\alpha$$
$$|[12][34]|_T = \sqrt{\tfrac{2}{3}}\,|[12]34| + \frac{1}{\sqrt{3}}\,|[123]4|$$

Relationships:

$$|(12)[13]| = -\frac{1}{\sqrt{2}}\,|11[23]|$$
$$|[12]13| = \sqrt{\tfrac{3}{2}}\,|11[23]|$$
$$|[13]23| = \frac{1}{\sqrt{6}}\,|33[12]|$$
$$|[12]33| = \sqrt{\tfrac{2}{3}}\,|33[12]|$$
$$|[123]3| = -\frac{2}{\sqrt{3}}\,|33[12]|$$
$$|(34)[12]| = \frac{1}{\sqrt{3}}\,|[12]34| - \sqrt{\tfrac{2}{3}}\,|[123]4|$$
$$|(13)[24]| = -\frac{1}{2}\,|(12)[34]| + \frac{\sqrt{3}}{2}\,|[12]34|$$
$$|(14)[23]| = \frac{1}{2}\,|(12)[34]| - \frac{1}{\sqrt{12}}\,|[12]34| - \sqrt{\tfrac{2}{3}}\,|[123]4|$$
$$|[12]43| = -\frac{1}{3}\,|[12]34| - \frac{2\sqrt{2}}{3}\,|[123]4|$$
$$|[34]12| = \frac{1}{\sqrt{3}}\,|(12)[34]| - \frac{2}{3}\,|[12]34| - \frac{\sqrt{2}}{3}\,|[123]4|$$
$$|[13]24| = \frac{\sqrt{3}}{2}\,|(12)[34]| + \frac{1}{2}\,|[12]34|$$
$$|[14]32| = \frac{1}{\sqrt{12}}\,|(12)[34]| - \frac{5}{6}\,|[12]34| + \frac{\sqrt{2}}{3}\,|[123]4|$$
$$|[124]3| = -\frac{2\sqrt{2}}{3}\,|[12]34| + \frac{1}{3}\,|[123]4|$$
$$|[134]2| = -\frac{2}{\sqrt{6}}\,|(12)[34]| - \frac{\sqrt{2}}{3}\,|[12]34| - \frac{1}{3}\,|[123]4|$$

2. The 0-Pair Wavefunction

Since all orbitals are taken to be orthogonal in the first place $\{\phi'\} = \{\phi\}$:

$$^{\circ}\psi = A_1 \left|(12)[34]\right| + A_2 \left|[12]34\right| + A_3 \left|[123]4\right|$$

where $A_1 = \mathcal{E}_1$, $A_2 = -\mathcal{E}_2$ and $A_3 = -\mathcal{E}_2$. Allowing for $\phi_1 \leftrightarrow \phi_2$ and $\phi_3 \leftrightarrow \phi_4$ orthogonal mixing:

$$\phi_1 \Rightarrow N(\phi_1 + C_{12}\phi_2);\quad \phi_2 \Rightarrow N(\phi_2 - C_{12}\phi_1)$$

$$\phi_3 \Rightarrow N'(\phi_2 + C_{34}\phi_4);\quad \phi_4 \Rightarrow N'(\phi_4 - C_{34}\phi_3)$$

$$\begin{aligned}
^{\circ}\psi = {} & A_1 (1 - C_{12}^2) \left|(12)[34]\right| - \sqrt{2}\, C_{12} A_1 \left(\left|11[34]\right| - \left|22[34]\right| \right) \\
& - \frac{(1+C_{12}^2)}{(1+C_{34}^2)} C_{34} \sqrt{\tfrac{2}{3}} \left(A_2 - \sqrt{2} A_3\right) \left(\left|33[12]\right| - \left|44[12]\right| \right) \\
& + (1+C_{12}^2) \left[A_2 - \frac{2}{3} C_{34}^2 \frac{(A_2 - \sqrt{2} A_3)}{1 + C_{34}^2} \right] \left|[12]34\right| \\
& + (1+C_{12}^2) \left[A_3 + \frac{2\sqrt{2}}{3} C_{34}^2 \frac{(A_2 - \sqrt{2} A_3)}{1 + C_{34}^2} \right] \left|[123]4\right| \\
= {} & b_1 \left(\left|11[34]\right| - \left|22[34]\right| \right) + b_3 \left|(12)[34]\right| + b_4 \left(\left|33[12]\right| - \left|44[12]\right| \right) \\
& + b_6 \left|[12]34\right| + b_7 \left|[123]4\right|
\end{aligned}$$

Thus, solving a 5 x 5 CI for b gives $\{A\}$, C_{12} and C_{34}:

$$C_{12} = \frac{b_3}{\sqrt{2}\, b_1} \pm \left[1 + \left(\frac{b_3}{\sqrt{2}\, b_1} \right)^2 \right]^{1/2} \quad ; \quad b_1 = 0 \Rightarrow C_{12} = 0$$

$$C_{34} = \frac{b_6 - \sqrt{2}\, b_7}{\sqrt{6}\, b_4} \pm \left[1 + \left(\frac{b_6 - \sqrt{2}\, b_7}{\sqrt{6}\, b_4} \right)^2 \right]^{1/2} \quad ; \quad b_4 = 0 \Rightarrow C_{34} = 0$$

$$\begin{aligned}
A_1 &= b_3 / (1 - C_{12}^2) \\
A_2 &= \left(b_6 - \sqrt{\tfrac{2}{3}}\, b_4 C_{34} \right) / (1 + C_{12}^2) \\
A_3 &= \left(b_7 + \tfrac{2}{\sqrt{3}}\, b_4 C_{34} \right) / (1 + C_{12}^2)
\end{aligned}$$

3. The 1-Pair Wavefunction

Since $\langle \phi_1' | \phi_2' \rangle \neq 0$ only, let $\phi_3' = \phi_3$, $\phi_4' = \phi_4$ and:

$$\phi_1' = \mathcal{N} (\phi_1 + \sqrt{\lambda}\, \phi_2) \quad ; \quad \phi_2' = \mathcal{N} (\phi_1 - \sqrt{\lambda}\, \phi_2) \qquad \langle \phi_1 | \phi_2 \rangle = 0$$

Hence:

$$\begin{aligned} {}^1\psi &= \varepsilon_1 \left(|11[34]| - \lambda\, |22[34]| \right) + \sqrt{2\lambda}\, \varepsilon_2\, |[12]34| + \sqrt{2\lambda}\, \varepsilon_3\, |[123]4| \\ &= A_1\, |11[34]| + A_2\, |22[34]| + A_3\, |[12]34| + A_4\, |[123]4| \end{aligned}$$

Allowing for $\phi_1 \leftrightarrow \phi_2$ and $\phi_3 \leftrightarrow \phi_4$ orthogonal mixing:

$$\begin{aligned} \phi_1 &\Rightarrow \mathcal{N} (\phi_1 + C_{12} \phi_2) \quad ; \quad \phi_2 \Rightarrow \mathcal{N} (\phi_2 - C_{12} \phi_1) \\ \phi_3 &\Rightarrow \mathcal{N}' (\phi_3 + C_{34} \phi_4) \quad ; \quad \phi_4 \Rightarrow \mathcal{N}' (\phi_4 - C_{34} \phi_3) \end{aligned}$$

$$\begin{aligned} {}^1\psi = {} & (A_1 + A_2 C_{12}^2)\, |11[34]| + (A_2 + A_1 C_{12}^2)\, |22[34]| + \sqrt{2}\,(A_1 - A_2) C_{12}\, |(12)[34]| \\ & - \frac{C_{34}\,(1 + C_{12}^2)(\sqrt{2} A_3 - 2A_4)}{\sqrt{3}\,(1 + C_{34}^2)} \left(|33[12]| - |44[12]| \right) \\ & + (1 + C_{12}^2) \left[A_3 - \frac{2 C_{34}^2 (A_3 - \sqrt{2} A_4)}{3 (1 + C_{34}^2)} \right] |[12]34| \\ & + (1 + C_{12}^2) \left[A_4 + \frac{2\sqrt{2}\, C_{34}^2 (A_3 - \sqrt{2} A_4)}{3 (1 + C_{34}^2)} \right] |[123]4| \\ = {} & b_1\, |11[34]| + b_2\, |22[34]| + b_3\, |(12)[34]| \\ & + b_4 \left(|33[12]| - |44[12]| \right) \\ & + b_6\, |[12]34| + b_7\, |[123]4| \end{aligned}$$

By solving for $\{b\}$ through a 6 x 6 CI, $\{A\}$, C_{12} and C_{34} can be obtained:

$$C_{12} = \frac{b_2 - b_1}{\sqrt{2}\, b_3} \pm \left[1 + \left(\frac{b_2 - b_1}{\sqrt{2}\, b_3} \right)^2 \right]^{1/2} \quad ; \quad b_3 = 0 \Rightarrow C_{12} = 0$$

$$C_{34} = \frac{b_6 - \sqrt{2}\, b_7}{\sqrt{6}\, b_4} \pm \left[1 + \left(\frac{b_6 - \sqrt{2}\, b_7}{\sqrt{6}\, b_4} \right)^2 \right]^{1/2} \quad ; \quad b_4 = 0 \Rightarrow C_{34} = 0$$

$$A_4 = \left(b_6 - \sqrt{\tfrac{2}{3}}\, c_{34}\, b_4\right) / \left(1 + c_{12}^2\right)$$
$$A_3 = \left(b_7 + \tfrac{2}{\sqrt{3}}\, c_{34}\, b_4\right) / \left(1 + c_{12}^2\right)$$
$$A_2 = \left(b_2 - b_1 c_{12}^2\right) / \left(1 - c_{12}^4\right)$$
$$A_1 = b_1 - A_2 c_{12}^2$$

4. The 2-Pair Wavefunction

Since $\langle\phi_1'|\phi_2'\rangle \neq 0$ and $\langle\phi_3'|\phi_4'\rangle \neq 0$, let:

$$\phi_1' = \mathcal{N}\left(\phi_1 + \sqrt{\lambda_1}\,\phi_2\right) \; ; \quad \phi_2' = \mathcal{N}\left(\phi_1 - \sqrt{\lambda_1}\,\phi_2\right) \qquad \langle\phi_1|\phi_2\rangle = 0$$
$$\phi_3' = \mathcal{N}'\left(\phi_3 + \sqrt{\lambda_2}\,\phi_4\right) \; ; \quad \phi_4' = \mathcal{N}'\left(\phi_3 - \sqrt{\lambda_2}\,\phi_4\right) \qquad \langle\phi_3|\phi_4\rangle = 0$$

Thus:

$$\begin{aligned} {}^2\Psi = {} & \sqrt{2\lambda_2}\,\varepsilon_1 \left(|11[34]| - \lambda_1 |22[34]| \right) - \sqrt{\tfrac{2\lambda_1}{3}} \left(\varepsilon_2 - \sqrt{2}\,\varepsilon_3\right) \left(|33[12]| \right. \\ & \left. - |44[12]| \right) + \tfrac{2}{3}\sqrt{\lambda_1\lambda_2} \left(\sqrt{2}\,\varepsilon_2 + \varepsilon_3\right) \left(\sqrt{2}\,|[12]34| + |[123]4| \right) \\ = {} & A_1 |11[34]| + A_2 |22[34]| + A_3 |33[12]| + A_4 |44[12]| + A_5 |[12][34]|_T \end{aligned}$$

Allowing for $\phi_1 \leftrightarrow \phi_2$ and $\phi_3 \leftrightarrow \phi_4$ orthogonal mixing:

$$\phi_1 \Rightarrow \mathcal{N}\left(\phi_1 + c_{12}\phi_2\right) \; ; \quad \phi_2 \Rightarrow \mathcal{N}\left(\phi_2 - c_{12}\phi_2\right)$$
$$\phi_3 \Rightarrow \mathcal{N}'\left(\phi_3 + c_{34}\phi_4\right) \; ; \quad \phi_4 \Rightarrow \mathcal{N}'\left(\phi_4 - c_{34}\phi_3\right)$$

$$\begin{aligned} {}^2\Psi = {} & b_1 |11[34]| + b_2 |22[34]| + b_3 |(12)[34]| + b_4 |33[12]| \\ & + b_5 |44[12]| + b_6 |[12]34| + b_7 |[123]4| \end{aligned}$$

where:

$$b_1 = \left(A_1 + A_2 c_{12}^2\right) / \left(1 + c_{12}^2\right)$$
$$b_2 = \left(A_2 + A_1 c_{12}^2\right) / \left(1 + c_{12}^2\right)$$
$$b_3 = \sqrt{2}\, c_{12} \left(A_1 - A_2\right) / \left(1 + c_{12}^2\right)$$
$$b_4 = \left(A_3 + A_4 c_{34}^2\right) / \left(1 + c_{34}^2\right)$$
$$b_5 = \left(A_4 + A_3 c_{34}^2\right) / \left(1 + c_{34}^2\right)$$
$$b_6 = \sqrt{\tfrac{2}{3}} \left[A_5 + c_{34}\left(A_3 - A_4\right) / \left(1 + c_{34}^2\right) \right]$$
$$b_7 = \tfrac{1}{\sqrt{3}} \left[A_5 - 2c_{34}\left(A_3 - A_4\right) / \left(1 + c_{34}^2\right) \right]$$

Upon solving a 7 x 7 CI for {b}:

$$C_{12} = \frac{b_2 - b_1}{\sqrt{2}\, b_3} \pm \left[1 + \left(\frac{b_2 - b_1}{\sqrt{2}\, b_3} \right)^2 \right]^{1/2} \quad ; \quad b_3 = 0 \Rightarrow C_{12} = 0$$

$$C_{34} = \frac{b_5 - b_4}{\sqrt{\frac{2}{3}}(b_6 - \sqrt{2} b_7)} \pm \left[1 + \left(\frac{b_5 - b_4}{\sqrt{\frac{2}{3}}(b_6 - \sqrt{5} b_7)} \right)^2 \right]^{1/2} \quad ; \quad b_6 - \sqrt{5} b_7 = 0 \Rightarrow C_{34} = 0$$

$$A_5 = (\sqrt{2} b_6 + b_7)/\sqrt{3}$$
$$A_4 = (b_5 - b_4 C_{34}^2)/(1 - C_{34}^2)$$
$$A_3 = b_4 (1 + C_{34}^2) - b_5 C_{34}^2$$
$$A_2 = (b_2 - b_1 C_{12}^2)/(1 - C_{12}^2)$$
$$A_1 = b_1 (1 + C_{12}^2) - b_2 C_{12}^2$$

5. Determination of Interpair Mixing Coefficients

$$\psi = b_1' \,|11[34]| + b_2' \,|22[34]| + b_3' \,|(12)[34]| + b_4' \,|33[12]| + b_5' \,|44[12]| + b_6' \,|[12]34| + b_7' \,|[123]4|$$

Letting:

$$\phi_1 \Rightarrow N_1^{-1/2} (\phi_1 + c_1 \phi_3 + c_2 \phi_4)$$
$$\phi_2 \Rightarrow N_2^{-1/2} (\phi_2 + c_3 \phi_3 + c_4 \phi_4)$$
$$\phi_3 \Rightarrow N_3^{-1/2} (\phi_3 - c_1 \phi_1 - c_3 \phi_2)$$
$$\phi_4 \Rightarrow N_4^{-1/2} (\phi_4 - c_2 \phi_1 - c_4 \phi_2)$$

$$b_1' = b_1 N_1 (N_3 N_4)^{1/2} \quad ; \quad b_2' = b_2 N_2 (N_3 N_4)^{1/2}$$
$$b_4' = b_4 N_3 (N_1 N_2)^{1/2} \quad ; \quad b_5' = b_5 N_4 (N_1 N_2)^{1/2}$$
$$b_i' = b_i (N_1 N_2 N_3 N_4)^{1/2} \quad i = 3, 6, 7$$

expanding ψ through second order in {c} gives

$$\psi = \theta_0 + \sum_i^4 c_i \theta_i + \sum_{i>j}^4 c_i c_j \theta_{ji}$$

where the definitions of the configurations $\{\theta\}$ are given in Table 2. After determining the new orbitals by quadratically solving for {c},

ϕ_2 is orthogonalized to ϕ_1 and ϕ_4 is orthogonalized to ϕ_3. If $\{b\}$ is to be redetermined for these new orbitals, these coefficients need not be redefined at this point. (If it is required that $b_1 = -b_2$ and/or $b_4 = -b_5$, reorthogonalization introduces only high-order errors).

6. The Basic SEF Configuration Transformation Matrix

If $\phi_\mu = \sum_i C_{i\mu} \chi_i$:

$$|(\mu\nu)[\gamma\varepsilon]| = \frac{1}{\sqrt{2}} \sum_i C^{\mu\nu}_{ii} \, |ii[\gamma\varepsilon]| + \sum_{i<j} C^{\mu\nu}_{ij} \, |(ij)[\gamma\varepsilon]|$$

$$= \frac{1}{\sqrt{2}} \sum_{\substack{i,\,k<l \\ i\neq k,l}} C^{\mu\nu\gamma\varepsilon}_{iikl} \, |ii[kl]| + \sum_{i<j,\,k<l} C^{\mu\nu\gamma\varepsilon}_{ijkl} \, |(ij)[kl]|$$

where $C^{\mu\nu}_{ij} = C_{i\mu}C_{j\nu} + C_{j\mu}C_{i\nu}$; $C^{\mu\nu\gamma\varepsilon}_{ijkl} = C^{\mu\nu}_{ij}\left(C_{k\gamma}C_{l\varepsilon} - C_{l\gamma}C_{k\varepsilon}\right)$

Since:

$$\sum_{i<j,\,k<l} C^{\mu\nu\gamma\varepsilon}_{ijkl} \, |(ij)[kl]| = \sum_{\substack{i<j,\,k<l \\ i,j\neq k,l}} C^{\mu\nu\gamma\varepsilon}_{ijkl} \, |(ij)[kl]| - \frac{1}{\sqrt{2}} \sum_{\substack{i,\,j<l \\ i\neq j,l}} \left(C^{\mu\nu\gamma\varepsilon}_{ijil} - C^{\mu\nu\gamma\varepsilon}_{ilij}\right) |ii[jl]|$$

$$\sum^{4}_{\substack{i<j,\,k<l \\ i,j\neq k,l}} C^{\mu\nu\gamma\varepsilon}_{ijkl} \, |(ij)[kl]| = \frac{1}{2}\Big[2C^{\mu\nu\gamma\varepsilon}_{1234} + C^{\mu\nu\gamma\varepsilon}_{1423} + C^{\mu\nu\gamma\varepsilon}_{2413} - C^{\mu\nu\gamma\varepsilon}_{1324}$$
$$- C^{\mu\nu\gamma\varepsilon}_{2314}\Big] \, |(12)[34]| + \frac{1}{2\sqrt{3}}\Big[3C^{\mu\nu\gamma\varepsilon}_{1324} - 3C^{\mu\nu\gamma\varepsilon}_{2314} + 2C^{\mu\nu\gamma\varepsilon}_{3412}$$
$$+ C^{\mu\nu\gamma\varepsilon}_{2413} - C^{\mu\nu\gamma\varepsilon}_{1423}\Big] \, |[12]34|$$
$$+ \sqrt{\tfrac{2}{3}}\Big[C^{\mu\nu\gamma\varepsilon}_{2413} - C^{\mu\nu\gamma\varepsilon}_{1423} - C^{\mu\nu\gamma\varepsilon}_{3412}\Big] \, |[123]4|$$

If:

$$D^{(\mu\nu)[\gamma\varepsilon]}_{ii[jl]} = \frac{1}{\sqrt{2}}\left[C^{\mu\nu\gamma\varepsilon}_{iijl} + C^{\mu\nu\gamma\varepsilon}_{ilij} - C^{\mu\nu\gamma\varepsilon}_{ijil}\right]$$
$$D^{(\mu\nu)[\gamma\varepsilon]}_{(ij)[kl]} = \frac{1}{2}\left[2C^{\mu\nu\gamma\varepsilon}_{ijkl} + 2C^{\mu\nu\gamma\varepsilon}_{iljk} + C^{\mu\nu\gamma\varepsilon}_{jlik} - C^{\mu\nu\gamma\varepsilon}_{ikjl} - C^{\mu\nu\gamma\varepsilon}_{jkil}\right]$$
$$D^{(\mu\nu)[\gamma\varepsilon]}_{[ij]kl} = \frac{1}{2\sqrt{3}}\left[3C^{\mu\nu\gamma\varepsilon}_{ikjl} - 3C^{\mu\nu\gamma\varepsilon}_{jkil} + 2C^{\mu\nu\gamma\varepsilon}_{klij} + C^{\mu\nu\gamma\varepsilon}_{jlik} - C^{\mu\nu\gamma\varepsilon}_{iljk}\right]$$
$$D^{(\mu\nu)[\gamma\varepsilon]}_{[ijk]l} = \sqrt{\tfrac{2}{3}}\left[C^{\mu\nu\gamma\varepsilon}_{jlik} - C^{\mu\nu\gamma\varepsilon}_{jlik} - C^{\mu\nu\gamma\varepsilon}_{klij}\right]$$

$$|(\mu\nu)[\gamma\varepsilon]| = \sum_{\substack{i,\,j<l \\ i\neq j,l}} D^{(\mu\nu)[\gamma\varepsilon]}_{ii[jl]} \, |ii[jl]|$$

$$+ \sum_{i<j<k<l} \Big[D^{(\mu\nu)[\gamma\varepsilon]}_{(ij)[kl]} \, |(ij)[kl]|$$

$$+ D^{(\mu\nu)[\gamma\varepsilon]}_{[ij]kl} \, |[ij]kl| + D^{(\mu\nu)[\gamma\varepsilon]}_{[ijk]l} \, |[ijk]l| \Big]$$

Therefore if:

$$D^{\mu\mu[\gamma\varepsilon]}_{\Theta} = \frac{1}{\sqrt{2}} D^{(\mu\mu)[\gamma\varepsilon]}_{\Theta}$$

$$D^{[\mu\nu]\gamma\varepsilon}_{\Theta} = \frac{1}{\sqrt{3}} D^{(\mu\nu)[\gamma\varepsilon]}_{\Theta} + \frac{2}{\sqrt{3}} D^{(\mu\gamma)[\nu\varepsilon]}_{\Theta}$$

$$D^{[\mu\nu\gamma]\varepsilon}_{\Theta} = -\frac{1}{\sqrt{2}} D^{[\mu\nu]\gamma\varepsilon}_{\Theta} - \sqrt{\frac{8}{2}} \, D^{(\gamma\varepsilon)[\mu\nu]}_{\Theta}$$

Then:

$$\Theta = \sum_{\substack{i,\,j<l \\ i\neq j,l}} D^{\Theta}_{ii[jl]} \, |ii[jl]| + \sum_{i<j<k<l} \Big[D^{\Theta}_{(ij)[kl]} \, |(ij)[kl]|$$

$$+ D^{\Theta}_{[ij]kl} \, |[ij]kl| + D^{\Theta}_{[ijk]l} \, |[ijk]l| \Big]$$

Table 2 Four-Electron Triplet Interpair CI Configurations

Θ	0	1	2	3	4	11	12	13	14	22	23	24	33	34	44
$\lvert 11[23]\rvert$	0	$-b_4$	$-X_2$	0	b_1	0	0	0	0	0	0	0	0	0	0
$\lvert 11[24]\rvert$	0	$\frac{1}{\sqrt{2}}(b_3-\sqrt{3}b_6)$	$-b_5$	$-b_1$	0	0	0	0	0	0	0	0	0	0	0
$\lvert 11[34]\rvert$	b_1	0	0	0	0	b_1	0	$\frac{1}{\sqrt{2}}(b_3-\sqrt{3}b_6)$	b_4	b_1	$-b_5$	X_2	0	0	0
$\lvert 22[13]\rvert$	0	0	b_2	b_4	$-X_1$	0	0	0	0	0	0	0	0	0	0
$\lvert 22[14]\rvert$	0	$-b_2$	0	$\frac{1}{\sqrt{2}}(b_3+\sqrt{3}b_6)$	b_5	0	0	0	0	0	0	0	0	0	0
$\lvert 22[34]\rvert$	b_2	0	0	0	0	0	0	$\frac{1}{\sqrt{2}}(b_3+\sqrt{3}b_6)$	b_5	0	$-b_4$	X_1	b_2	0	b_2
$\lvert 33[12]\rvert$	b_4	0	0	0	0	b_4	$\frac{1}{\sqrt{2}}(\sqrt{3}b_6-b_3)$	0	b_1	0	$-b_2$	0	b_4	$\frac{1}{\sqrt{2}}(b_3+\sqrt{3}b_6)$	0
$\lvert 33[14]\rvert$	0	$-b_1$	0	$-\frac{1}{\sqrt{2}}(b_3+\sqrt{3}b_6)$	b_4	0	0	0	0	0	0	0	0	0	0
$\lvert 33[24]\rvert$	0	$\frac{1}{\sqrt{2}}(\sqrt{3}b_6-b_3)$	$-b_4$	$-b_2$	0	0	0	0	0	0	0	0	0	0	0
$\lvert 44[12]\rvert$	b_5	0	0	0	0	0	X_2	0	b_2	b_5	$-b_1$	0	0	$-X_1$	b_5
$\lvert 44[13]\rvert$	0	0	b_1	b_5	X_1	0	0	0	0	0	0	0	0	0	0
$\lvert 44[23]\rvert$	0	$-b_5$	X_2	0	b_2	0	0	0	0	0	0	0	0	0	0
$\lvert (12)[34]\rvert$	b_3	0	0	0	0	$\frac{1}{2}(b_3+\sqrt{3}b_6)$	$\frac{1}{\sqrt{2}}(b_5-b_4$	$\frac{1}{\sqrt{2}}(b_1+b_2)$	0	$\frac{1}{\sqrt{2}}X_1$	0	$\frac{1}{\sqrt{2}}(b_1+b_2)$	$\frac{1}{2}(b_3-\sqrt{3}b_6)$	$\frac{1}{\sqrt{2}}(b_4-b_5)$	$\frac{1}{\sqrt{2}}X_2$
$\lvert [12]34\rvert$	b_6	0	0	0	0	$\frac{1}{2}(\sqrt{3}b_3-b_6)$	$\sqrt{\frac{3}{2}}b_4-\frac{b_5}{\sqrt{6}}$	$\sqrt{\frac{3}{2}}(b_2-b_1)$	0	$\frac{1}{\sqrt{12}}b_3+X_3$	0	$\frac{1}{\sqrt{6}}(b_2-b_1)$	$-\frac{1}{2}(\sqrt{3}b_3+b_6)$	$\sqrt{\frac{3}{2}}b_4-\frac{b_5}{\sqrt{6}}$	$-\frac{b_3}{\sqrt{12}}+X_3$
$\lvert [123]4\rvert$	b_7	0	0	0	0	b_7	$-2b_5/\sqrt{5}$	0	0	$\frac{2b_3}{\sqrt{6}}-X_4$	0	$\frac{2}{\sqrt{3}}(b_2-b_1)$	b_7	$-2b_5/\sqrt{3}$	$-\frac{2b_3}{\sqrt{6}}-X_4$

$X_1=\frac{1}{\sqrt{2}}b_3+\frac{1}{\sqrt{6}}b_6+\frac{2}{\sqrt{3}}b_7$ $\quad X_3=\frac{5}{6}b_6-\frac{\sqrt{2}}{3}b_7$

$X_2=\frac{1}{\sqrt{2}}b_3-\frac{1}{\sqrt{6}}b_6-\frac{2}{\sqrt{3}}b_7$ $\quad X_4=\frac{\sqrt{2}}{3}b_6-\frac{1}{3}b_7$

D. Energy Coefficients

The general 3-electron doublet, 4-electron singlet and 4-electron triplet wavefunctions are:

$$\Psi_{3D} = A_1\,|113| + A_2\,|223| + A_3\,|(12)3| + A_4\,|[12]3|$$

where

$$A_1 = A_2 = 0 \quad \text{for } {}^0\Psi_{3D} \;;\quad A_3 = 0 \quad \text{for } {}^1\Psi_{3D}$$

$$\begin{aligned}\Psi_{4S} = {} & A_1\,|1133| + A_2\,|1144| + A_3\,|2233| + A_4\,|2244| \\ & + A_5\,|[12][34]| + A_6\,|11(34)| + A_7\,|22(34)| + A_8\,|(12)(34)|\end{aligned}$$

where

$$\begin{aligned} & A_1 = A_2 = A_3 = A_4 = A_6 = A_7 = 0 && \text{for } {}^0\Psi_{4S} \\ & A_1 = A_2 = A_3 = A_4 = A_8 = 0 && \text{for } {}^1\Psi_{4S} \\ & A_6 = A_7 = A_8 = 0 && \text{for } {}^2\Psi_{4S}\end{aligned}$$

$$\begin{aligned}\Psi_{4T} = {} & A_1\,|11[34]| + A_2\,|22[34]| + A_3\,|33[12]| + A_4\,|44[12]| \\ & + A_5\,|[12]34| + A_6\,|[123]4| + A_7\,|(12)[34]| + A_8\,|[12][34]|_T\end{aligned}$$

where

$$\begin{aligned} & A_1 = A_2 = A_3 = A_4 = A_8 = 0 && \text{for } {}^0\Psi_{4T} \\ & A_3 = A_4 = A_7 = A_8 = 0 && \text{for } {}^1\Psi_{4T} \\ & A_5 = A_6 = A_7 = 0 && \text{for } {}^2\Psi_{4T}\end{aligned}$$

Calculating the energies of these wavefunctions, omitting necessarily zero terms and casting these equations in the general form:

$$\begin{aligned} E = {} & \sum_{i}^{N}\left[2f_i\,h_{ii} + a_{ii}\,J_{ii}\right] + 2\sum_{i>j}^{N}\left[a_{ij}\,J_{ij} + b_{ij}\,K_{ij}\right] \\ & + \sum_{m}^{NP}\sum_{\nu\neq m_1,m_2}^{N} c_{m\nu}\,\langle m_1|K_\nu|m_2\rangle + \sum_{n>m}^{NP}\left[d_{mn}\,(m_1n_1|m_2n_2) + e_{mn}\,(m_1n_2|m_2n_1)\right]\end{aligned}$$

gives the definitions of the coefficients $\{f, a, b, c, d, e\}$ in terms of the spin-pair coefficients $\{A\}$ shown in Table 3, where it is assumed that $\{A\}$ is normalized to $\sum_i A_i^2 = 1$.

Table 3a

Three-Electron Doublet Energy Coefficients

f_1	$A_1^2 + \frac{1}{2}(A_3^2 + A_4^2)$
f_2	$A_2^2 + \frac{1}{2}(A_3^2 + A_4^2)$
f_3	$\frac{1}{2}$
a_{11}	A_1^2
a_{22}	A_2^2
a_{33}	0
a_{12}	$\frac{1}{2}(A_3^2 + A_4^2)$
a_{13}	f_1
a_{23}	f_2
b_{12}	$A_1 A_2 + \frac{1}{2}(A_3^2 - A_4^2)$
b_{13}	$\frac{1}{4}(A_4^2 - A_3^2 - 2A_1^2) - \frac{\sqrt{3}}{2} A_3 A_4$
b_{23}	$\frac{1}{4}(A_4^2 - A_3^2 - 2A_1^2) + \frac{\sqrt{3}}{2} A_3 A_4$
c_{13}	$\sqrt{6} A_4 (A_1 - A_2)$

Table 3b

Four-Electron Singlet and Triplet Energy Coefficients

COEF.	SINGLET	TRIPLET
f_1	$A_1^2+A_2^2+A_6^2+\frac{1}{2}(A_5^2+A_8^2)$	$\frac{1}{2}(1+A_1^2-A_2^2)$
f_2	$A_3^2+A_4^2+A_7^2+\frac{1}{2}(A_5^2+A_8^2)$	$\frac{1}{2}(1+A_2^2-A_1^2)$
f_3	$A_1^2+A_3^2+\frac{1}{2}(A_5^2+A_6^2+A_7^2+A_8^2)$	$\frac{1}{2}(1+A_3^2-A_4^2)$
f_4	$A_2^2+A_4^2+\frac{1}{2}(A_5^2+A_6^2+A_7^2+A_8^2)$	$\frac{1}{2}(1+A_4^2-A_3^2)$
a_{11}	$A_1^2+A_2^2+A_6^2$	A_1^2
a_{22}	$A_3^2+A_4^2+A_7^2$	A_2^2
a_{33}	$A_1^2+A_3^2$	A_3^2
a_{44}	$A_2^2+A_4^2$	A_4^2
a_{12}	$\frac{1}{2}(A_5^2+A_8^2)$	$\frac{1}{2}(1-A_1^2-A_2^2)$
a_{13}	$2A_1^2+A_6^2+\frac{1}{2}(A_5^2+A_8^2)$	$\frac{1}{2}(1+A_1^2-A_2^2+A_3^2-A_4^2)$
a_{14}	$2A_2^2+A_6^2+\frac{1}{2}(A_5^2+A_8^2)$	$\frac{1}{2}(1+A_1^2-A_2^2-A_3^2+A_4^2)$
a_{23}	$2A_3^2+A_7^2+\frac{1}{2}(A_5^2+A_8^2)$	$\frac{1}{2}(1-A_1^2+A_2^2+A_3^2-A_4^2)$
a_{24}	$2A_4^2+A_7^2+\frac{1}{2}(A_5^2+A_8^2)$	$\frac{1}{2}(1-A_1^2+A_2^2-A_3^2+A_4^2)$
a_{34}	$\frac{1}{2}(A_5^2+A_6^2+A_7^2+A_8^2)$	$\frac{1}{2}(1-A_3^2-A_4^2)$
b_{12}	$A_1A_3+A_2A_4+A_6A_7+\frac{1}{2}(A_8^2-A_5^2)$	$A_1A_2+A_7^2-\frac{1}{2}(1-A_1^2-A_2^2)$
b_{13}	$\frac{1}{4}(A_5^2-A_8^2)-A_1^2-\frac{1}{2}A_6^2+\frac{\sqrt{3}}{2}A_5A_8$	$\frac{1}{4}(A_5^2-A_7^2)-\frac{1}{2}(A_1^2+A_3^2+A_6^2+\sqrt{3}A_5A_7)$
b_{14}	$\frac{1}{4}(A_5^2-A_8^2)-A_2^2-\frac{1}{2}A_6^2-\frac{\sqrt{3}}{2}A_5A_8$	$\frac{1}{12}(2A_6^2-5A_5^2+4\sqrt{2}A_5A_6)-\frac{1}{2}(A_1^2+A_4^2+\frac{1}{2}A_7^2)-\frac{A_7}{2\sqrt{3}}(A_5+2\sqrt{2}A_6)$
b_{23}	$\frac{1}{4}(A_5^2-A_8^2)-A_3^2-\frac{1}{2}A_7^2-\frac{\sqrt{3}}{2}A_5A_8$	$\frac{1}{4}(A_5^2-A_7^2)-\frac{1}{2}(A_2^2+A_3^2+A_6^2-\sqrt{3}A_5A_7)$
b_{24}	$\frac{1}{4}(A_5^2-A_8^2)-A_4^2-\frac{1}{2}A_7^2+\frac{\sqrt{3}}{2}A_5A_8$	$\frac{1}{12}(2A_6^2-5A_5^2+4\sqrt{2}A_5A_6)-\frac{1}{2}(A_1^2+A_4^2+\frac{1}{2}A_7^2)+\frac{A_7}{2\sqrt{3}}(A_5+2\sqrt{2}A_6)$
b_{34}	$A_1A_2+A_3A_4+\frac{1}{2}(A_6^2+A_7^2+A_8^2-A_5^2)$	$A_3A_4-\frac{1}{2}(A_1^2+A_2^2+A_7^2+A_8^2)+\frac{1}{6}(A_5^2-A_6^2-4\sqrt{2}A_5A_6)$
c_{13}	$\sqrt{6}A_5(A_6-A_7)$	$(\sqrt{6}A_5+A_8)(A_1-A_2)$
c_{14}	$-\sqrt{6}A_5(A_6-A_7)$	$2(A_8+\frac{1}{\sqrt{6}}A_5+\frac{2}{\sqrt{3}}A_6)(A_1-A_2)$
c_{21}	0	$2A_8(A_4-A_3)$
c_{22}	0	$2A_8(A_4-A_3)$
d_{12}	$2\sqrt{3}A_5(A_2+A_3)$	$-2(A_1A_3+A_2A_4)$
e_{12}	$2\sqrt{3}A_5(A_1+A_4)$	$2(A_1A_4+A_2A_3)$

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PROPOSITIONS

1.

Ordering of Two-Electron Integrals For Configuration Interaction Calculations

Abstract

Through use of a new 2-electron integral ordering sequence, it is proposed that CI matrices can be evaluated much more efficiently than is possible with the usual canonical ordering.

I. INTRODUCTION

Development of an efficient method for generating CI matrices over sets of general antisymmetrized orbital-product configurations (AOPs)[*] involving reasonably large numbers of orthogonal orbitals has been made very difficult owing to the horrendous number of 2-electron integrals involved. Since there are $\frac{1}{4}(M^2(M+1)^2/2 + M(M+1))$ such integrals for M orbitals, their number easily exceeds any central storage computer capabilities for all but small values of M (e.g. $M<25$). As a consequence, these integrals must usually be held in peripheral storage during CI matrix construction, with only a fraction being available in core at any one time. However, when dealing with moderately large numbers of configurations, practical considerations require that a given matrix element, or a small group of them, be completely evaluated and stored peripherally before calculating other elements. Therefore, all integrals needed to calculate a given matrix element must be readily available at the same time. Because of this, all procedures which start with an integral list in the usual can-

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[*] An AOP has the general form:

$$\mathcal{A}\Phi\chi$$

where $\mathcal{A}$ is the antisymmetrizer (determinant operator), Φ is a product of doubly- and singly-occupied orbitals, and χ is any compatible spin function.

onical[*] order must, in one way or another, involve highly inefficient multi-pass methods in which those integrals currently needed are first identified and then brought into central storage after scanning the peripherally stored integral list for them. When dealing with large numbers of orbitals and configurations, such procedures can be extremely time consuming and expensive. A procedure which can avoid this problem will now be proposed. This approach involves abandoning the customary canonical integral ordering. Instead, the integrals are ordered in a different, but nontheless general, way which permits complete evaluation of all matrix elements requiring any integral currently in central storage.

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[*] The IJKL canonical index for the 2-electron integral $(IJ|KL)$ written in $(11|22)$ form is:

$$\begin{aligned} IJKL &= IJ\,(IJ-1)/2 + KL \qquad && IJ \geqslant KL \\ IJ &= I\,(I-1)/2 + J && I \geqslant J \\ KL &= K\,(K-1)/2 + L && K \geqslant L \end{aligned}$$

II. DISCUSSION

If we define a spatial configuration as simply being some set of doubly- and singly-occupied orthogonal orbitals from which one or more AOPs are to be constructed, then all CI matrix elements between all possible AOPs for spatial configurations Φ_A and Φ_B can, of course, be evaluated using only those 2-electron integrals which involve only those orbitals appearing in Φ_A and Φ_B. Moreover, since all orbitals are orthogonal, of these, only certain specific integrals are actually ever required. The number and type of these integrals depends upon how Φ_A and Φ_B differ from each other:[1]

A) Zero Excitation:

If $\Phi_A = \Phi_B$, only the coulomb and exchange integrals involving the orbitals of Φ_A will ever be needed to calculate any matrix elements:

$$J_{ij} = \langle i \,|J_j|\, i\rangle = \langle \phi_i \phi_j | \tfrac{1}{r_{12}} | \phi_i \phi_j \rangle$$
$$K_{ij} = \langle i \,|K_j|\, i\rangle = \langle \phi_i \phi_j | \tfrac{1}{r_{12}} | \phi_j \phi_i \rangle$$

where $\phi_i, \phi_j \in \Phi_A$

B) Single Excitation:

If Φ_A and Φ_B differ by orbitals ϕ_a and ϕ_b respectively, the only 2-electron integrals ever needed are of the form:

$$\langle a \,|\, J_\mu \,|\, b\rangle, \quad \langle a \,|\, K_\nu \,|\, b\rangle$$

where $\phi_\mu \in \Phi_A$ and $\phi_\nu \in \Phi_A \neq \phi_a, \phi_b$

C) Double Excitation:

If Φ_A differs from Φ_B by orbitals ϕ_{a_1} and ϕ_{a_2} while Φ_B differs from Φ_A by orbitals ϕ_{b_1} and ϕ_{b_2}, the following subclassifications are possible:

1) Core Excitation:

If $\phi_{a_1} = \phi_{a_2}$ and $\phi_{b_1} = \phi_{b_2}$, only the exchange integral $K_{a_1 b_1}$ will ever be required.

2) 1-Integral Double:

If $\phi_{a_1} = \phi_{a_2}$, but $\phi_{b_1} \neq \phi_{b_2}$, all possible matrix elements can be calculated using only the integral:

$$\langle b_1 \,|\, K_{a_1} \,|\, b_2 \rangle$$

3) 2-Integral Double:

If $\phi_{a_1} \neq \phi_{a_2}$ and $\phi_{b_1} \neq \phi_{b_2}$, the only two integrals ever needed are:

$$(a_1 b_1 | a_2 b_2) = \langle \phi_{a_1} \phi_{a_2} | \tfrac{1}{r_{12}} | \phi_{b_1} \phi_{b_2} \rangle$$

$$(a_1 b_2 | a_2 b_1) = \langle \phi_{a_1} \phi_{a_2} | \tfrac{1}{r_{12}} | \phi_{b_2} \phi_{b_1} \rangle$$

D) Higher Excitations:

Since all orbitals are orthogonal, if Φ_A and Φ_B differ by more than a double excitation, all matrix elements must be zero.

Thus, we see that in evaluating all possible AOP CI matrix elements between pairs of spatial configurations differing by specific types of excitations, only specific types of 2-electron integrals need be available:

A) Type 1 - All integrals involving just one or two orbitals:

$$J_{ii}\ ,\ J_{ij}\ ,\ K_{ij} \qquad i<j\leq M$$

With these, all zero and core spatial excitations can be handled.

B) Type 2 - All integrals involving three different orbitals:

$$\langle i|J_\mu|j\rangle\ ,\ \langle i|K_\nu|j\rangle \qquad i<j\leq M \quad \mu\leq M \quad \nu\neq i,j\leq M$$

With these, all single and 1-integral double spatial excitations can be handled.

C) Type 3 - All integrals involving four different orbitals:

$$(ij|kl),\ (ik|jl),\ (il|jk) \qquad l<k<j<i\leq M$$

With these, all 2-integral double spatial excitations can be handled.

Hence, if central storage could accommodate each one of these three groups separately, CI matrices could be generated by simply calculating all matrix elements resulting from those spatial excitations requiring integrals of the particular type currently at hand.

Since there are only M^2 type 1 integrals, it is safe to assume that these can all be held in central storage simultaneously. Unfortunately, this cannot be presumed to be the case for the much more numerous type 2 and type 3 integrals. This problem, however, can easily be solved by ordering these integrals in a specific manner.

Any spatial excitation requiring type 2 integrals really only needs integrals from a subset of the form:

$$\langle i | J_\mu | j \rangle, \ \langle i | K_\nu | j \rangle \qquad \mu \leqslant M \qquad \nu \neq i, j \leqslant M$$

where i and j ($i > j$) are fixed. Thus, if type 2 integrals are grouped into such subsets, all matrix elements which require any integrals in those complete subsets currently held in core can be evaluated completely.

Any spatial excitation requiring type 3 integrals can really only need integrals from a triad of the form:

$$(ij|kl),\ (ik|jl),\ (il|jk)$$

where $M \geqslant i > j > k > l$. Thus, if type 3 integrals are grouped into such triads, all matrix elements requiring any integrals in those complete triads currently in core can be evaluated completely.

Thus, we find that if the 2-electron integral list is arranged in the order:

$$\{J_{ii}\}\ \{J_{ij}\}\ \{K_{ij}\}\ \{\langle i|J_u|j\rangle, \langle i|K_\nu|j\rangle\}\ \{(ij|kl), (ik|jl), (il|jk)\}$$

where

$$M \geqslant i > j > k > l\ ;\quad u \leqslant M\ ;\quad \nu \neq i,j \leqslant M$$

then all CI matrix elements involving an integral held in central storage at any one time can be completely evaluated since all other integrals which might be required can also be present. Rearranging a random 2-electron integral list into this order is relatively easy and requires no more effort than is needed to obtain the customary canonical ordering.

Efficient use of this integral order is, of course, contigent upon knowing all the pairs of spatial configurations between which matrix elements require integrals of that group currently held in central storage. This can be best accomplished by first checking all pairs of spatial configurations and categorizing them according to which integral group they will require (Type 1? Which type 2 group? Which type 3 group?). These pair numbers, plus other essential information obtained during the categorization process, can be stored peripherally by category for later retrieval as each group of integrals becomes available.

III. CONCLUSION

A method making possible efficient generation of AOP CI matrices for spatial configurations constructed from reasonably large sets of orthogonal orbitals has been outlined. This procedure involves ordering of the 2-electron integrals in such a way that when taken together with prior spatial configuration pair categorization, it becomes possible to completely evaluate all matrix elements involving that fraction of 2-electron integrals currently in central storage.

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2.

Investigation Of a Localized Orbital Model For Singlet-Pair Transfer Processes

Abstract

Despite initial appearances to the contrary, it is proposed that the Generalized Valence-Bond description of singlet-pair transfer processes may distill into a simple localized orbital model.

I. INTRODUCTION

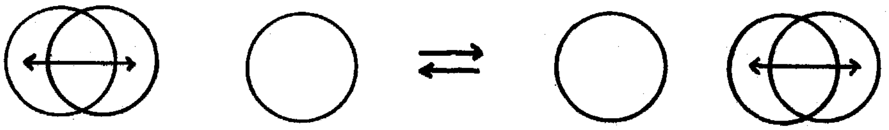
In any attempt to uncover those key factors essential to the development of a theoretically based model of chemical reactivity, studies of reactions involving basicly three electrons are of fundamental importance. This is because such reactions represent the simplest examples of processes involving disruption of one chemical bond and formation of a new bond. This occurs in colinear exchange reactions such as:

$$H_2 + D \rightleftarrows H + HD$$
$$LiH + H \rightleftarrows Li + H_2$$

Also fitting into this category are simple molecule formation reactions such as:

$$Be + H \rightarrow BeH\ ({}^{2}\Sigma^{+})$$
$$B + H \rightarrow BH\ ({}^{1}\pi, {}^{3}\pi)$$
$$C + H \rightarrow CH\ ({}^{2}\Delta, {}^{4}\Sigma^{-}, \cdots)$$

in which the initial 'bond' involves two electrons of the same atom. As all of these reactions involve low-lying atomic and (covalent) molecular states, an orbital description of each (with each electron having its own orbital) begins and ends with two highly overlapping singlet paired orbitals such that if the original pair is to the left of center, then the product pair is to the right of center;*



For this reason, we will categorize these reactions as being singlet-pair transfer (or bond transfer) processes. Considering the three π-orbitals of allyl radical to be trapped midway through such a process also provides us with an opportunity to investigate the phenomena of resonance stabilization as well.

Since these processes are of such basic importance, it is essential that any physical concepts advanced to explain them be based upon theoretical calculations (i.e. a wavefunction) capable of describing the energetics involved in at least a semiquantitative manner. Obviously, such a wavefunction must also be physically interpretable. Since the ultimate goal is to develop a physical model capable of predicting chemical mechanisms without detailed calculations, it is equally important to extract from such a wavefunction those key factors leading to a definitive description of the processes involved.

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* The presence of additional nonparticipating electrons is ignored.

It has been known for some time that Generalized Valence-Bond (GVB) wavefunctions[1] are capable of adequately describing singlet-pair transfer processes. However, there has been some confusion regarding the most useful interpretation of these results. Based upon qualitative arguments presented in the following section, it is proposed to investigate the possibility that these GVB results distill essentially into a simple localized-orbital model, despite initial appearances to the contrary.

II. DISCUSSION

Since singlet-pair transfer processes begin and end with singlet coupling between two highly overlapping orbitals, let us first consider the simple wavefunction in which singlet pairing is preserved throughout:

$$\psi_{PP} = \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 \\ \cline{1-1}\end{array} = \mathcal{A}\ \phi_1\phi_2\phi_3\,(\alpha\beta-\beta\alpha)\alpha \qquad (1)$$

where no restrictions are placed on any of the orbitals (Note that if $\phi_1 = \phi_2$, this reduces to the Hartree-Fock wavefunction). As is illustrated in Fig. 1 and 2, singlet-pair migration can be accomplished in a straightforward manner through delocalization and subsequent relocalization of ϕ_2 and ϕ_3. As these two orbitals move in opposite directions, ϕ_2 can always maintain high overlap with ϕ_1, while ϕ_3 can always remain essentially orthogonal to both of these orbitals. Since ϕ_1 and ϕ_2 are always singlet paired <u>and</u> highly overlapping, while ϕ_3 is always nearly orthogonal to this pair (to which it is antisymmetrically coupled), repulsive interactions between these orbitals are always kept to a minimum. Thus, this wavefunction provides us with a physical model for singlet-pair transfer which is not only simple, but quite reasonable as well.

Within this model, the original singlet-pair simply moves intact from one region of space to another. The unpaired orbital simultaneously moves in the other direction, developing antibonding character (i.e. a nodal plane) as it readjusts to achieve favorable small overlap with this pair. Hence, in simple exchange reactions, we are led to the notion that instead of one bond breaking as another is formed, what actually occurs is that the original bond is simply transferred intact from reactants to products. Assuming that the π-orbitals of ground state allyl radical are trapped midway through such a process, the resonance energy of this molecule can be attributed to delocalization of a bonding (no nodes) singlet-pair over the entire system, with the unpaired orbital exhibiting typical antibonding character (a central nodal plane).

Thus, we have the makings of a simple model for describing chemical reactions and resonating systems. However, upon closer scrutiny it is found that there are serious problems with the Perfect-Pairing (PP) wavefunctions upon which this model is based. While wavefunctions (1) adequately describe both reactants and products, they typically give energies much higher than would be preferred in intermediate regions. Of much greater importance, however, is the simple fact that, in general, PP wavefunctions cannot continuously describe singlet-pair transfer. This was revealed in PP calculations for formation of the $^2\Delta$ and $^4\Sigma^-$ states of CH, where it was found that it was not possible to go smoothly from reactants to products (Fig. 3) . The reason for these inadequacies will be discussed later. For now, it suffices to say that since any physical model we develop must be based upon a wavefunction which at least behaves properly, we must look for another wavefunction from which to extract physical concepts.

Above, we let the orbitals themselves change, but kept the coupling between them fixed. Therefore, the logical thing to do next is to unrestrict this coupling as well. Wavefunctions in which both the orbitals themselves and the coupling between them are unrestricted are Generalized Valence-Bond (GVB) wavefunctions. For the three electron doublets considered here, this wavefunction can be written as a linear combination of any two linearly independent couplings between these orbitals. For later convenience, let us choose these to be the $\boxed{\phi_1 \phi_2}$ and $\boxed{\phi_1 \phi_3}$ singlet pair couplings:

$$\psi_{GVB} = \mathcal{E}_1 \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + \mathcal{E}_2 \begin{array}{|c|c|}\hline \phi_1 & \phi_3 \\ \hline \phi_2 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \qquad (2)$$

where ϕ_1 and ϕ_2 comprise the reactant singlet-pair. In all cases investigated thus far, GVB wavefunctions have been found to behave properly[2](i.e. go smoothly from reactants to products) and always give much better intermediate energies than PP wavefunctions. Typically, the orbitals change as shown in Fig. 1 and 2. That is, they behave qualitatively the same as in PP wavefunctions (The differences involve relative degrees of delocalization). Thus, ϕ_2 and ϕ_3 still effectively exchange original identities through delocalization-re-localization, with ϕ_2 maintaining high overlap with ϕ_1 and ϕ_3 remaining nearly orthogonal to these two orbitals. However, while this is going on, the coupling between these orbitals also changes significantly (Fig. 4 & 5). Upon analysis of these coupling changes, it is always found that during delocalization, ϕ_1 and ϕ_2 become increasingly less symmetrically (singlet) coupled as ϕ_1 and ϕ_3 become increasingly more symmetrically (singlet) coupled (This is not only because $|\varepsilon_1|$ decreases as $|\varepsilon_2|$ increases, but also because these coefficients are opposite in sign) Once ϕ_2 and ϕ_3 have become fully delocalized and begin to relocalize, this trend (which is toward triplet coupling between ϕ_2 and ϕ_3) reverses itself as $\boxed{\phi_1\phi_2}$ pairing corresponds to product coupling.

Thus, we have found that singlet-pair transfer can always be described by a GVB wavefunction, but not by a PP wavefunction. We have found that this GVB description involves both the orbital changes expected for a PP description and significant orbital recoupling in intermediate regions. There is, in fact, only one problem. During delocalization, the overlap between orbitals ϕ_1 and ϕ_2 does not decrease, but the symmetric coupling between them does decrease. Moreover, while ϕ_1 and ϕ_3 remain nearly orthogonal during delocalization, the symmetric coupling between them increases. Hence, it would seem that repulsive interactions between orbitals are greater in the GVB wavefunction than they are in the inadequate PP wavefunction. Upon what bases then can we extract generally applicable physical concepts from these GVB results?

In both the PP and GVB descriptions of singlet-pair transfer, ϕ_1 remains essentially localized throughout. If ϕ_2 and ϕ_3 are initially localized to the left and right of ϕ_1 respectively, with ϕ_1 and ϕ_2 comprising the reactant singlet-pair, then during delocalization-relocalization of ϕ_2 and ϕ_3 , ϕ_2 develops more and more right-hand character as ϕ_3 develops more and more left-hand character. Therefore, let's assume that these two orbitals can always be expressed as:

$$\phi_2 = \lambda_{l_2}\phi_l + \lambda_{r_2}\phi_r \quad ; \quad 1 = \lambda_{l_2}^2 + \lambda_{r_2}^2 + 2\lambda_{l_2}\lambda_{r_2}\langle\phi_l|\phi_r\rangle \quad ; \quad \lambda_{l_2}\lambda_{r_2} \geqslant 0$$
$$\phi_3 = \lambda_{r_3}\phi_r - \lambda_{l_3}\phi_l \quad ; \quad 1 = \lambda_{l_3}^2 + \lambda_{r_3}^2 - 2\lambda_{l_3}\lambda_{r_3}\langle\phi_l|\phi_r\rangle \quad ; \quad \lambda_{l_3}\lambda_{r_3} \geqslant 0$$

where ϕ_l and ϕ_r are localized orbitals allowed full variational freedom within their respective regions. That is, ϕ_l decays to the right of ϕ_1, changing smoothly from ϕ_2 (initial) to ϕ_3 (final) and ϕ_r decays to the left of ϕ_1, changing from ϕ_3 (initial) to ϕ_2 (final). Renaming ϕ_1 as ϕ_c to indicate its regional localization, the PP wavefunction in terms of these <u>localized</u> orbitals is:

$$\Psi_{PP} = \begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 \\ \cline{1-1}\end{array}$$

$$= \underbrace{\lambda_{l_2}\lambda_{r_3}\begin{array}{|c|c|}\hline \phi_c & \phi_l \\ \hline \phi_r \\ \cline{1-1}\end{array} - \lambda_{l_3}\lambda_{r_2}\begin{array}{|c|c|}\hline \phi_c & \phi_r \\ \hline \phi_l \\ \cline{1-1}\end{array}}_{\text{covalent}} + \underbrace{\lambda_{l_2}\lambda_{l_3}\mathcal{A}\,\phi_l^2\phi_c\alpha\beta\alpha - \lambda_{r_2}\lambda_{r_3}}_{\text{ionic}}\overset{(3)}{\mathcal{A}}\,\phi_r^2\phi_c\alpha\beta\alpha$$

whereas the GVB wavefunction is:

$$\Psi_{GVB} = \varepsilon_1\begin{array}{|c|c|}\hline \phi_1 & \phi_2 \\ \hline \phi_3 \\ \cline{1-1}\end{array} + \varepsilon_2\begin{array}{|c|c|}\hline \phi_1 & \phi_3 \\ \hline \phi_2 \\ \cline{1-1}\end{array}$$

$$= (\varepsilon_1\lambda_{l_2}\lambda_{r_3} - \varepsilon_2\lambda_{l_3}\lambda_{r_2})\underbrace{\begin{array}{|c|c|}\hline \phi_c & \phi_l \\ \hline \phi_r \\ \cline{1-1}\end{array} + (\varepsilon_2\lambda_{l_2}\lambda_{r_3} - \varepsilon_1\lambda_{l_3}\lambda_{r_2})}_{\text{covalent}}\begin{array}{|c|c|}\hline \phi_c & \phi_r \\ \hline \phi_l \\ \cline{1-1}\end{array}$$

$$+ (\varepsilon_1+\varepsilon_2)\Big[\underbrace{\lambda_{l_3}\lambda_{l_2}\mathcal{A}\,\phi_l^2\phi_c\alpha\beta\alpha - \lambda_{r_2}\lambda_{r_3}\mathcal{A}\,\phi_r^2\phi_c\alpha\beta\alpha}_{\text{ionic}}\Big] \qquad (4)$$

$$\varepsilon_1\varepsilon_2 \leqslant 0$$

Examining the covalent part of each wavefunction which can be written as:

$$\psi_{\text{COVALENT}} = \gamma_1 \begin{array}{|c|c|}\hline \phi_c & \phi_\ell \\ \hline \phi_r \\ \cline{1-1}\end{array} + \gamma_2 \begin{array}{|c|c|}\hline \phi_c & \phi_r \\ \hline \phi_\ell \\ \cline{1-1}\end{array} \qquad (5)$$

we find that in going from reactants, in which ϕ_c and ϕ_ℓ are singlet paired, to the products, in which ϕ_c and ϕ_r are singlet paired, $|\gamma_1|$ decreases from unity as $|\gamma_2|$ increases from zero to finally approach unity. Moreover, these coefficients always differ in sign. Therefore, as ϕ_c and ϕ_r overlap more and more, they also become increasingly singlet coupled. In addition, as ϕ_c and ϕ_ℓ overlap less and less, the singlet coupling between them decreases. Thus, as far as the covalent part of each wavefunction goes, the changes in the (localized) orbitals and the changes in the coupling between these orbitals are consistent with minimizing repulsive interactions between them.

Considering the low-lying atomic states we are dealing with, in and of themselves the ionic configurations appearing in each wavefunction obviously have high energies. Therefore, it is safe to assume that these ionic terms should never contribute greatly to the wavefunction. However, in the PP wavefunction (3) there are only two independent parameters to control the relative contributions of the four configurations involved. Hence, the extensive delocalization <u>needed</u> to go from reactants to products necessarily forces the wavefunction to take on an inordinant amount of ionic character. For example, the PP description of allyl radical considered earlier would correspond to equal amounts of covalent and ionic character:

$$\psi_{PP} = \begin{array}{|c|c|}\hline \phi_c & \phi_\ell \\ \hline \phi_r & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} - \begin{array}{|c|c|}\hline \phi_c & \phi_r \\ \hline \phi_\ell & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + a\,\phi_\ell^2\phi_c\alpha\beta\alpha - a\,\phi_r^2\phi_c\alpha\beta\alpha$$

It is not surprising then that PP wavefunctions give energies too high in intermediate regions. This enforced ionic character also explains why PP wavefunctions do not continuously describe singlet-pair transfer. Initial delocalization occurs so as to keep excessive ionic contributions to a minimum. The mode of delocalization, however, depends upon whether we start from reactants or products. As a consequence, continual change in this initial mode (least change path) need not lead to the desired limit.

In the GVB wavefunction (4), each one of these four configurations can contribute independently. Moreover, we know that the common coefficient for each ionic term, ($\varepsilon_1 + \varepsilon_2$), continually decreases as delocalization increases. Thus, despite increasing delocalization, it would seem that these ionic contributions (which are really the only consequence of delocalization) do remain relatively small at all times. For example, in the GVB description of allyl radical, covalent terms account for over 80% of the wavefunction:[3]

$$\psi = \begin{array}{|c|c|}\hline \phi_c & \phi_l \\ \hline \phi_r & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} - \begin{array}{|c|c|}\hline \phi_c & \phi_r \\ \hline \phi_l & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} + 0.2\left[\mathcal{A}\,\phi_l^2\phi_c\alpha\beta\alpha - \mathcal{A}\,\phi_r^2\phi_c\alpha\beta\alpha\right]$$

Thus, by partitioning these wavefunctions into covalent and ionic parts in terms of localized orbitals (able to distort, but always retaining their initial identities) we have found that in GVB wavefunctions the relative covalent and ionic contributions can vary independently. Since the sole effect of the observed orbital delocalization is to impart ionic character to these GVB wavefunctions and since the simultaneously occurring orbital recoupling appears to keep ionic contributions small despite extensive delocalization, it is quite possible that the overall result of these drastic orbital changes is only to offset to a minor extent unfavorable interactions developing within the covalent wavefunction (5). If this assumption is correct, it would seem only logical to base any physical model of singlet-pair transfer (reactions and resonance in general?) upon the localized-orbital GVB wavefunction (5). As mentioned previously, this wavefunction describes singlet-pair transfer as involving dissolution of the reactant bond with simultaneous formation of the product bond. The changes in both the orbitals and the coupling between them in going from reactants to products are consistent with those basic premises which have had great success in analyzing the GVB descriptions of the low-lying states of many molecules (equilibrium geometries):[4]

1) Orbitals remain largely atomiclike, distorting somewhat owing to their molecular environment.
2) Repulsive interaction between orbitals are minimized by:
    A) Symmetric coupling between orbitals having high overlap.
    B) Antisymmetric coupling between orbitals having small overlap

Hence, by suitably modifying this localized-orbital description to account for ionic perturbations (if necessary), it may be possible to distill from raw GVB results the essential elements needed to develop a generally applicable model for chemical reactions and resonating systems.

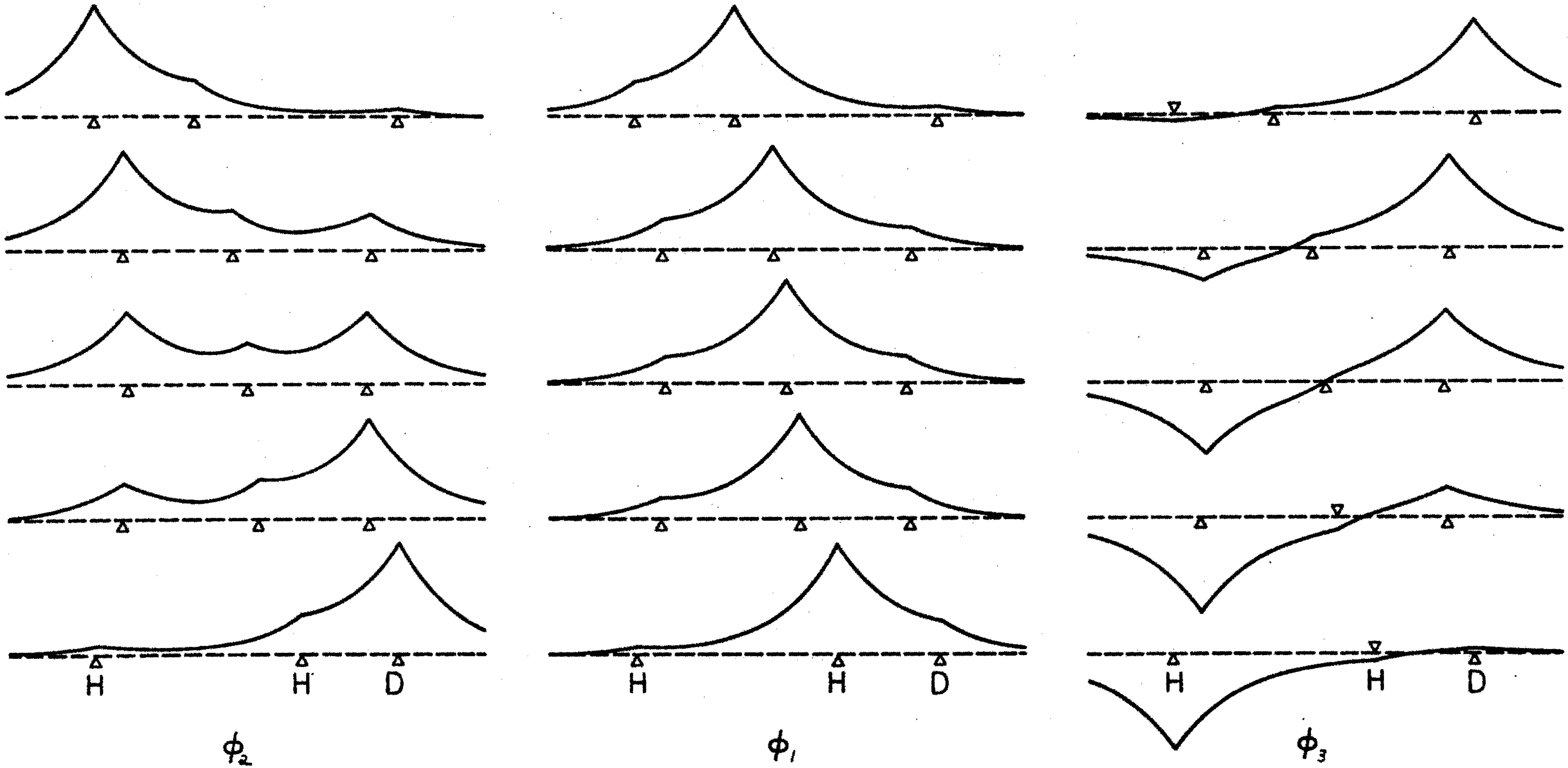
Therefore, it is proposed to make a thorough investigation of singlet-pair transfer processes in terms of these covalent and ionic contributions to determine if the assumptions which have been made are valid, and if so, to what extent the localized-orbital model needs to be modified. In order to do this, several essential questions must be answered:

1) Can a localized-orbital description of singlet-pair transfer go continuously from reactants to products?
2) How much worse would a localized-orbital description be? Are the essential features of the potential energy curves preserved or severely distorted?
3) How does ionic character change during delocalization? Is it more important at full delocalization or just after delocalization begins?
4) How system-dependent is the degree of ionic character which develops?
5) If ionic contributions are essential, is there a simple way to account for them within a localized-orbital model?

Analysis of existing GVB results may help answer some of these questions. However, new calculations designed to get to the heart of the matter will also be required. CI calculations using frozen atomic orbitals may be helpful, provided they can adequately describe both reactants and products. Most likely, calculations in which the orbitals are allowed to vary between their initial and final localized forms will also be required. This can be done by restricting the space available to each orbital in actual GVB calculations or through use of simple iterative CI techniques in which each orbital is expressed as a linear combination of its initial and final forms.

III. CONCLUSION

Based upon qualitative arguments, it would appear likely that the well-behaved GVB description of 3-orbital singlet-pair transfer processes is best described by a simple localized-orbital model, despite the extensive orbital delocalizations observed. This is because the simultaneous orbital coupling changes tend to minimize the net effect of these drastic orbital changes. Within such a model, which may require modification to account for ionic perturbations, the reactant bond gradually breaks as the product bond forms. It has been shown that this model is consistent with minimization of repulsive interactions between atomic-like orbitals; the very concept upon which the GVB description of many low-lying molecular states have been successfully based. This is in contrast to the incorrect model one would arrive at based solely on the observed orbital changes, in which the reactant bond (i.e. two highly overlapping singlet paired orbitals) is simply transferred intact to the products. It has been proposed to verify the assumptions made through localized orbital calculations from which the relative covalent and ionic contributions to the wavefunction can be easily ascertained. It is felt that through such a representation, the basic essentials involved in these processes will become apparent and may help lead toward the development of a generally applicable physical model for chemical reactions and resonating systems.



$H_2 + D \rightleftarrows H + HD$

FIG. 1

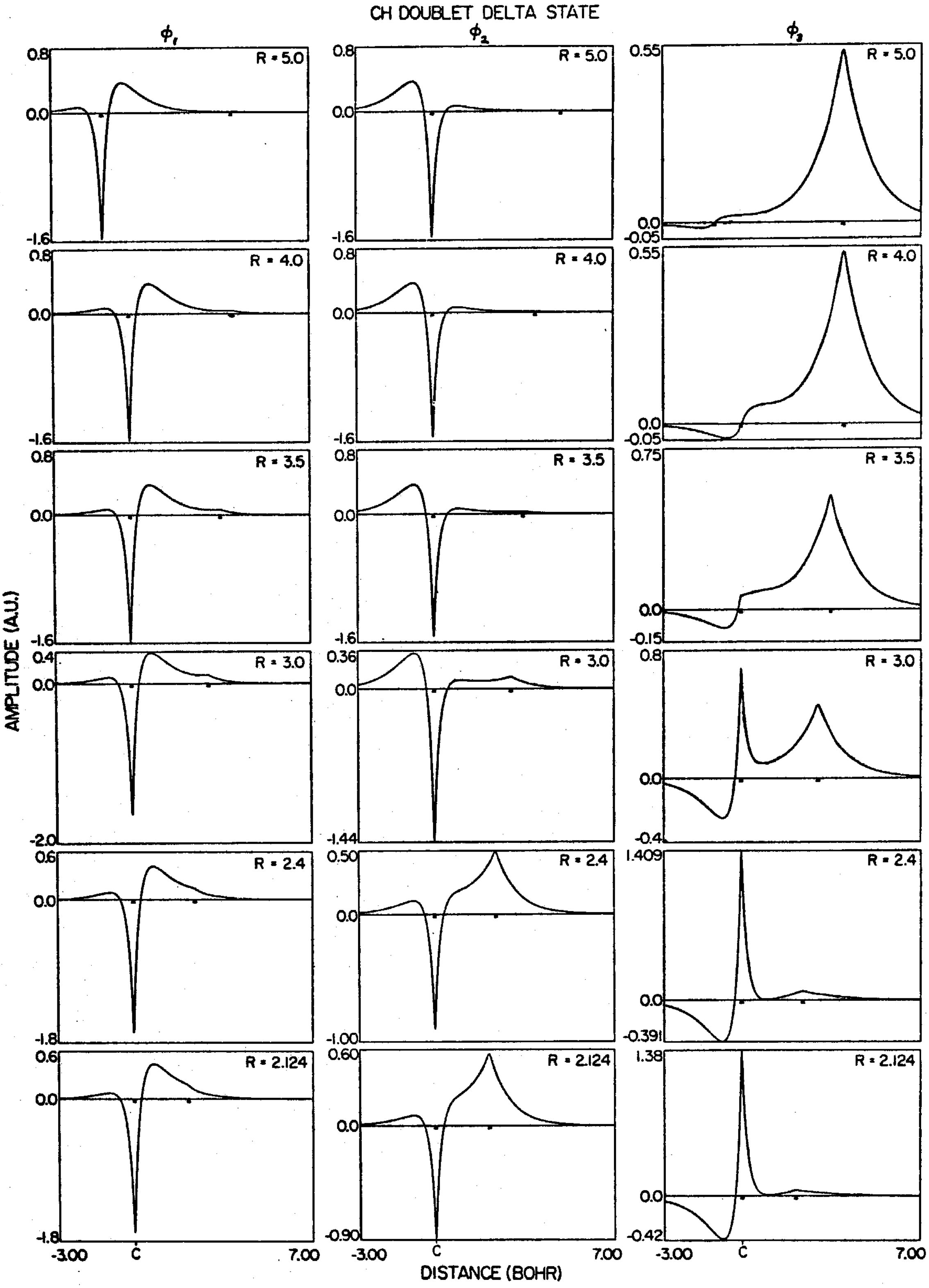

CH DOUBLET DELTA STATE
φ1
φ2
φ3
AMPLITUDE (A.U.)
DISTANCE (BOHR)
R = 5.0
R = 4.0
R = 3.5
R = 3.0
R = 2.4
R = 2.124
0.8
0.0
-1.6
0.4
-2.0
0.6
-1.8
0.36
-1.44
0.50
-1.00
0.60
-0.90
0.55
-0.05
0.75
-0.15
-0.4
1.409
-0.391
1.38
-0.42
-3.00
C
7.00

FIG. 2

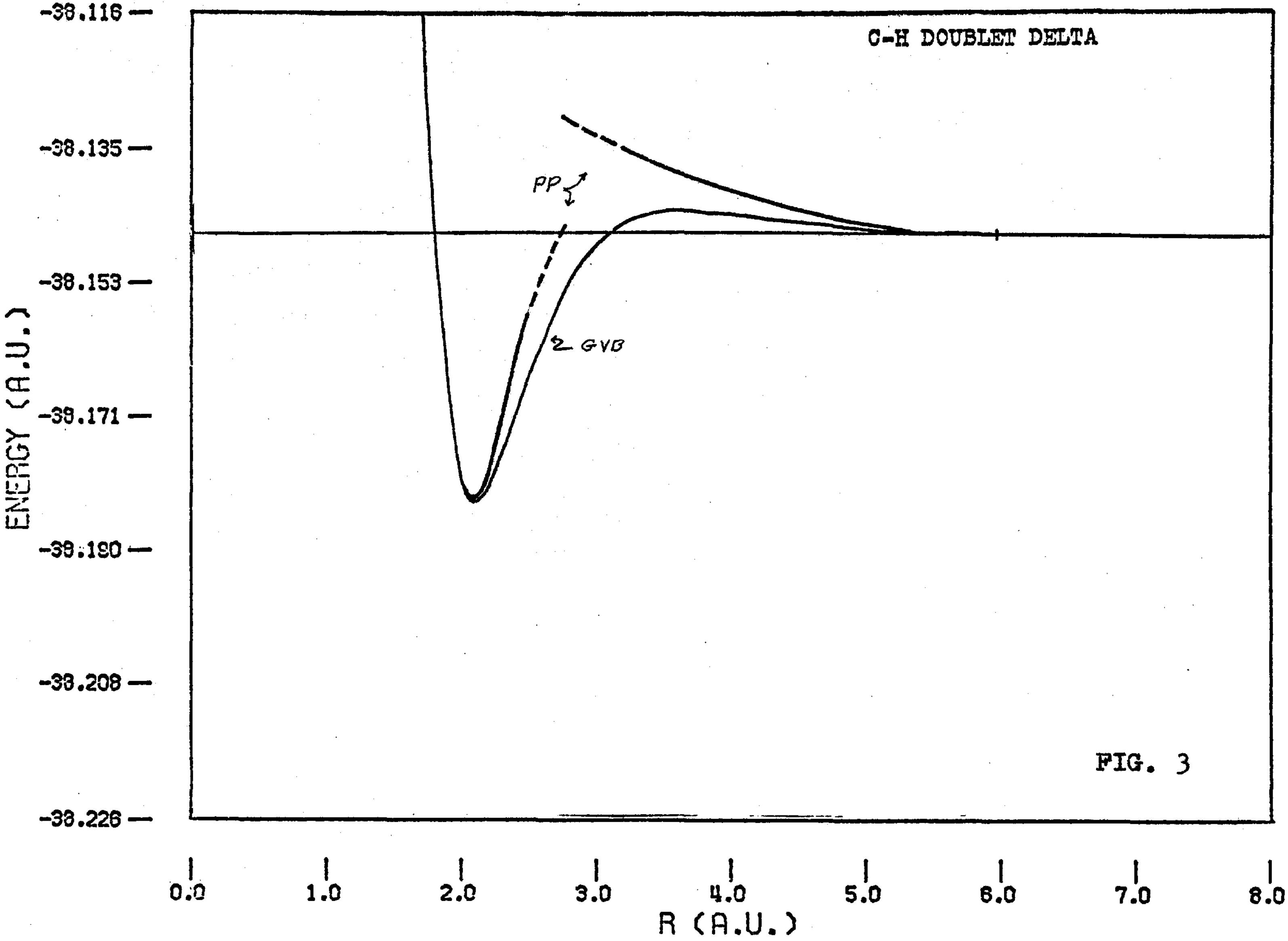

C-H DOUBLET DELTA
PP
GVB
ENERGY (A.U.)
-38.116
-38.135
-38.153
-38.171
-38.190
-38.208
-38.226
R (A.U.)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

FIG. 3

H_2 + D SPIN-COUPLING ε_{max} PLOT

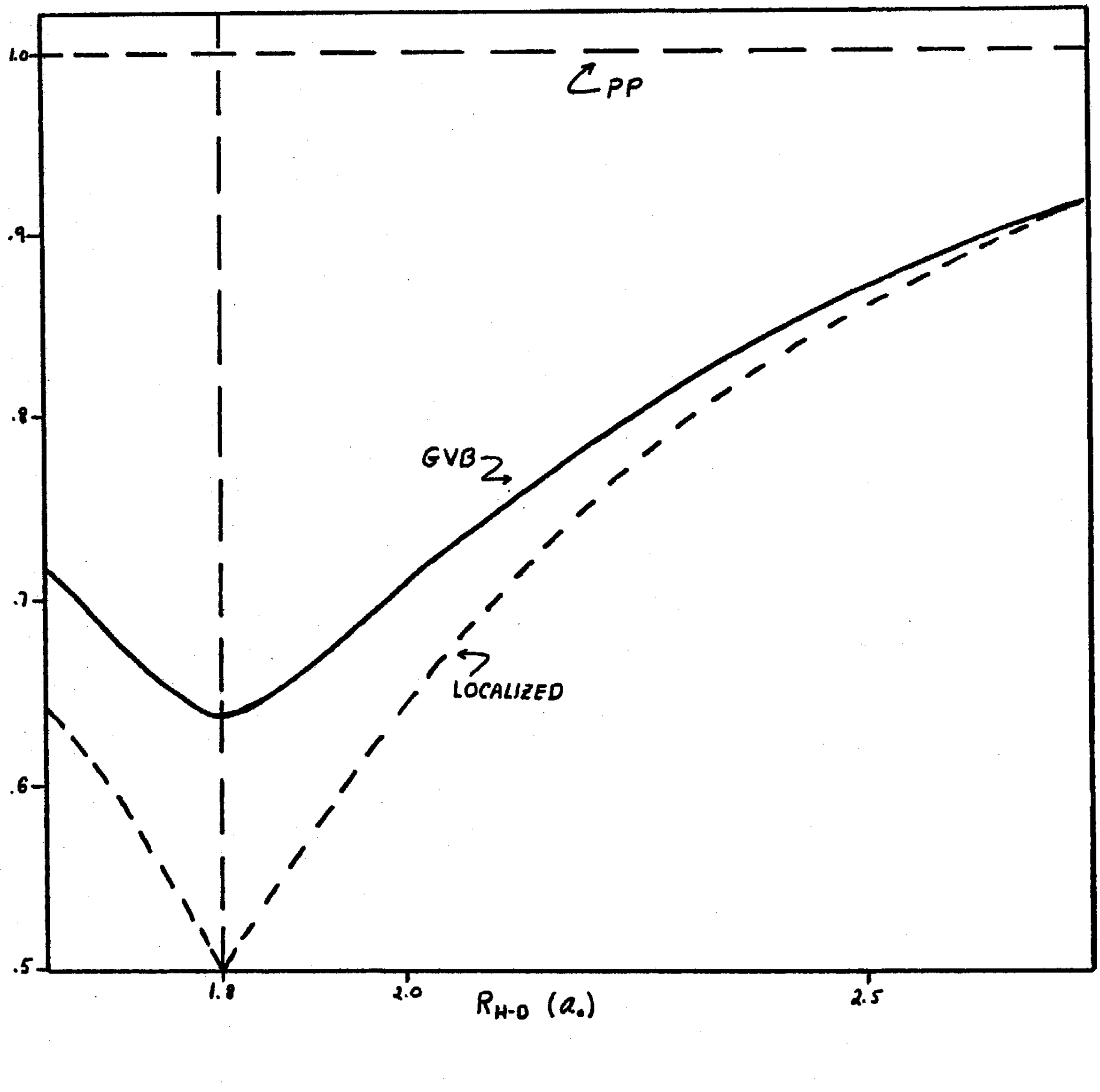


FIG. 4

CH ²Δ COUPLING COEFFICIENTS

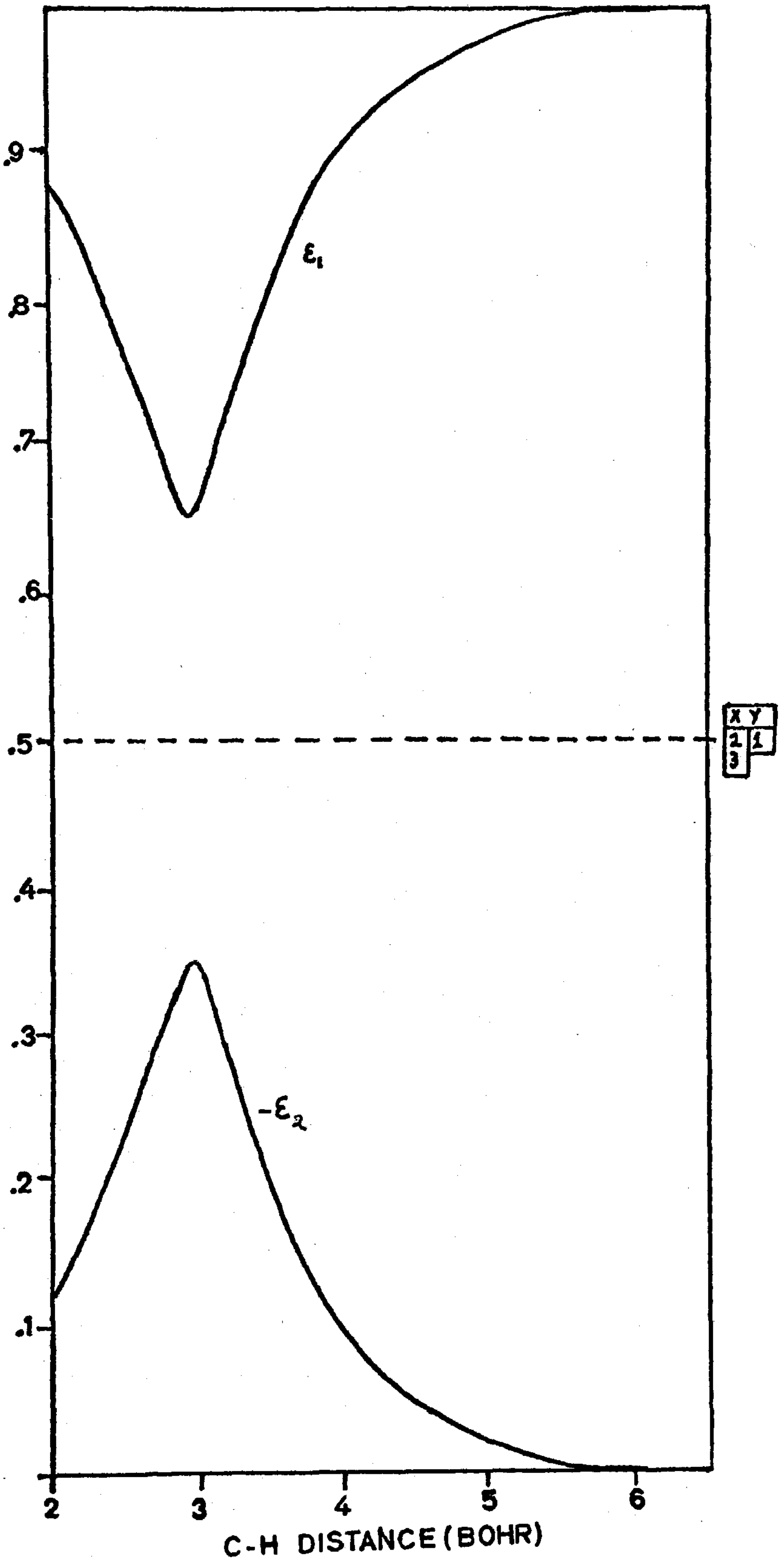


FIG. 5

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3.

Generalized Orthogonal-Orbital Variational Equations

Abstract

The orbital variational equations for any many-electron wavefunction involving orthogonal orbitals are rigorously derived. Based upon the resulting quadratically convergent orbital optimization equation, it may be possible to devise a practical computational method which will be more rapidly convergent than those procedures currently employed.

I. INTRODUCTION

Starting with an energy expression valid for any many-electron wavefunction, a set of general orthogonal-orbital variational equations are derived. In so doing, the variational condition (the equation satisfied by the optimal orbitals) is rigorously obtained, without resorting to use of Lagrange Multipliers[1], by implicitly requiring that all orbital variations must preserve overall orbital orthogonality. In addition, this approach permits derivation of a quadratically-convergent equation for orbital optimization which cannot be obtained from the variational condition alone. Finally, using this result, the equation which couples optimization of a single orbital with simultaneously required changes in all other orbitals is derived through second-order. **Based upon this equation** , it may be possible to devise a practical computational method for orbital optimization which will be more rapidly convergent than those procedures currently employed.[2]

II. DERIVATIONS

The energy of any many-electron wavefunction (actual or contrived) involving N orthonormal orbitals $\{\phi\}$ can always be written as:

$$\begin{aligned} E = & \sum_{i}^{N} \left[2 f_{ii}\, h_{ii} + a_{ii}\, J_{ii} \right] \\ & + \sum_{i>j}^{N} \left[4 f_{ij} h_{ij} + 2 \left(a_{ij} J_{ij} + b_{ij} K_{ij} \right) + 4 \sum_{k \neq i,j}^{N} \langle i | c_{ij}^{k} J_k + d_{ij}^{k} K_k | j \rangle \right] \\ & + 4 \sum_{i \neq j}^{N} e_{j}^{i} \langle i | J_i | j \rangle + 4 \sum_{\substack{i>j,\, k>l \\ ij > kl \\ i \neq j \neq k \neq l}}^{N} \gamma_{ij}^{kl} (ij|kl) \end{aligned} \qquad (1)$$

where:

$$\langle i | j \rangle = \langle \phi_i | \phi_j \rangle = \delta_{ij}$$
$$h_{ij} = \langle i | h | j \rangle = \langle \phi_i | t + v_n | \phi_j \rangle$$

If $(ij|kl)$ is a 2-electron integral involving orbitals ϕ_i, ϕ_j, ϕ_k and ϕ_l written in (11|22) form:

$$\begin{aligned} \langle i | J_k | j \rangle &= (ij|kk) \\ \langle i | K_k | j \rangle &= (ik|jk) \\ J_{ij} &= \langle i | J_j | i \rangle \\ K_{ij} &= \langle i | K_j | i \rangle \end{aligned}$$

The coefficients $\{a, b, c, d, e, f, \gamma\}$ depend upon the form of the wavefunction we are dealing with. These may be fixed or may depend upon optimization of adjustable parameters within the wavefunction. Since we will not be concerned with such matters here, these coefficients will simply be regarded as being fixed parameters. Starting with equation (1), the equations needed to variationally optimize the orthonormal orbitals will be derived. For simplicity, all orbitals will be taken to be real (extension to complex orbitals is trivial).

A. The Variational Condition

The optimum orbitals are those for which the energy is stationary with respect to their allowed changes (i.e. orbital orthogonality preservation). To see what this implies, let's allow each orbital to vary outside its current space in such a way so as to preserve orbital orthonormality:

$$\phi_i' = (\phi_i + \delta_i)/(1 + \langle \delta_i | \delta_i \rangle)^{1/2}$$
$$\langle \phi_i | \delta_i \rangle = 0$$
$$\langle \phi_i' | \phi_j' \rangle = \delta_{ij}$$

Upon substituting these orbitals in (1) [Note that we can do this since $\{\phi'\}$ are orthonormal] and expanding, we obtain an equation having the general form:

$$E' = E + \sum_i^N \left[\langle \delta_i | H_i | \phi_i \rangle + \langle \delta_i | R_i \rangle \right] + O_\delta^{(2)}$$

where $O_\delta^{(2)}$ contains terms second-order and high in the orbital variations $\{\delta\}$. Hence, the first-order change in the energy owing to orbital variations is:

$$\delta E = \sum_i^N \left[\langle \delta_i | H_i | \phi_i \rangle + \langle \delta_i | R_i \rangle \right]$$

If $\{\phi\}$ are the optimal orbitals, this energy change must be zero. Therefore, the variational condition for the optimal orbitals is:

$$0 = \sum_{i}^{N} \left[\langle \delta_i | H_i | \phi_i \rangle + \langle \delta_i | R_i \rangle \right] \qquad (2)$$

where the variations $\{\delta\}$ in the orthonormal orbitals must be such so as to preserve orbital orthonormality at least through first-order (second-order and **higher** non-orthonormalities cannot contribute to first-order energy changes). Since this equation tells us when the optimal orbitals have been obtained, any equation we derive for orbital optimization must be capable of converging to a set of orbitals satisfying (2).

B. Definition of the Field Terms H and R

We will now define the field terms $\{H, R\}$ appearing in (2). Isolating from (1) those terms which depend upon orbital ϕ_ν, we obtain:

$$E_\nu = 2f_{\nu\nu} h_{\nu\nu} + a_{\nu\nu} J_{\nu\nu} + 2\sum_{j\neq\nu} \Big[a_{j\nu} J_{j\nu} + b_{j\nu} K_{j\nu} + 2\sum_{i>j\neq\nu} \langle i | c_{ij}^{\nu} J_\nu + d_{ij}^{\nu} K_\nu | j \rangle$$
$$+ 2 \langle \nu | f_{j\nu} h + e_j^{\nu} J_\nu + e_\nu^{j} J_j + \sum_{i,j\neq\nu} (c_{j\nu}^{i} J_i + d_{j\nu}^{i} K_i) + \sum_{\substack{k>l \\ k,l\neq j,\nu}} \gamma_{j\nu}^{kl} \textstyle\int kl | j \rangle \Big]$$

where $\langle \nu | \int kl | j \rangle = (\nu j | kl)$. Substituting $\phi_\nu' = (\phi_\nu + \delta_\nu)/(1 + \langle \delta_\nu | \delta_\nu \rangle)^{1/2}$ in the above and expanding, the first-order change in E_ν owing to δ_ν is:

$$\tfrac{1}{4}\, \delta E_\nu = \langle \delta_\nu | f_{\nu\nu} h + a_{\nu\nu} J_\nu + \sum_{i\neq\nu} [a_{i\nu} J_i + b_{i\nu} K_i] + 2\sum_{i>j\neq\nu} c_{ij}^{\nu} \textstyle\int ij | \nu \rangle$$
$$+ \sum_{i>j\neq\nu} d_{ij}^{\nu} \left[(\delta_\nu i | \nu j) + (\nu i | \delta_\nu j) \right] + \sum_{j\neq\nu} \langle \delta_\nu | f_{j\nu} h + e_\nu^{j} J_j + e_j^{\nu} (J_\nu + 2K_\nu)$$
$$+ \sum_{i\neq j,\nu} (c_{j\nu}^{i} J_i + d_{j\nu}^{i} K_i) + \sum_{\substack{k>l \\ k,l\neq j,\nu}} \gamma_{j\nu}^{kl} \textstyle\int kl | j \rangle$$

If ϕ_ν is optimal, E_ν is stationary with respect to variations in ϕ_ν (which preserve overall orbital orthogonality). Therefore, the variational condition for orbital ϕ_ν is:

$$0 = \langle \delta_\nu | f_{\nu\nu} h + a_{\nu\nu} J_\nu + \sum_{i \neq \nu} (a_{i\nu} J_i + b_{i\nu} K_i) + \sum_{i > j \neq \nu} [2c_{ij}^{\nu} \int^{ij} + d_{ij}^{\nu} (K_{i+j} - K_i - K_j)] | \nu \rangle$$
$$+ \sum_{j \neq \nu} \langle \delta_\nu | f_{j\nu} h + e_\nu^j J_j + c_j^\nu (J_\nu + 2K_\nu) + \sum_{i \neq j,\nu} (c_{j\nu}^i J_i + d_{j\nu}^i K_i) + \sum_{k>l;\ k,l \neq j,\nu} \gamma_{j\nu}^{kl} \int^{kl} | j \rangle$$

where we have used the relationship:

$$(\delta_\nu i | \nu j) + (\nu i | \delta_\nu j) = \langle \delta_\nu | K_{i+j} - K_i - K_j | \nu \rangle$$

From (2), we have:

$$0 = \langle \delta_\nu | H_\nu | \nu \rangle + \langle \delta_\nu | R_\nu \rangle$$

Therefore, we can define H$_\nu$ and R$_\nu$ as:

$$H_\nu = f_{\nu\nu} h + a_{\nu\nu} J_\nu + \sum_{i \neq \nu} \left[a_{i\nu} J_i + \left(b_{i\nu} - \sum_{j \neq i,\nu} d_{ij}^{\nu} \right) K_i \right] + \sum_{i > j \neq \nu} [2c_{ij}^{\nu} \int^{ij} + d_{ij}^{\nu} K_{i+j}] \qquad (3)$$

$$R_\nu = \sum_{j \neq \nu} \left[f_{j\nu} h + e_\nu^j J_j + c_j^\nu (J_\nu + 2K_\nu) + \sum_{i \neq j,\nu} (c_{j\nu}^i J_i + d_{j\nu}^i K_i) + \sum_{\substack{k>l \\ k,l \neq j,\nu}} \gamma_{j\nu}^{kl} \int^{kl} \right] | j \rangle \qquad (4)$$

C. The Energy in Terms of the H and R Operators

Now that $\{H, R\}$ have been defined in terms of the parameters of the energy expression (1), let's rewrite (1) using these field terms:

$$\sum_i [\langle i | H_i | i \rangle + \langle i | R_i \rangle] = \sum_i [f_{ii} h_{ii} + a_{ii} J_{ii}]$$
$$+ \sum_{i \neq j} (a_{ij} J_{ij} + b_{ij} K_{ij}) + 2 \sum_{i,\ j > k \neq i} \langle j | c_{jk}^i J_i + d_{jk}^i K_i | k \rangle$$
$$+ \sum_{i \neq j} [f_{ij} h_{ij} + e_i^j \langle i | J_j | j \rangle + 3c_j^i \langle i | J_i | j \rangle]$$
$$+ \sum_{i \neq j \neq k} \langle j | c_{jk}^i J_i + d_{jk}^i K_i | k \rangle + \sum_{\substack{k>l \\ i \neq j \neq k \neq l}} \gamma_{ij}^{kl} (ij | kl)$$

$$= \sum_{i} \left[f_{ii} h_{ii} + a_{ii} J_{ii} \right] + 2 \sum_{i>j} \left(a_{ij} J_{ij} + b_{ij} K_{ij} \right) + 4 \sum_{\substack{i,j,k \\ i \neq j,k}} \langle j | c_{jk}^{i} J_{i}$$

$$+ d_{jk}^{i} K_{i} | k \rangle + 2 \sum_{i>j} f_{ij} h_{ij} + 4 \sum_{i \neq j} e_{j}^{i} \langle i | J_{i} | j \rangle + 4 \sum_{\substack{i>j,\, k>l \\ ij>kl \\ i \neq j \neq k \neq l}} \gamma_{ij}^{kl} (ij|kl)$$

$$= E - \sum_{i} f_{ii} h_{ii} - 2 \sum_{i>j} f_{ij} h_{ij}$$

Therefore:

$$E = \sum_{i} \left[\langle i | H_{i} | i \rangle + \langle i | R_{i} \rangle + \sum_{j} f_{ij} h_{ij} \right] \qquad (5)$$

D. The Orbital Optimization Equation

We must now derive an equation capable of leading from some set of orthonormal orbitals $\{\phi^{\circ}\}$ to a set for which the energy is stationary [i.e. satisfies the variational condition (2)]. If $\{\phi\}$ are the desired orthogonal orbitals, then the proper orbital changes $\{\Delta\}$ are given by:

$$\phi_{i} = \left(\phi_{i}^{\circ} + \Delta_{i} \right) / \left(1 + \Delta_{i}^{2} \right)^{1/2}$$

$$\langle \Delta_{i} | \phi_{i}^{\circ} \rangle = 0$$

$$\langle \Delta_{i} | \phi_{j}^{\circ} \rangle + \langle \Delta_{j} | \phi_{i}^{\circ} \rangle + \langle \Delta_{i} | \Delta_{j} \rangle = 0 \qquad i \neq j$$

Substituting these orbitals in (1) and expanding in terms of field terms involving $\{\phi^{\circ}\}$, we obtain after deleting terms which involve only $\{\phi^{\circ}\}$ and dividing by 2:

$$E_{\Delta} = \sum_{i} \left[\langle i | H_{i_0} | i \rangle + 2 \langle i | R_{i_0} \rangle \right] + 2 \sum_{i} a_{ii} \left(\Delta_{i} i_{0} | \Delta_{i} i_{0} \right)$$

$$+ 2 \sum_{i>j} \Big\{ f_{ij} h_{\Delta_i \Delta_j} + 2 a_{ij} \left(i_{0} \Delta_{i} | j_{0} \Delta_{j} \right) + b_{ij} \left[\left(i_{0} j_{0} | \Delta_{i} \Delta_{j} \right) + \left(i_{0} \Delta_{j} | j_{0} \Delta_{i} \right) \right]$$

$$+ \sum_{k \neq i,j} \Big[c_{ij}^{k} \left\{ 2 \left(i_{0} \Delta_{j} | k_{0} \Delta_{k} \right) + 2 \left(\Delta_{i} j_{0} | k_{0} \Delta_{k} \right) + \left(\Delta_{i} \Delta_{j} | k_{0} k_{0} \right) \right\}$$

$$+ d_{ij}^{k} \left\{ \left(\Delta_{i} k_{0} | k_{0} \Delta_{j} \right) + \left(\Delta_{i} k_{0} | j_{0} \Delta_{i} \right) + \left(\Delta_{i} \Delta_{k} | j_{0} k_{0} \right) + \left(i_{0} \Delta_{k} | \Delta_{j} k_{0} \right) \right.$$

$$\left. + \left(i_{0} k_{0} | \Delta_{j} \Delta_{k} \right) \right\} \Big] \Big\} + 2 \sum_{i \neq j} c_{j}^{i} \Big\{ 2 \left[\left(i_{0} \Delta_{i} | \Delta_{i} j_{0} \right) + \left(\Delta_{i} i_{0} | i_{0} \Delta_{j} \right) \right]$$

$$+ (i_0 j_0|\Delta_i \Delta_i) + (i_0 i_0|\Delta_i \Delta_j)\} + 2 \sum_{\substack{i>j,\, k>l \\ ij>kl \\ i\neq j\neq k\neq l}} \gamma_{ij}^{kl} \Big[(\Delta_i \Delta_j|k_0 l_0)$$

$$+ (\Delta_i j_0|\Delta_k l_0) + (\Delta_i j_0|k_0 \Delta_l) + (i_0 \Delta_j|\Delta_k l_0) + (i_0 \Delta_j|k_0 \Delta_l) + (i_0 j_0|\Delta_k \Delta_l)\Big]$$

where $O_\Delta^{(3)}$ contains terms third-order and higher in $\{\Delta\}$. This equation was obtained using the relationships:

$$J_{ij} = J_{i_0 j} + J_{i j_0} - J_{i_0 j_0} + 4\,(i_0 \Delta_i|j_0 \Delta_j) + \cdots$$

$$K_{ij} = K_{i_0 j} + K_{i j_0} - K_{i_0 j_0} + 2\,(i_0 j_0|\Delta_i \Delta_j) + 2\,(i_0 \Delta_j|j_0 \Delta_i) + \cdots$$

$$\begin{aligned} \langle i|J_k|j\rangle = {} & \langle i|J_{k_0}|j_0\rangle + \langle i_0|J_{k_0}|j\rangle + \langle i_0|J_k|j_0\rangle \\ & - 2\langle i_0|J_{k_0}|j_0\rangle + 2\,(i_0 \Delta_j|k_0 \Delta_k) + 2\,(\Delta_i j_0|k_0 \Delta_k) \\ & + (\Delta_i \Delta_j|k_0 k_0) + \cdots \end{aligned}$$

$$\begin{aligned} \langle i|K_k|j\rangle = {} & \langle i|K_{k_0}|j_0\rangle + \langle i_0|K_{k_0}|j\rangle + \langle i_0|K_k|j_0\rangle - 2\langle i_0|K_{k_0}|j_0\rangle \\ & + \langle \Delta_i|K_{k_0}|\Delta_j\rangle + (\Delta_i k_0|j_0 \Delta_k) + (\Delta_i \Delta_k|j_0 k_0) \\ & + (i_0 \Delta_k|\Delta_j k_0) + (i_0 k_0|\Delta_j \Delta_k) + \cdots \end{aligned}$$

$$\begin{aligned} \langle i|J_i|j\rangle = {} & \langle i_0|J_{i_0}|j\rangle + \langle i|J_{i_0}|j_0\rangle + 2\,(i i_0|i_0 j_0) - \langle i_0|J_{i_0}|j_0\rangle \\ & + 2\,(i_0 \Delta_i|\Delta_j i_0) + 2(i_0 \Delta_i|\Delta_i j_0) + (i_0 j_0|\Delta_i \Delta_i) + (i_0 i_0|\Delta_i \Delta_j) + \cdots \end{aligned}$$

$$\begin{aligned} (ij|kl) = {} & (i_0 j_0|k_0 l) + (i_0 j_0|k l_0) + (i_0 j|k_0 l_0) + (i j_0|k_0 l_0) \\ & - 3\,(i_0 j_0|k_0 l_0) + (\Delta_i \Delta_j|k_0 l_0) + (\Delta_i j_0|\Delta_k l_0) \\ & + (\Delta_i j_0|k_0 \Delta_l) + (i_0 \Delta_j|\Delta_k l_0) + (i_0 \Delta_j|k_0 \Delta_l) \\ & + (i_0 j_0|\Delta_k \Delta_l) + \cdots \end{aligned}$$

$$h_{ij} = h_{i_0 j} + h_{i j_0} + h_{\Delta_i \Delta_j} - h_{i_0 j_0} + \cdots$$

$$\begin{aligned} \sum_i \Big[\langle i|H_{i_0}|i) + 2\,\langle i|R_{i_0}\rangle \Big] = {} & \sum_i \Big[f_{ii}\, h_{ii} + a_{ii}\, J_{i i_0} \Big] \\ & + \sum_{i\neq j} \Big[a_{ij}\, J_{i j_0} + b_{ij}\, K_{i j_0} \Big] + 2 \sum_{\substack{k,\, i>j \\ k\neq i,j}} \langle i_0|\, C_{ij}^{k}\, J_k \end{aligned}$$

$$+ d_{ij}^{k} K_k | j_0 \rangle + 2 \sum_{i \neq j} \Big[f_{ij} h_{i_0 j} + e_i^j \langle i | J_{j_0} | j_0 \rangle$$

$$+ c_j^i \langle i | J_{i_0} + 2 K_{i_0} | j_0 \rangle + \sum_{k \neq i,j} \langle i | c_{ij}^k J_{k_0} + d_{ij}^k K_{k_0} | j_0 \rangle \Big]$$

$$+ 2 \sum_{\substack{i \neq j, k > l \\ k,l \neq i,j}} \gamma_{ij}^{kl} (i j_0 | k_0 l_0)$$

If $\Delta H_i (j \to \Delta_j)$ and $\Delta R_i (j \to \Delta_j)$ are the first-order changes in H_i and R_i owing to the change in orbital j :

$$H_i - H_{i_0} = \sum_j \Delta H_j (j \to \Delta_j) + \cdots \quad = \Delta H_i + \cdots$$

$$R_i - R_{i_0} = \sum_j \Delta R \; (j \to \Delta_j) + \cdots \quad = \Delta R_i + \cdots$$

then:

$$\sum_i \langle \Delta_i | \Delta H_i | i_0 \rangle = 2 \sum_i a_{ii} \; (\Delta_i i_0 | \Delta_i i_0)$$

$$+ \sum_{i \neq j} \Big[2 a_{ij} \; (\Delta_i i_0 | j_0 \Delta_j) + b_{ij} \; (\Delta_i j_0 | i_0 \Delta_j) + b_{ij} \; (\Delta_i \Delta_j | i_0 j_0) \Big]$$

$$+ \sum_{\substack{k, i > j \\ i,j \neq k}} \Big\{ 2 c_{ij}^k \big[(\Delta_k k_0 | \Delta_i j_0) + (\Delta_k k_0 | j_0 \Delta_i) \big] + d_{ij}^k \big[(\Delta_k i_0 | k_0 \Delta_j)$$

$$+ (\Delta_k \Delta_i | k_0 j_0) + (k_0 i_0 | \Delta_k \Delta_j) + (k_0 \Delta_i | \Delta_k j_0) \big] \Big\}$$

and:

$$\sum_i \langle \Delta_i | \Delta R_i \rangle = \sum_{i \neq j} \Big\{ f_{ij} h_{\Delta_i \Delta_j} + e_i^j \big[2 (\Delta_i j_0 | j_0 \Delta_j)$$

$$+ (\Delta_i \Delta_j | j_0 j_0) \big] + 2 e_j^i \big[(\Delta_i j_0 | \Delta_i i_0) + (\Delta_i i_0 | \Delta_j i_0)$$

$$+ (\Delta_i \Delta_i | j_0 i_0) + (\Delta_i i_0 | j_0 \Delta_i) + \tfrac{1}{2} (\Delta_i \Delta_j | i_0 i_0) \big]$$

$$+ \sum_{k \neq i,j} \Big(c_{ij}^k \big[(\Delta_i \Delta_j | k_0 k_0) + 2 (\Delta_i j_0 | k_0 \Delta_k) \big] + d_{ij}^k \big[(\Delta_i k_0 | k_0 \Delta_j)$$

$$+ (\Delta_i \Delta_k | k_0 j_0) + (\Delta_i k_0 | \Delta_k j_0) \big] \Big) + \sum_{k > l ; \, k,l \neq i,j} \gamma_{ij}^{kl} \big[(\Delta_i \Delta_j | k_0 l_0)$$

$$+ (\Delta_i j_0 | \Delta_k l_0) + (\Delta_i j_0 | k_0 \Delta_l) \big] \Big\}$$

Therefore, the equation for E_Δ becomes:

$$E_\Delta = \sum_i \Big[\langle i | H_{i_0} | i \rangle + 2 \langle i | R_{i_0} \rangle + \sum_j \Big(\langle \Delta_i | \Delta H_i (j \rightarrow \Delta_j) | i_0 \rangle + \langle \Delta_i | \Delta R_i (j \rightarrow \Delta_j) \rangle + O_\Delta^{(3)}$$

$$= \sum_i (1 + \Delta_i^2)^{-1} \Big\{ \langle i_0 | H_{i_0} | i_0 \rangle + 2 \langle i_0 | R_{i_0} \rangle + 2 \big[\langle \Delta_i | H_{i_0} | i_0 \rangle + \langle \Delta_i | R_{i_0} \rangle \big] + \langle \Delta_i | H_{i_0} | \Delta_i \rangle + \Delta_i^2 \langle i_0 | R_{i_0} \rangle + \sum_j \big[\langle \Delta_i | \Delta H_i (j \rightarrow \Delta_j) | i_0 \rangle + \langle \Delta_i | \Delta R_i (j \rightarrow \Delta_j) \rangle \big] \Big\} + O_\Delta^{(3)}$$

where we note that this equation is consistent with the variational condition (2) since the first-order change in E_Δ is:

$$\delta E_\Delta = 2 \sum_i \big[\langle \Delta_i | H_{i_0} | i_0 \rangle + \langle \Delta_i | R_{i_0} \rangle \big]$$

Assuming an iterative procedure, if $\{\phi^0\}$ are at all a reasonable starting guess for the final orbitals it is safe to assume that $O_\Delta^{(3)}$ can be deleted:

$$E_\Delta = \sum_i (1 + \Delta_i^2)^{-1} \Big\{ \langle i_0 | H_{i_0} | i_0 \rangle + 2 \langle i_0 | R_{i_0} \rangle + 2 \big[\langle \Delta_i | H_{i_0} | i_0 \rangle + \langle \Delta_i | R_{i_0} \rangle \big] + \langle \Delta_i | H_{i_0} | \Delta_i \rangle + \Delta_i^2 \langle i_0 | R_{i_0} \rangle + \sum_j \big[\langle \Delta_i | \Delta H_i (j \rightarrow \Delta_j) | i_0 \rangle + \langle \Delta_i | \Delta R_i (j \rightarrow \Delta_j) \rangle \big] \Big\} \qquad (6)$$

In theory, this equation can be used to obtain the desired orbitals through second-order provided the initial orbitals $\{\phi^0\}$ are reasonable starting guesses and the orbital changes $\{\Delta\}$ are constrained to preserve orbital orthogonality at least through second-order.

E. Application of the Optimization Equation to a Single Orbital

Finally, let's consider optimization of orbital ν with respect to the *entire* space available. If this space is defined by the orthonormal functions $\{\chi\}$, with the first N of them being the current orbitals $\{\phi^\circ\}$:

$$\phi_\nu = [\phi_\nu^\circ + \sum_{j\neq\nu} \lambda_j \chi_j] / [1 + \sum_{j\neq\nu} \lambda_j^2]^{1/2}$$

Since orbital orthogonality must be preserved, the change in this orbital must be accompanied by changes in all the other orbitals as well. Orthogonality can be maintained through second-order if we take these changes to be:

$$\phi_i = [\phi_i^\circ - \lambda_i \phi_\nu^\circ - \sum_{\substack{j<i \\ i,j\neq\nu}} \lambda_i \lambda_j \phi_j^\circ + \cdots] / [1 + \lambda_i^2 + \cdots]^{1/2} \qquad i \neq \nu$$

Therefore:

$$\Delta_\nu = \sum_{j\neq\nu} \lambda_j \chi_j$$

$$\Delta_i = -\lambda_i \chi_\nu - \sum_{\substack{j<i \\ i,j\neq\nu}} \lambda_i \lambda_j \chi_j \qquad i \neq \nu$$

Substituting these orbital changes in (6) and expanding to give a normalization-scaled equation for E_{Δ_ν} valid through second-order we obtain:

$$E_{\Delta_\nu} = \sum_{i,j} \lambda_i' \lambda_j' H_{ij} / \sum_i \lambda_i'^2$$

where:

$$\lambda_i' = \lambda_i \lambda_\nu'$$

$$\mathcal{H}_{\nu\nu} = \sum_i^N \epsilon_i$$

$$\mathcal{H}_{\nu i} = \langle \nu | H_\nu - H_i | i \rangle + \langle i | R_\nu \rangle - \langle \nu | R_i \rangle \qquad i \leqslant N$$

$$\mathcal{H}_{\nu i} = \langle \nu | H_\nu | i \rangle + \langle i | R_\nu \rangle \qquad i > N$$

$$\begin{aligned} \mathcal{H}_{ii} = {} & \langle i | H_\nu | i \rangle + \langle \nu | H_i | \nu \rangle + \langle \nu | R_\nu \rangle + \langle i | R_i \rangle \\ & + \langle \nu | \Delta H_{\nu-i} \tbinom{\nu\to i}{i\to-\nu} | i \rangle + \langle i | \Delta R_\nu \tbinom{\nu\to i}{i\to-\nu} \rangle \\ & - \langle \nu | \Delta R_i \tbinom{\nu\to i}{i\to-\nu} \rangle + \sum_{j\neq\nu,i} \epsilon_j \qquad i \leqslant N \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ii} = {} & \langle i | H_\nu | i \rangle + \langle \nu | R_\nu \rangle + \langle i | \Delta H_\nu (\nu\to i) | \nu \rangle \\ & + \langle i | \Delta R_\nu (\nu\to i) \rangle + \sum_{j\neq\nu} \epsilon_j \qquad i > N \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ij} = {} & \langle i | H_\nu - H_i | j \rangle - \langle j | R_i \rangle + \tfrac{1}{2} \Big[\langle i | \Delta H_{\nu-i} \tbinom{\nu\to j}{j\to-\nu} | \nu \rangle \\ & + \langle j | \Delta H_{\nu-j} \tbinom{\nu\to i}{i\to-\nu} | \nu \rangle + \langle i | \Delta R_\nu \tbinom{\nu\to j}{j\to-\nu} \rangle \\ & + \langle j | \Delta R_\nu \tbinom{\nu\to i}{i\to-\nu} \rangle - \langle \nu | \Delta R_i \tbinom{\nu\to j}{j\to-\nu} + \Delta R_j \tbinom{\nu\to i}{i\to-\nu} \rangle \Big] \qquad j < i \leqslant N \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ij} = {} & \langle i | H_\nu | j \rangle + \tfrac{1}{2} \Big[\langle i | \Delta H_\nu \tbinom{\nu\to j}{j\to-\nu} | \nu \rangle + \langle i | \Delta R_\nu \tbinom{\nu\to j}{j\to-\nu} \rangle \\ & + \langle j | \Delta H_{\nu-j} (\nu\to i) | \nu \rangle + \langle j | \Delta R_{\nu-j} (\nu\to i) \rangle \Big] \qquad i > N,\ j \leqslant N \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{ij} = {} & \langle i | H_\nu | j \rangle + \tfrac{1}{2} \Big[\langle i | \Delta H_\nu (\nu\to j) | \nu \rangle + \langle j | \Delta H_\nu (\nu\to i) | \nu \rangle \\ & + \langle i | \Delta R_\nu (\nu\to j) \rangle + \langle j | \Delta R_\nu (\nu\to i) \rangle \Big] \qquad i > j > N \end{aligned}$$

$$\epsilon_i = \langle i | H_i | i \rangle + 2 \langle i | R_i \rangle \qquad i \leqslant N$$

$$\Delta H_{i-j} = \Delta H_i - \Delta H_j$$

$$\Delta R_{i-j} = \Delta R_i - \Delta R_j$$

Thus, by solving (in matrix notation):

$$\underline{E_{\Delta\nu}}\ \underline{\lambda'} = \underline{\mathcal{H}}\ \underline{\lambda'}$$

for the desired root, orbital ν can be optimized with respect to the entire space available subject to simultaneously required changes in all other orbitals.

In general, construction of the H matrix would be quite difficult. However, it may be possible to make some simplifying approximations which will not adversely affect overall convergence. For example, orbital optimization with respect to the space orthogonal to the current orbitals, $\{\chi_i, i > N\}$, is generally rapid using only linearly convergent procedures.[3] Therefore, it should be possible to ignore field term corrections $\{\Delta H, \Delta R\}$ involving these basis functions during $\underline{H}$ construction. While optimization with respect to occupied space usually requires a quadratically convergent solution,[4] it may be possible to ignore off-diagonal H element correction terms not involving orbital since these are of less importance than the H and H elements. Moreover, for simple wavefunctions such as Hartree-Fock or Perfect -

Pairing GVB, only the diagonal 1-electron integrals and the coulomb and exchange 2-electron integrals have non-zero coefficients in (1). As a consequence, construction of the H matrix for such wavefunctions is much easier than in the general case since many terms vanish.

III. CONCLUSION

The orbital variational equations for any many-electron wavefunction involving orthonormal orbitals have been derived by starting with a general energy expression. A quadratically convergent equation for optimization of a single orbital with respect to the entire space available subject to simultaneously required changes in all other orbitals has been given. This equation can be solved through simple matrix diagonalization. The extent to which simplifying approximations to this equation can be made requires investigation.

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4.

Investigations of Reactions of Atomic, Diatomic and Triatomic Carbon

Abstract

Despite extensive experimental studies, little is conclusively known concerning reactions of C_n species. For the most part, this is due to unsupported assumptions concerning reaction conditions and the nature of the precursors involved. These weak points are discussed and possible experimental procedures which may clarify the situation are proposed.

I. INTRODUCTION

Mechanisms of reactions involving highly reactive species such as carbon atom, diatomic carbon, and triatomic carbon are only poorly understood. Aside from being interesting in themselves, a thorough knowledge of these reactions may shed some light on the correlation between electronic structure and chemical reactivity of highly excited states in general. The reactions of C_1, C_2, and C_3 with various organic substrates have been extensively studied by Skell _et al_ and others using carbon vapor as a source of these species. Reactions of atomic carbon have also been studied using carbon-11 generated by nuclear processes. However, even though much experimental data has been accumulated, little of it has led to firmly established reaction mechanisms. For the most part, this has been due to an inability to firmly establish the precise nature of the reacting species involved and a lack of clear evidence in support of proposed mechanisms. It is the purpose here to uncover these weak points and propose possible experiments which would eliminate them. The results of these experiments could either support hypotheses already proposed or indicate the need to reevaluate previous work. In an effort to expand upon studies already done, areas which have not yet been fully explored will also be discussed. In a few instances, results will be reinterpreted in the light of what is now known about the electronic structure of these species.

II. DISCUSSION

Reactions of carbon atoms, diatomic carbon, and triatomic carbon with various substrates have been investigated using carbon vapor generated from a 16-volt (a.c.) carbon arc. These C_n species are produced simultaneously in both their ground and metastable electronic states. The C_n distribution of this vapor is deduced from yields of C_n CL_m products obtained upon reaction with chlorine. On this basis the vapor was determined to be 40% C_1, 30% C_2, and 14% C_3.[4, 14] A material balance was not obtained and no $C_{n>3}$ CL_m products were observed although C_4 and C_5 are surely present. This analysis is based on the assumption that all species in all electronic states are reactive and that no combination and/or fragmentation of intermediates occurs. None of these assumptions have been verified. It is interesting to note that the $C_2\% > C_3\%$ is contrary to reliable mass spectroscopic results obtained for thermally generated vapors at a variety of temperatures.[1] The claim that reaction of chlorine with thermally generated vapor (temperature unspecified) gives practically the same results is thus somewhat disturbing. In view of these results and the assumptions upon which they are based, a mass spectroscopic determination should be made. A discrepancy may even demonstrate the invalidity of the basic assumption made in all studies: namely, that if a product contains n arc atoms it must be derived from C_n.

Spectroscopic studies have shown that in thermally generated carbon vapor essentially all species are present in their ground electronic state.[2] No such studies have been made on 16-volt arc generated vapor. It has been assumed that C_1 is present largely in its ^1S and ^1D metastable states (ratio unknown) and that C_2 and C_3 are present in their lowest singlet and triplet states. Other metastable states such as the ^5S state of carbon atom have been completely ignored. Since rationalizations of product formation are solidly based on these assumptions, a spectroscopic study of the vapor is of utmost importance. This can be accomplished by first imbedding the vapor in an inert matrix. To assign C_n in a given electronic state as the sole precursor of a product it should at least first be established that this species is present in sufficient quantities to account for this product.

No attempts have been made to willfully vary vapor composition although it is well known that its C_n

distribution depends upon the temperature of vaporization and whether or not equilibrium is established. In addition, variation of the arc voltage should affect the population of the various electronic states. Obviously, changes in product distribution following known changes in vapor composition would provide much needed information concerning the nature of the precursors of these products.

Carbon vapor is not the only source of atomic carbon. Carbon-11 and carbon-14 generated by nuclear processes have also been used.[3] However, owing to the very high kinetic energy of these species, extensive fragmentation/rearrangement occurs; thus making meaningful mechanistic studies extremely difficult. The situation is further complicated by radiation-induced side reactions. Because of the method of generation, prior thermalization of these atoms has not been possible. For the same reason it has not been possible to determine the electronic state (s) of these species. In fact, it has not even been conclusively proven that neutral atoms, and not ions, are the actual reacting species. Hence, although this source is not contaminated with higher C_n species, conclusions based solely on results using this source cannot be accepted without reservation.

The most desirable approach would be to exclude all vapor species other than the one chosen for study. This can be accomplished by ionizing the vapor and separating the ions prior to neutralization. This technique was once explored as a potential source of high energy carbon atoms but was abandoned owing to loss of kinetic energy during neutralization.[3] Since high kinetic energy species are not wanted here, this aspect presents no problem. This approach requires considerable instrumentation and would probably present many technical difficulties. However, its use on even a limited scale would resolve many of the ambiguities inherent with use of the mixed vapor.

Once generated, the carbon vapor is always reacted with a large excess of substrate via codeposition on the reactor walls held at -196° C. Thermalization is assumed to be rapid and all reactions have been presumed to occur in the solid phase at or near this temperature. The carbon electrodes are usually enriched with carbon-14 and from the molar activity of a product, its C_n precursor is inferred. That is, the possibility of combination and/or fragmentation of intermediates is discounted. Yields are based on the C_n distribution deduced from reaction with chlorine. Questions concerning the validity of these assumptions have already been raised.

Mechanisms which have been proposed for formation of a product from a presumed C_n precursor are generally quite straightforward. However, in most cases, no labeling studies have been preformed. Until such studies are carried out, these mechanisms, for the most part, must be regarded as being unsupported.

No reactions under different experimental conditions have been carried out. Confinement to liquid nitrogen temperatures is based on the assumption that all reactions require little or no activation energy and that this temperature serves only to prevent fragmentation/rearrangement of initial products. This presumption is questionable, especially in cases where little or no products are observed. In such instances the need to change reaction conditions is evident.

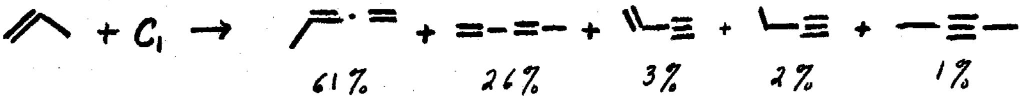
It has also been assumed that product distributions are phase independent. While this may be true for carbon-11 reactions, extension to carbon vapor reactions is unlikely since such phase independence is presumed to be indicative of high energy reactions; a situation which the carbon vapor source was intended to eliminate. Hence, product distributions may very well be phase dependent. In connection with relative rate studies this has become apparent. Such studies conducted in the solid phase often give ambiguous results, presumably because the physical characteristics of the matrices cloud true chemical reactivity.

In all studies so far reported, yields based on the total amount of carbon vaporized are quite low. However, no attempt has been made to obtain a material balance through recovery of unreacted carbon. Hence, it has never been conclusively demonstrated that all the products in a given reaction have been accounted for. Since it is not unusual for over sixty percent of the vaporized carbon to be unaccounted for , this point, as a check on isolation and identification techniques, deserves special attention.

Carbon vapor has been reacted with olefins, alkanes, alcohols, carbonyl compounds, and other oxygenated organic substrates. The results of these studies will be briefly summarized with the aim towards not only recapitulating what is already known, but also to enumerate the areas which require further study. The need for verification of the assumptions made will also be pointed out. For convenience of discussion, the assumption that no combination and/or fragmentation of intermediates occurs will not be questioned in each instance, realizing, however, that this assumption has in no way been verified and is a critical point.

A. Reactions with Olefins [4, 5]

Arc vapor has been reacted with simple olefins. Of the variety of products observed, most contain only one arc atom and are therefore presumed to have atomic carbon as their sole precursor. These products are allenes, dienes and small amounts of alkynes. For example, reaction with proplene gives:

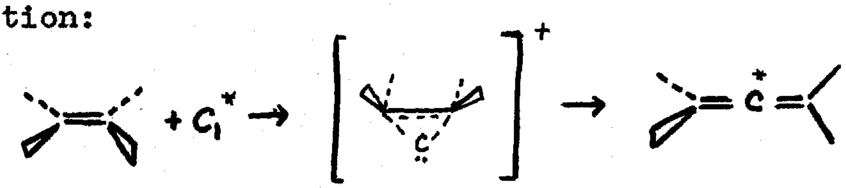


where yields are based upon a presumed 40% C_1 vapor content.

The dienes are assumed to be formed by hydrogen migration after an initial allylic C-H insertion:

$$R_2C=CR-CH_3 + C_1^* \rightarrow R_2C=CR-CH_2-\underset{*}{\ddot{C}}-H \xrightarrow{\sim H} R_2C=CR-CH=\overset{*}{C}H_2$$

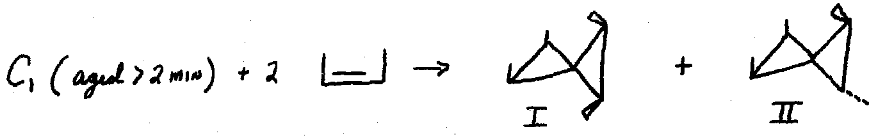
Allenes are assumed to result from direct double bond insertion:



No labeling studies have been performed to demonstrate that these are the only mechanisms involved despite the fact that some of these products can also be formed via initial vinylic C-H insertion; a mechanism which appears to be operative in carbon-11 studies. Also, with regard to allene formation, it has been maintained that cyclopropylidene intermediates are not formed per se owing to the inability to trap such intermediates. However, considering the simple olefins used, this is not surprising. To establish whether or not this C_1 precursor can react to initially give cyclopropylidenes, an olefin such as diphenylethylene should be used so that the corresponding cyclopropylidene, if formed, would be stable enough to permit trapping.

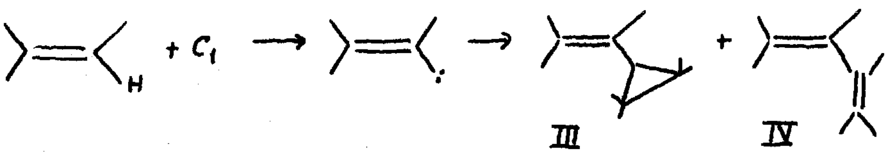
As use of thermally generated carbon vapor gave no C_1 products under identical experimental conditions, it is assumed that a metastable carbon atom is the solely reactive species. On the basis of highly suspect time-delay studies in which the vapor was 'aged' on a neopentene surface prior to substrate addition, it was concluded that the ^1S state was solely responsible for allene formation (Dienes not mentioned in this study).[6] Conclusions based on these studies, however, are of questionable validity for reasons which will be discussed below. Hence, the states responsible for these products remain unknown. A spectral determination of the $^1S/^1D$ content of the vapor would be most helpful. Also, variation of the arc voltage to alter the population of these states would shed light on this matter. While the ^3P (ground) state of carbon is apparently unreactive under the experimental conditions employed, this does not imply that it would be unreactive under other conditions. This is one example of where an investigation under different conditions of temperature and/or phase is warranted.

Formation of spiropentanes has been reported only in connection with the above mentioned time-delay studies. After 'aging' the vapor longer than two minutes, the only C_1 products observed were spiropentanes formed in a nonstereospecific manner:[7]



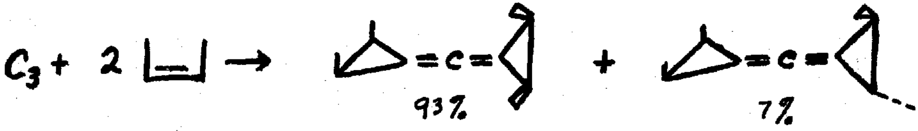
When aging was decreased to less than two minutes, the stereospecific product I predominated. Hence, it was concluded that while the ^1S state was responsible for allenes, the ^1D state reacted with olefins to give a stereospecific spiropentane and the ^3P state reacted to give the nonstereospecifically derived product.[8] However, although arc vapor surely contains ^1D atoms, no trace of spiropentanes were found when there was no aging and, as mentioned above, ^3P atoms generated thermally failed to react with olefins at all. Therefore, these time-delay studies involve more than just the electronic state of the atoms. Surface effects and/or complex formation might prevent collapse of an initially formed cyclopropylidene. In the absence of such effects, allenes might be formed. Such effects would also retard C-H insertion reactions. Hence, no definite conclusions concerning the differences in reactivity between the ^1S and ^1D states can be reached from these studies. However, a nonstereospecific product after long aging strongly indicates that the ^3P state is the precursor despite the unreactivity of thermally produced vapor. While surface catalysis is possible, it is more likely that this is due to different reaction conditions (e.g. temperature, due to rapid addition of a large excess of olefin). Reacting thermally generated vapor under different conditions of temperature and phase should establish this point. It would also be interesting to react arc vapor with an olefin which is unlikely to give an allene, such as cyclopentene, to see if spiropentanes would be formed instead.

Other C_1 + 2 olefin products which have not been generally observed might also be formed. For example:

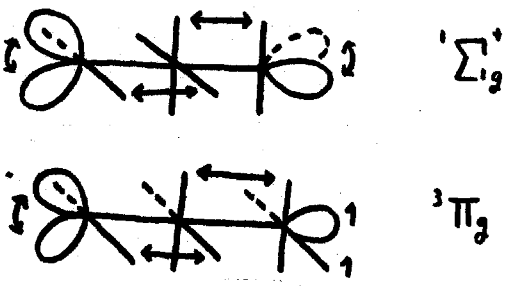


Product III has been observed in reactions with isobutylene, but this mechanism was not considered. Product IV has not been observed. Analogous products derived from other olefins have likewise not yet been reported.

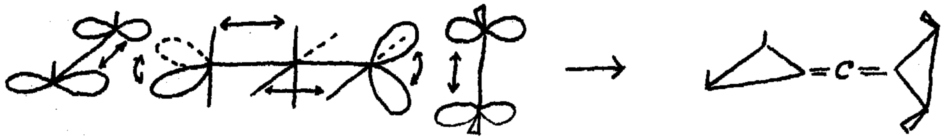
The only other observed products in carbon vapor-olefin reactions are bisethanoallenes, which are presumed to have C_3 as their sole precursor.[9] No reliable yields are available. Early reported yields of 40-45% based on the total carbon vaporized are inconsistent with the presumed 14% C_3 vapor content. This matter, of course, requires clarification. Some nonstereospecificity was noted in the reactions of cis- and trans-2-butenes:

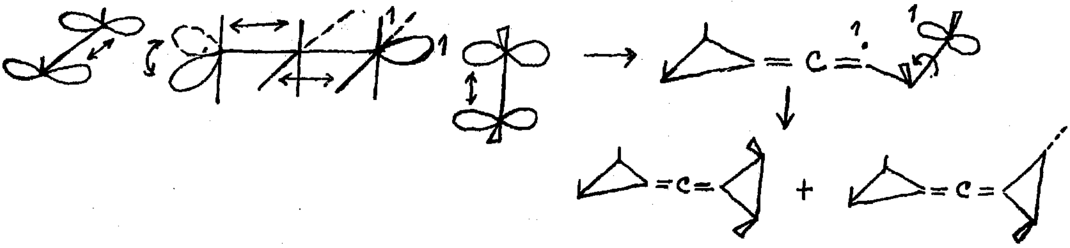


Since thermally generated vapor, which presumably contains only ground state C_3 , gave only the stereospecific product, the nonstereospecific product was attributed to the lowest triplet state of C_3. If these states have the electronic structures:



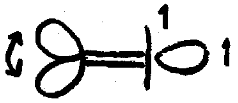
$\longleftrightarrow$ indicates the two orbitals are singlet coupled then formation of these products can be envisioned as:



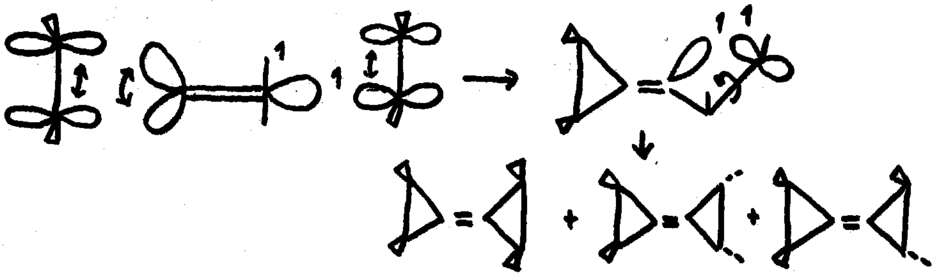


No C_2 derived products have as yet been observed despite the fact that C_2 preportedly comprises 30% of the arc vapor and should be present in both its ground state ($^1\Sigma_g^+$) and lowest triplet state ($^3\pi_u$). If the ground state has the electronic structure:

it is difficult to imagine formation of any products. The triplet state, however, should have the structure:



and it can be speculated that bisethanoethylenes might be formed in a nonstereospecific manner:

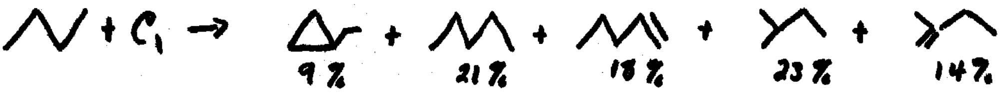


Hence, it would be of interest to identify any C_2 derived products which are formed.

Although C_4 and C_5 are usually present in carbon vapor, no products containing this many arc atoms have ever been isolated. The fate of these species remains unknown.

B. Reactions with Alkanes[10,1]

Arc vapor reportedly reacts with simple alkanes to give products containing an additional carbon atom. Since thermally generated vapor is apparently unreactive, it is likely that metastable carbon atoms are the reactive species. Whether these are ^1S and/or ^1D atoms is not known. The products observed are typically alkanes, cyclopropanes and olefins. Yields based on a 40% C_1 vapor content are quite good. For example, reaction with n-butane gives:

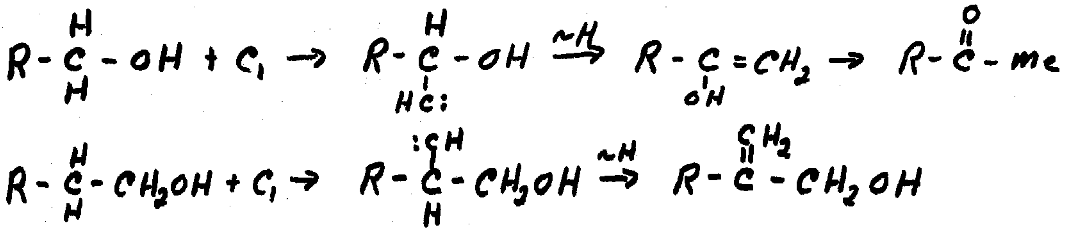


These products have been proposed to be formed via hydrogen abstraction, internal C-H insertion, and hydrogen migration mechanisms involving an initially formed monoalkylcarbene. Labeling studies have not been reported in support of these simple mechanisms. Formation of saturated hydrocarbons is contrary to all other monoalkylcarbene investigations. While it is possible that initially formed methylene may be responsible for this, it is curious that this is the only carbon vapor reaction study in which products having a possible methylene precursor have been observed. In any event, reasons for this peculiarity warrant further study.

As with olefins, no variations in reaction conditions have been carried out to determine any phase dependence or to determine the conditions under which other vapor components are reactive.

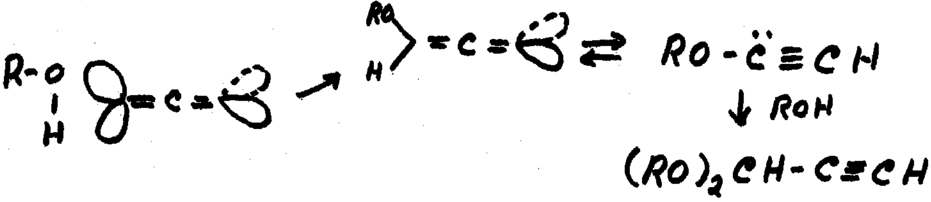
C. Reactions with Alcohols [11]

In carbon vapor-alcohol reactions several C_1 derived products are observed. The products are presumed to result from either initial C-H or O-H insertion reactions. The major products formed via O-H insertion are dialkoxymethanes. The products formed from C-H insertion are methyl ketones or alkene-ols depending on the site of insertion:

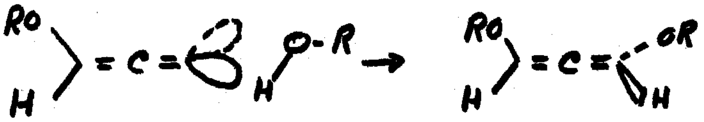


These same products have also been observed in carbon-11 studies.[12] The major product in both cases, however, is carbon monoxide. The mechanism involved in this deoxygenation is unknown. Identification of products derived from the alkyl residues should shed light on this matter. Here again, the reactive species is presumed to be a metastable electronic state of unclear nature.

The C_3 products observed are propargyl aldehyde acetals, allene, propylene, propyne, and propane.[13] Use of thermally generated vapor gives only propargyl aldehyde acetals. Hence, this product is assumed to have ground state C_3 as its precursor. The other products are derived from an excited state via as yet unknown hydrogen abstraction mechanisms. While it has been proposed that propargyl aldehyde acetal formation involves both a 1, 1- and 1,3-addition, a more likely mechanism would be a rearrangement following an initial 1, 1-addition prior to another 1, 1-addition:

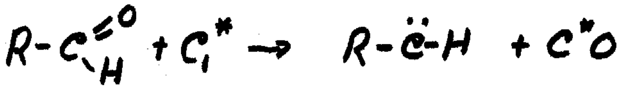


Although they have not been observed, 1, 3-dialkoxyallenes might also be found:



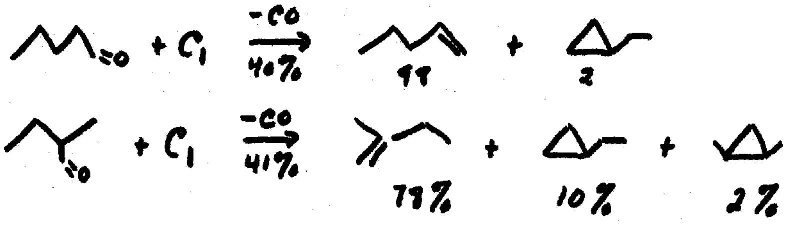
D. Reactions with Aldehyde and Ketones [14]

Monoalkylcarbenes are also posited to be formed in reactions of arc vapor with aldehydes in which carbon monoxide (arc carbon) is liberated:



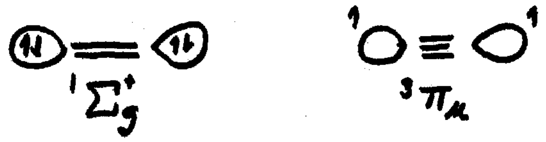
$$R\text{-}C\overset{\displaystyle O}{\underset{H}{\lessgtr}} + C_1^* \rightarrow R\text{-}\ddot{C}\text{-}H + C^*O$$

A metastable carbon atom (^1S and/or ^1D) is the assumed sole precursor for carbon monoxide liberation. For the aldehydes studied, the products observed are generally the same as those found when monoalkylcarbenes are generated in more conventional ways. Namely, these products are cyclopropanes and olefins. No alkanes are observed whatsoever. For example:

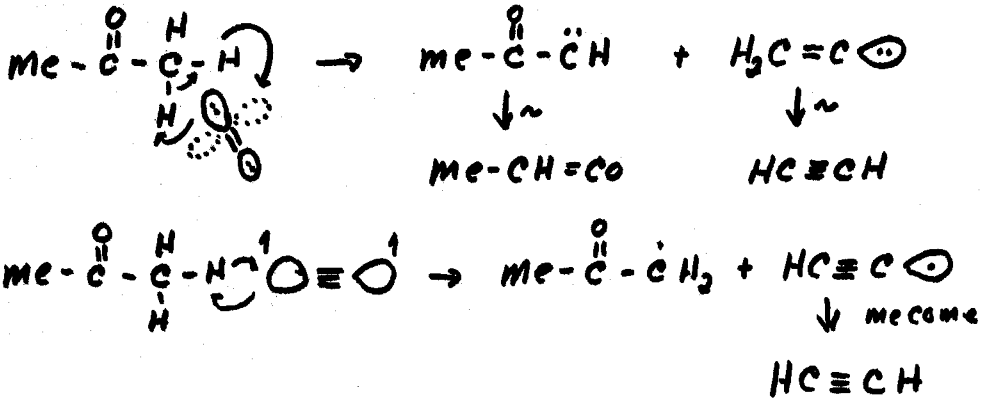


When carbon arc vapor is reacted with ketones, carbon monoxide is also liberated. Cyclopropanes and olefins consistent with initial dialkylcarbene formation are the observed products. Also noted in these reactions are some allene, propylene, propyne, and propane. These products contain three arc atoms and are therefore assigned a C_3 precursor. The details concerning the formation of these products have not been explored.

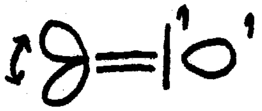
In reactions of all oxygenated organic substrates acetylene, which contains two arc atoms, has been observed. These are the only instances in which a C_2 product has ever been observed. A detailed study was made using acetone and acetyldehyde as substrates.[15] Results from studies employing a mixture of deuterated and undeuterated substrate seem to indicate that two mechanisms are operative; one which is intramolecular and the other intermolecular. The intramolecular product generally accounts for over 70% of the acetylene. It was assumed that ground state C_2 (${}^1\Sigma_g^+$) was responsible for the intramolecular reaction and the lowest triplet state (${}^3\pi_u$) was responsible for the intermolecular reaction. The structures of these states were assumed to be:



And the mechanisms to be (using acetone):

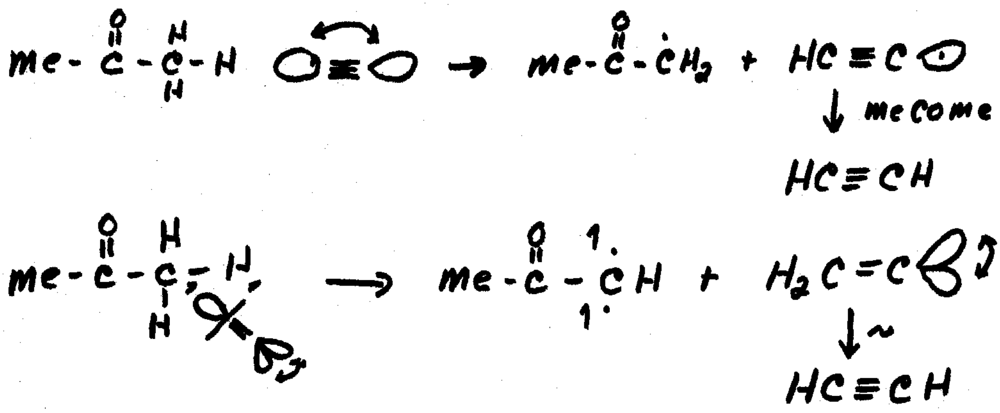


However, there are several problems with these conclusions. In the first place, the proposed structure for the $^3\pi_u$ state corresponds to a $^3\Sigma_u^+$ state. The actual structure of the $^3\pi_u$ state is most likely to be:



Secondly, theoretical calculations indicate the $^1\Sigma_g^+$ is not as given above, but corresponds to:

It is therefore difficult to imagine how the $^1\Sigma_g^+$ state can participate in the intramolecular reaction. If anything, it might be expected to react in an intermolecular manner. It is, rather, the $^3\pi_u$ state which would most likely remove two protons from the same molecule:



Which of these hypotheses is correct might be determined by using thermally generated vapor, which should contain a vast predominance of the $^1\Sigma_g^+$ state.

III. CONCLUSION

Despite the fact that carbon vapor reactions have been actively studied for several years, a great many questions remain unanswered. One of the biggest problems involves the assumptions made concerning the composition of this vapor. Mass spectroscopic and spectral investigations would help resolve these ambiguities. Questions have also arisen concerning the assumption that no combination and/or fragmentation of intermediates occurs. Ways of varying the vapor composition (up to complete removal of all but one C_n species) have been suggested as a means of determining this. The need for supporting evidence for proposed mechanisms has been demonstrated. Questions have also been raised about possible phase dependence of product distribution.

However, even if all the assumptions which have previously been made are shown to be valid, many areas are still open to study. Although all atomic carbon reactions appear to involve a metastable electronic state (s), the differences in reactivity between the ^1S and ^1D states are unclear. Studies using vapors having different $^1S/^1D$ contents could shed light on this matter. It would be of interest to know whether the ^1S state undergoes reactions different from the ^1D state only because of the higher energy of the ^1S state or if these species undergo uniquely different reactions owing to their different electronic structures. No reactions involving ground state carbon atoms (^3P) have yet been definitely observed. Hence, questions concerning the conditions required for and the products formed in these reactions are unanswered. The same is true for C_2 , for which only one reaction has been observed. The interpretation of this reaction itself has also been questioned. The fate of the higher polymers, C_4 and C_5 are as yet completely unknown.

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5.

Avoiding Complete Integral Transformations in Iterative Configuration Interaction MC-SCF Procedures

Abstract

One of the major obstacles preventing practical application of iterative Configuration Interaction procedures for solving for multiconfigurational wavefunctions is the presumed need to transform all 1- and 2-electron integrals after every iteration. It is shown that such transformations are not really necessary and a simple procedure for avoiding this problem is presented.

I. INTRODUCTION

Consider some multiconfigurational wavefunction involving N orthonormal orbitals having the form:

$$\Psi = \sum_m \varepsilon_m \psi_m \qquad (1)$$

where $\{\psi\}$ is a set of orthogonal configurations and ε_m is the CI coefficient of the M^{th} configuration. If $\{\phi\}$ are the optimal orbitals for (1) and $\{\phi^\circ\}$ are our current guesses for them, then the required changes $\{\Delta\}$ needed to go from $\{\phi^\circ\}$ to $\{\phi\}$ are given by:

$$\begin{aligned} &\phi_i = (\phi_i^\circ + \Delta_i)/(1+\Delta_i^2)^{1/2} \qquad i = 1, N \\ &\langle \Delta_i | \Delta_i \rangle = \Delta_i^2 \\ &\langle \Delta_i | \phi_i^\circ \rangle = 0 \\ &\langle \Delta_i | \phi_j^\circ \rangle + \langle \Delta_j | \phi_i^\circ \rangle + \langle \Delta_i | \Delta_j \rangle = 0 \qquad i \neq j \end{aligned}$$

Substituting these orbitals in (1) and expanding in terms of $\{\phi^\circ, \Delta\}$, we obtain:

$$\begin{aligned} &\Psi = \Psi_0 + \sum_i \Psi_i^{\Delta_i} + O_\Delta^{(2)} \qquad (2) \\ &\Psi_0 = \sum_m \varepsilon_m \psi_m^\circ \\ &\Psi_i^{\Delta_i} = \sum_n \varepsilon_{ni} \psi_i^{\Delta_i} \end{aligned}$$

where Ψ_0 is the wavefunction in terms of $\{\phi^\circ\}$. $\Psi_i^{\Delta_i}$ is the first-order change in the wavefunction in going from ϕ_i° to ϕ_i which is composed of those wavefunctions involving orbital i in which ϕ_i° is <u>singly</u> replaced by Δ_i. $O_\Delta^{(2)}$

contains all terms second-order and higher in $\{\Delta\}$.

If we assume that $\{\Psi\}$ is complete with respect to the orbitals, the orbital changes need only involve expansion into the space orthogonal to the current orbitals. If this space is defined by the orthonormal ' virtuals ' $\{\chi\}$, then:

$$\phi_i = \left(\phi_i^\circ + \sum_j \lambda_{ji}\chi_j\right) \Big/ \left(1 + \sum_j \lambda_{ji}^2\right)^{1/2}$$
$$\langle \chi_i | \phi_j^\circ \rangle = 0$$
$$\langle \chi_i | \chi_j \rangle = \delta_{ij}$$

Thus, (2) becomes:

$$\Psi = \Psi_0 + \sum_i^N \sum_j \lambda_{ji} \Psi_i^{\chi_j} + O_\lambda^{(2)}$$

If $\{\phi^\circ\}$ are reasonable guesses for the optimal orbitals, it should be possible to determine the orbital changes iteratively in a linearly convergent manner by simply ignoring high-order terms and solving:

$$\Psi = \Psi_0 + \sum_i \sum_j \lambda_{ji} \Psi_i^{\chi_j} \qquad (3)$$

for $\{\lambda\}$. Hence, we can obtain $\{\lambda\}$ and therefore new orbitals for the next iteration (after removal of high-order nonorthogonalities) by solving (in matrix notation):

$$\underline{H}\,\underline{\lambda}' = \underline{E}\,\underline{S}\,\underline{\lambda}' \qquad (4)$$

where:

$$\lambda_i' = \lambda_0' \lambda_i$$

$$\mathcal{H}_{00}^{00} = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_{m,n} \varepsilon_m \varepsilon_n \langle \psi_m^0 | H | \psi_n^0 \rangle = \sum_{m,n} \varepsilon_m \varepsilon_n H_{m,n}^{00}$$

$$\mathcal{H}_{0\nu}^{0\chi_i} = \langle \Psi_0 | H | \Psi_\nu^{\chi_i} \rangle = \sum_m \sum_n \varepsilon_m \varepsilon_{n\nu} \langle \psi_m^0 | H | \psi_{n\nu}^{\chi_i} \rangle$$
$$= \sum_m \sum_n \varepsilon_m \varepsilon_{n\nu} H_{0,n\nu}^{0\chi_i}$$

$$\mathcal{H}_{\nu,\mu}^{\chi_i \chi_j} = \langle \Psi_\nu^{\chi_i} | H | \Psi_\mu^{\chi_j} \rangle = \sum_m \sum_n \varepsilon_{n\nu} \varepsilon_{m\mu} \langle \psi_{n\nu}^{\chi_i} | H | \psi_{m\mu}^{\chi_j} \rangle$$
$$= \sum_m \sum_n \varepsilon_{n\nu} \varepsilon_{m\mu} H_{n\nu,m\mu}^{\chi_i \chi_j}$$

$$\mathcal{A}_{00}^{00} = \langle \Psi_0 | \Psi_0 \rangle = \sum_m \varepsilon_m^2 = 1$$
$$\mathcal{A}_{0\nu}^{0\chi_i} = \langle \Psi_0 | \Psi_\nu^{\chi_i} \rangle = 0$$
$$\mathcal{A}_{\nu,\mu}^{\chi_i \chi_j} = \delta_{ij} \langle \Psi_\nu^{\chi_i} | \Psi_\mu^{\chi_i} \rangle = \delta_{ij} \sum_m \sum_n \varepsilon_{n\nu} \varepsilon_{m\mu} \langle \psi_{n\nu}^{\chi_i} | \psi_{m\mu}^{\chi_i} \rangle$$

Thus, we can solve for the optimum orbitals and CI coefficients of (1) using a very simple iterative Configuration Interaction (CI) procedure whereby we alternately solve (1) to obtain $\{\varepsilon\}$ for a given set of orbitals and then solve (3) for given $\{\varepsilon\}$ to obtain new orbitals until convergence is achieved.

Even if $\{\psi\}$ is incomplete so that orthogonal mixing between orbitals must also be considered, this method provides us with a very simple and straightforward way of solving for general multiconfigurational wave - functions. However, despite the almost trivial formalism involved, this approach has only recently begun to receive much attention.[1] The reason for this is that generation of primitive H matrix elements needed to construct the H matrix of (4) is practical only if all configurations of (3) involve orthonormal basis functions. It has therefore been generally supposed that after every iteration all 1-and 2-electron integrals must be transformed to a new basis consisting of the new-found orbitals $\{\phi^{\circ}\}$ and their corresponding ' virtuals ' $\{\chi\}$. Since complete transformation of all 2-electron integrals can be extremely time consuming even for moderately sized basis sets, iterative CI procedures would appear to be too costly to be of practical value.

However, it will now be shown that it is really only necessary to redefine these integrals for just the new orbitals after every iteration and not for the entire basis set. Thus, by using the proposed procedure outlined in the following section, one of the major stumbling blocks toward practical application of iterative CI techniques for solving for multiconfigurational wavefunctions can be removed.

II. DISCUSSION

Assume one current set of NB basis functions $\{y\}$ for which we have 1- and 2- electron integrals consists of the N current orthonormal orbitals $\{\phi^0\}$ and NB-N original normalized basis functions which are neither orthogonal to each other nor to the orbitals. Since the ith orthonormal virtual χ_I can always be written in terms of this basis:

$$\chi_I = \sum_i^{NB} c_{iI}\, y_i$$

$$\langle \chi_I | \phi_j^0 \rangle = 0$$

$$\langle \chi_I | \chi_J \rangle = \delta_{IJ}$$

then configuration $\Psi_{n\nu}^{\chi_I}$ is:

$$\Psi_{n\nu}^{\chi_I} = \sum_i c_{iI}\, \Psi_{n\nu}^{y_i}$$

Thus, the CI matrix element between $\Psi_{n\nu}^{\chi_I}$ and $\Psi_{m\mu}^{\chi_J}$ is:

$$H_{n\nu,m\mu}^{\chi_I \chi_J} = \sum_{i,j} c_{iI}\, c_{jJ} \langle \Psi_{n\nu}^{y_i} | H | \Psi_{m\mu}^{y_j} \rangle = \sum_{i,j} c_{iI}\, c_{jJ}\, \mathcal{H}_{n\nu,m\mu}^{y_i y_j}$$

Since we can write $\mathcal{H}_{n\nu,m\mu}^{y_i y_j}$ as:

$$\begin{aligned} \mathcal{H}_{n\nu,m\mu}^{y_i y_j} = \langle \Psi_{n\nu}^{y_i} | H | \Psi_{m\mu}^{y_j} \rangle = {} & H_{n\nu,m\mu}^{y_i y_j} + A_{n\nu,m\mu} (1-\delta_{ij}) \langle y_i | y_j \rangle \\ & + \sum_{\omega} B_{\omega,i} \langle \phi_\omega^0 | y_j \rangle + \sum_{\omega} B'_{\omega,j} \langle y_i | \phi_\omega^0 \rangle \\ & + \sum_{\omega,\omega'} D_{\omega,\omega'} \langle y_i | \phi_\omega^0 \rangle \langle \phi_{\omega'}^0 | y_j \rangle \end{aligned}$$

where:

$H_{n\nu,m\mu}^{y_i y_j}$ is the value of the matrix element assuming y_i and y_j are orthonormal

$A_{n\nu,m\mu}$	is that linear combination of integrals involving only $\{\phi^\circ\}$ having $\langle y_i \vert y_j\rangle$ $(i \neq j)$ as its coefficient
$B_{\omega,i}$ $(B'_{\omega,j})$	is that linear combination of integrals involving $\{\phi^\circ\}$ and y_i (y_j) having $\langle \phi^\circ_\omega \vert y_j\rangle$ $(\langle y_i \vert \phi^\circ_\omega\rangle)$ as its coefficient
$D_{\omega,\omega'}$	is that linear combination of integrals involving $\{\phi^\circ\}$ having $\langle \phi^\circ_\omega \vert y_j\rangle \langle \phi^\circ_{\omega'} \vert y_i\rangle$ as its coefficient

Hence:

$$
\begin{aligned}
H^{\chi_I \chi_J}_{n\nu,m\mu} = {} & \sum_{i,j} c_{iI} c_{jJ} H^{y_i y_j}_{n\nu,m\mu} + A_{n\nu,m\mu} \sum_{i \neq j} c_{iI} c_{jJ} \langle y_i | y_j \rangle \\
& + \sum_i \sum_\omega B_{\omega,i} c_{iI} \sum_j c_{jJ} \langle \phi^\circ_\omega | y_j \rangle \\
& + \sum_j \sum_\omega B'_{\omega,j} c_{jJ} \sum_i c_{iI} \langle y_i | \phi^\circ_\omega \rangle \\
& + \sum_{\omega,\omega'} D_{\omega,\omega'} \sum c_{iI} \langle y_i | \phi^\circ_\omega \rangle \sum_j c_{jJ} \langle \phi^\circ_{\omega'} | y_j \rangle \\
= {} & \sum_{i,j} c_{iI} c_{jJ} H^{y_i y_j}_{n\nu,m\mu} + A_{n\nu,m\mu} \sum_{i \neq j} c_{iI} c_{jJ} \langle y_i | y_j \rangle \\
& + \sum_i \sum_\omega B_{\omega,i} c_{iI} \langle \phi^\circ_\omega | \chi_J \rangle + \sum_j \sum_\omega B'_{\omega,j} c_{jJ} \langle \chi_I | \phi^\circ_\omega \rangle \\
& + \sum_{\omega,\omega'} D_{\omega,\omega'} \langle \phi^\circ_{\omega'} | \chi_J \rangle \langle \chi_I | \phi^\circ_\omega \rangle
\end{aligned}
$$

Since $\langle \chi | \phi^\circ \rangle = 0$:

$$H^{\chi_I \chi_J}_{n\nu,m\mu} = \sum_{i,j} c_{iI} c_{jJ} H^{y_i y_j}_{n\nu,m\mu} + A_{n\nu,m\mu} \sum_{i \neq j} c_{iI} c_{jJ} \langle y_i | y_j \rangle$$

Letting:

$$\sum_{i \neq j} c_{iI} c_{jJ} \langle y_i | y_j \rangle = \langle \chi_I | \chi_J \rangle - \sum_i c_{iI} c_{iJ} = \delta_{IJ} - \sum_i c_{iI} c_{iJ} = D_{IJ}$$

$$H^{\chi_I \chi_J}_{n\nu,m\mu} = \sum_{i,j} c_{iI} c_{jJ} H^{y_i y_j}_{n\nu,m\mu} + D_{IJ} A_{n\nu,m\mu}$$

We are, however, not really interested in these matrix elements per se, but rather in the $\mathcal{H}$ elements constructed from them:

$$\begin{aligned}
\mathcal{H}^{\chi_I \chi_J}_{\nu,\mu} &= \sum_n \sum_m \varepsilon_{n\nu}\varepsilon_{m\mu} H^{\chi_I \chi_J}_{n\nu,m\mu} \\
&= \sum_{i,j} C_{iI} C_{jJ} \sum_n \sum_m \varepsilon_{n\nu}\varepsilon_{m\mu} H^{y_i y_j}_{n\nu,m\mu} + O_{IJ} \sum_n \sum_m \varepsilon_{n\nu}\varepsilon_{m\mu} A_{n\nu,m\mu} \\
&= \sum_{i,j} C_{iI} C_{jJ} \mathcal{H}^{y_i y_j}_{\nu,\mu} + D_{IJ} \mathcal{A}_{\nu,\mu}
\end{aligned}$$

By applying similar arguments, we find that the desired $\mathcal{H}^{o\,\chi_I}_{o\,\nu}$ elements are:

$$\begin{aligned}
\mathcal{H}^{o\,\chi_I}_{o\,\nu} &= \sum_i C_{iI} \sum_m \sum_n \varepsilon_m \varepsilon_{n\nu} H^{o\,y_i}_{o\,n\nu} \\
&= \sum_i C_{iI} \mathcal{H}^{o\,y_i}_{o\,\nu}
\end{aligned}$$

Thus, the desired matrix elements needed to construct the $\mathcal{H}$ matrix of (4) are:

$$\begin{aligned}
\mathcal{H}^{oo}_{oo} &= \sum_m \sum_n \varepsilon_m \varepsilon_n H^{oo}_{mn} \\
\mathcal{H}^{o\,\chi_I}_{o\,\nu} &= \sum_i C_{iI} \sum_m \sum_n \varepsilon_m \varepsilon_{n\nu} H^{o\,y_i}_{o\,m} \\
&= \sum_i C_{iI} \mathcal{H}^{o\,y_i}_{o\,\nu} \\
\mathcal{H}^{\chi_I \chi_J}_{\nu,\omega} &= \sum_{i,j} C_{iI} C_{jJ} \sum_m \sum_n \varepsilon_{n\nu}\varepsilon_{m\mu} H^{y_i y_j}_{n\nu,m\mu} + D_{IJ} \sum_m \sum_n \varepsilon_{n\nu}\varepsilon_{m\mu} A_{n\nu,m\mu} \\
&= \sum_{i,j} C_{iI} C_{jJ} \mathcal{H}^{y_i y_j}_{\nu,\mu} + D_{IJ} \mathcal{A}_{\nu,\omega}
\end{aligned}$$

Therefore, we can construct the desired $\mathcal{H}$ matrix needed for orbital optimization from integrals over the nonorthogonal basis $\{y\}$ in the following manner:

1) Assuming an orthonormal basis consisting of $\{\phi^{\circ}\}$ and $\{y\}$, generate an $\mathcal{H}$ matrix in the usual manner.

2) Transform the matrix over to $\{\chi\}$ using $\{c\}$.
3) Calculate the $A_{n\nu,m\mu}$ values needed by evaluating $\langle \psi_{n\nu}^{z_i} | H | \psi_{m\mu}^{z_j} \rangle$ where z_i and z_j are 'dummy' functions, all of whose integrals are zero. Proceeding just as in 1) generate the required $\mathcal{A}$ matrix.
4) Calculate the D matrix.
5) Correct the transformed $\mathcal{H}$ matrix elements $\mathcal{H}_{\nu,\mu}^{\chi_I \chi_J}$ by adding $D_{IJ} A_{\nu,\mu}$ to each element.

Since the $\mathcal{A}$ and D 'correction' matrices are easily constructed and since transformation of the primitive $\mathcal{H}$ matrix can be accomplished as each H element is being calculated, the above procedure can be quite rapid and should prove to be much more efficient than transforming all 1- and 2- electron integrals after every iteration. Thus, by utilizing this simple procedure, it becomes only necessary to update only those integrals involving the orbitals themselves.

III. CONCLUSION

It has been shown that application of iterative CI techniques in solving for multiconfigurational wavefunctions does not have to involve complete transformation of all 1- and 2-electron integrals after every iteration. Since the need for such transformations has been one of the major problems associated with this potentially powerful approach, the simple procedure outlined here may be of aid in developing a practical computational method within this framework.

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