

APPROXIMATE SPIN EXTENDED HARTREE-FOCK THEORY,

by

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Dissertation submitted to the Graduate Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry

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May, 1978
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ACKNOWLEDGEMENTS

The author wishes to acknowledge his research advisor, Dr. John C. Schug, for his patience and guidance during the completion of this work. Moreover, the author thanks the members of his committee Drs. Dillard, Ross, Sanzone and Viers for their encouragement and aid.

Finally, special thanks to
and for typing this manuscript.

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INTRODUCTION

The electronic structure and reactivity of chemical systems are most conveniently interpreted in the framework of a valence bond or an independent particle model. Unfortunately, the simplest formulation of the independent particle model, the Restricted Hartree-Fock (RHF) method, often fails to provide qualitatively acceptable descriptions of fundamental chemical phenomena such as 1) bond dissociation, 2) the ordering of electronic energy states observed in molecular spectra and 3) hyperfine splitting occurring in the electron paramagnetic resonance spectra. In order for a quantum calculation to provide a more useful description of these phenomena, one must resort to some variation of Configuration Interaction, Perturbation, or Multi-Configuration Self-Consistent-Field Theory. All of these more accurate approaches are limited to systems of modest size by the time required to process two-electron integrals during the calculations.

In an Approximate Spin-Extended Hartree-Fock (ASEHF) calculation, one addresses this problem by spin projecting an open shell wavefunction and then minimizing the energy of the spin projected wavefunction by shifting electron density among the configurations generated by the spin projection operator. In this method, the Natural Orbitals used to construct these configurations are not varied. Computational schemes in which the energy of spin projected wavefunctions are minimized in a self-consistent-field calculation are termed spin extended

or generalized independent particle calculations, and are a variation of Multi-Configuration Self-Consistent-Field theory. The two-electron integrals which must be updated on each iteration in a spin extended calculation need only be calculated once in ASEHF Theory. Therefore, this procedure is more efficient than spin extended calculations and may be applied to larger systems. The foundation of this approach is the expectation that Natural Orbitals obtained from an open shell calculation adequately approximate the Natural Orbitals resulting in the spin extended calculation. Moreover, there is some flexibility available in choosing the form of the ASEHF wavefunction. In most applications, the ASEHF wavefunction may be chosen to be identical in form to a Generalized Valence Bond (GVB) wavefunction; therefore, the results of these calculations may be easily interpreted in terms of common molecular orbitals or valence bond concepts.

In this work, a new GVB energy expression is derived and various methods for generating the approximate Natural Orbitals required in a ASEHF calculation are presented. An algorithm used to minimize the energy of the spin projected wavefunction in the ASEHF procedure is also developed. The results of a number of Ab-Initio and semi-empirical ASEHF calculations are then compared with Multi-Configuration Self-Consistent-Field calculations and experimental quantities.

THE GENERALIZED INDEPENDENT PARTICLE MODEL

In the Generalized Independent Particle Model, the solution to the non-relativistic time-independent Schrodinger equation,

$$H\Psi = E\Psi \quad (1)$$

is of the form¹

$$\Psi = A\Phi\chi \quad (2)$$

where A is the normalized antisymmetrizer, Φ is a product of one-electron spatial orbitals and χ is a linear combination of products of one-electron spin functions. The terms occurring in the non-relativistic n -electron Hamiltonian are conveniently partitioned as a sum of one and two-electron operators,

$$H = h + g \quad (3)$$

$$h = \sum_i^n h(i) = \sum_i (\nabla_i^2 + \sum_{\alpha} \frac{Z_{\alpha}}{R_{i\alpha}}) \quad (4)$$

$$g = \sum_{i>j}^n g(i,j) = \sum_{i>j} 1/|\bar{r}_i - \bar{r}_j| \quad (5)$$

where Z_{α} is the charge of the α th nucleus and $R_{i\alpha}$ is the distance between the α th nucleus and the i th electron. By requiring that the expectation value of the Hamiltonian be stationary with respect to first order variations of the spatial orbitals comprising Ψ , one generates n one-particle eigenvalue equations. The eigenvalue problem,

$$F_i^{\chi}\psi_i = \epsilon_i\psi_i \quad (6)$$

is then solved iteratively for the n one-electron spatial orbitals.

F_i^χ is a generalized Fock operator whose structure depends on the spin function χ .

Each electron may be thought of as moving in an average potential field generated by the remaining $n-1$ electrons even though Ψ is not constrained to be a single determinantal function. In most applications, the one-electron spatial orbitals, ψ_i , are approximated as linear combinations of Slater or Gaussian functions, expanded about the atomic centers in the system.

If $\Psi = \psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)\dots\psi_{n/2}(n-1)\psi_{n/2}(n)$ and $\chi = \alpha(1)\beta(2)\alpha(3)\beta(4)\dots\alpha(n-1)\beta(n)$, Ψ is a closed shell single determinant and the Fock matrix may be partitioned as follows:²

$$F_i^\alpha = F_i^\beta = h + 2 J_c(i) - K_c(i) \quad (7)$$

where $J_c(i)$ and $K_c(i)$ are the well known coulomb and exchange operators respectively,

$$J_c(1)\psi_j(1) = \sum_{k=1}^n \langle \psi_k(2) | g(1,2) | \psi_k(2) \rangle \psi_j(1) \quad (8)$$

$$K_c(1)\psi_j(1) = \sum_{k=1}^n \langle \psi_k(2) | g(1,2) | \psi_j(2) \rangle \psi_k(1) \quad (9)$$

$$\langle \psi_i(1) | f(1) | \psi_j(1) \rangle \equiv \int \psi_i(1)f(1)\psi_j(1)d\tau \quad (10)$$

With these restrictions on Φ and χ , the closed shell Hartree-Fock method is generated.

By removing the pairing restrictions on Φ , the Unrestricted Hartree-Fock (UHF) method is generated. The Fock operator arising in UHF

theory may also be partitioned³

$$F_i^\alpha = h + J_T(i) - K_\alpha(i) \quad (11)$$

$$F_i^\beta = h + J_T(i) - K_\beta(i) \quad (12)$$

$$J_T(1)\psi_i(1) = \sum_{k=1}^n \langle \psi_k(2) | g(1,2) | \psi_k(2) \rangle \psi_i(1) \quad (13)$$

$$K_\alpha(1)\psi_i(1) = \sum_{k=1,3,5}^n \langle \psi_k(2) | g(1,2) | \psi_i(2) \rangle \psi_k(1) \quad (14)$$

$$K_\beta(1)\psi_i(1) = \sum_{k=2,4,6}^n \langle \psi_k(2) | g(1,2) | \psi_i(2) \rangle \psi_k(1) \quad (15)$$

The UHF wavefunction provides a better description of bond dissociation and the spin properties of molecules, but the UHF wavefunction is not an eigenfunction of S^2 , the operator for the square of the total spin angular momentum.

$$S^2 = S \cdot S \quad (16)$$

$$S = \sum_i s(i) = \sum_i \{s_x(i)\hat{i} + s_y(i)\hat{j} + s_z(i)\hat{k}\} \quad (17)$$

$$S_z = \sum_i s_z(i) \quad (18)$$

where

$$[s_x(j), s_y(k)] = i s_z(j) \delta_{jk} \quad (\text{cyclic}) \quad (19)$$

$$s^2(i)\xi(i) = (1/2)(1/2+1)\pi^2\xi(i), \quad \xi(i) = \alpha(i) \text{ or } \beta(i) \quad (20)$$

$$s_z(i)\xi(i) = (1/2)\pi\xi(i), \quad \text{if } \xi(i) = \alpha(i) \quad (21)$$

$$s_z(i)\xi(i) = -(1/2)\pi\xi(i), \quad \text{if } \xi(i) = \beta(i) \quad (22)$$

Since

$$[H, S^2] = [S^2, S_z] = [H, S_z] = 0 \quad (23)$$

the eigenfunctions of the Hamiltonian operator must also be simultaneous eigenfunctions of S^2 and S_z .

In order for ψ to be an eigenfunction of S^2 when ϕ is a general product of spatial orbitals, the spin function χ can no longer be a simple product of one-electron spin functions.¹ We can construct suitable spin functions by noting⁴

$$[S^2, P_\sigma] = [H, P_\sigma] = 0 \quad (24)$$

where P_σ is an arbitrary permutation of the coordinates on the N electrons. These equations follow from the fact that both S^2 and H are totally symmetric with respect to arbitrary permutations of electron coordinates. The set of all permutations of N objects form a group and the spin functions which are symmetry adapted to this group must also be eigenfunctions of S^2 . The eigenfunctions of S^2 can then be generated by applying Wigner Operators,⁵ $\rho_{\ell,k}^g$, to a general product of one-electron spin functions.

$$\rho_{\ell,k}^g = \frac{\ell g}{h} \sum_R \Gamma_{\ell,k}^g(R) \tau_R^+ \quad (25)$$

where

ℓg = the dimension of the g th irreducible
representation

h = the order of the group

$\Gamma_{\ell,k}^g(R)^+$ = the ℓ, k element of the Hermitian
conjugate of the matrix representing
the operator R in the g th irreducible
representation

Σ = the sum over all operators, R , in the
 R
group.

The Symmetric or Permutation group has been used to generate spin eigenfunctions for a number of small systems,⁶⁻⁸ in a N -electron problem there are $N!$ group operations appearing in the definition of the Wigner Operators. For this reason, the construction of spin eigenfunctions by this procedure becomes a very time consuming task as the number of electrons increases.

Traditionally, this problem has been circumvented by using a character projection operator, ρ_c^g .⁹

$$\rho_c^g = \frac{\ell_g}{h} \sum_{R_c} \chi^g(R_c) R_c, \quad \chi(R_c) = \sum_i \Gamma_{ii}^g(R_c) \quad (26)$$

where the sum extends only over all classes in the group and R_c is any element in the class c . Löwdin has demonstrated that this projection operator has a particularly simple form when applied to the problem of constructing spin eigenfunctions.¹⁰

$$\Theta_L^s = \prod_{k \neq s} \frac{s^2 - k(k+1)}{s(s+1) - k(k+1)} \quad (27)$$

The wavefunction obtained by applying Lowdin's projection to an open shell single determinant is of the form^{10,11}

$$\Psi_L = \sum_{k=0}^{\nu} C_k^{s,m} T_k \quad (28)$$

where $C_k^{s,m}$ are the Sasaki-Ohno coefficients¹² and T_k is a sum of Slater determinants,

$$T_k = \Phi [\alpha^{\mu-k} \beta^k \mid \beta^{\nu-k} \alpha^k]. \quad (29)$$

Here, Φ is a product of one-electron spatial functions and $[\alpha^{\mu-k} \beta^k \mid \beta^{\nu-k} \alpha^k]$ is the spin function generated by all of the possible products that can be formed from $\nu-k$ beta spin functions and k alpha spin functions times all of the possible products that can be formed from k beta spin functions and $\mu-k$ alpha spin functions.

The spatial function Φ may be transformed to a "Corresponding Orbital"¹³ basis

$$\Phi = a_1(1)a_2(2)\dots a_{\mu}(\mu)b_1(\mu+1)b_2(\mu+2)\dots b_{\nu}(\mu+\nu) \quad (30)$$

$$\langle a_i \mid a_j \rangle = \langle b_i \mid b_j \rangle = \delta_{ij} \quad (31)$$

$$\langle a_i \mid b_j \rangle = d_i \delta_{ij} \quad (32)$$

The energy expression for this wavefunction has been derived by Harriman.^{11,14} He was able to demonstrate that the natural orbitals which diagonalized the Charge Density Matrix R_C^T are unchanged by spin projection of a single Slater determinant.

$$R^T = N \int \Psi^* \Psi d\tau_2 d\tau_3 \dots d\tau_N, \quad N = \mu + \nu$$

For an unprojected single determinant consisting of μ alpha spin orbitals and ν beta spin orbitals, R^T is of the form;

$$\begin{aligned} R^T &= \sum_i^{\mu} | \psi_i^\alpha \rangle \langle \psi_i^\alpha | + \sum_{j=1}^{\nu} | \psi_j^\beta \rangle \langle \psi_j^\beta | \\ &= \sum_{i=1}^{\mu} | a_i \rangle \langle a_i | + \sum_{j=1}^{\nu} | b_j \rangle \langle b_j |. \end{aligned} \quad (33)$$

The Natural Orbitals may be conveniently expressed in the Corresponding Orbital basis,¹¹

$$| \psi_i \rangle = (| a_i \rangle + | b_i \rangle) / \sqrt{2+2d_i}; \quad i \leq \nu \quad (34)$$

$$| \psi_i \rangle = (| a_i \rangle - | b_i \rangle) / \sqrt{2-2d_i}; \quad i \leq \nu \quad (35)$$

$$| \psi_t \rangle = | a_t \rangle; \quad \mu \geq t > \nu. \quad (36)$$

In practice, these Natural Orbitals are most conveniently obtained by first forming the Alpha and then the Beta Corresponding Orbitals.

The Alpha Corresponding Orbitals are obtained by diagonalizing

$R^{\alpha \beta \alpha}$,¹³

$$R^{\alpha} = \sum_{i=1}^{\mu} | a_i \rangle \langle a_i | \quad (37)$$

$$R^{\beta} = \sum_j^{\nu} | b_j \rangle \langle b_j | \quad (38)$$

$$R^{\alpha \beta \alpha} | a_i \rangle = d_i^2 | a_i \rangle \quad (39)$$

and the Beta Corresponding Orbitals are obtained by matrix multiplication

$$R^\beta | a_i \rangle = d_i | b_i \rangle \quad (40)$$

Constructing the Natural Orbitals in this manner, rather than diagonalizing R^T directly, eliminates several problems incurred when degenerate Occupation Numbers are present. The Natural Orbitals form the most convenient basis for evaluation of the energy expression,¹⁵

$$E = E_1 + E_2 \quad (41)$$

$$E_1 = \sum_{i=1}^{\nu} (\gamma_i \langle \psi_i | h | \psi_i \rangle + \gamma_i \langle \psi_i | h | \psi_i \rangle) + \sum_{j=\nu+1}^{\mu} \langle \psi_j | h | \psi_j \rangle \quad (42)$$

$$E_2 = \sum_{i,j,k,\ell=1}^n \Gamma_{ijkl} \langle \psi_i \psi_j | g | \psi_k \psi_\ell \rangle \quad (43)$$

$$\langle \psi_i \psi_j | g | \psi_k \psi_\ell \rangle \equiv \int \psi_i(1) \psi_j(2) g(1,2) \psi_k(1) \psi_\ell(2) dv_1 dv_2$$

The elements of the one and two-electron spinless density matrices, γ_m and Γ_{ijkl} respectively, are functions of the overlap integrals between Corresponding Orbitals and the Sasaki-Ohno coefficients. These density matrix elements will be discussed in more detail in a later section of the thesis.

The generalized Fock operator needed to perform the spin extended calculations based on Lowdin's wavefunction has been derived by Kaldor,¹⁶ Goddard,¹⁷ Mayer¹⁸ and also by Mesteschkin.¹⁹ The expressions for these Fock operators are quite lengthy and will not be reproduced here. Sando and Harriman²⁰ have also developed an algorithm based on a Newton-Raphson minimization of the energy functional in

which no generalized Fock operator is constructed. These procedures require that two-electron integrals between linear combinations of atomic orbitals be updated on each iteration. This is a very time consuming task, and for this reason, spin extended studies have only been carried out on relatively small systems or have entailed the use of semi-empirical parameters.

There is one other spin projected wavefunction which can be constructed quite simply without directly involving the Symmetric Group. This is the Generalized Valence Bond (GVB) wavefunction, which was first studied by Serber.^{21,22} For even-electron systems where $S_z = 0$.

$$\begin{aligned} \Psi_{\text{GVB}}^{s=0} = A(\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))\dots \quad (44) \\ \dots(\psi_{n-1}(n-1)\psi_n(n) + \psi_n(n-1)\psi_{n-1}(n))(\alpha(n-1)\beta(n) - \\ \beta(n-1)\alpha(n)) \end{aligned}$$

$$\begin{aligned} \Psi_{\text{GVB}}^{s=1} = \Psi_{\text{GVB}}^{s=0}(\psi_{n+1}(n+1)\psi_{n+2}(n+2) - \psi_{n+2}(n+1)\psi_{n+1}(n+2)) \times \quad (45) \\ (\alpha(n+1)\beta(n+2) + \beta(n+1)\alpha(n+2)) \end{aligned}$$

and for systems where $S_z \neq 0$

$$\begin{aligned} \Psi_{\text{GVB}}^{s=q/2} = \Psi_{\text{GVB}}^{s=0} \psi_{n+1}(n+1)\alpha(n+1)\psi_{n+2}(n+2)\alpha(n+2)\dots \quad (46) \\ \dots \psi_{n+q}(n+q)\alpha(n+q) \end{aligned}$$

In the simplest formulation of GVB theory, the spatial functions are Corresponding Orbitals and the wavefunction may be transformed to the Natural Orbital basis in a simple fashion. The energy expression for this wavefunction, as well as its transformation properties, will be discussed in a later section of the thesis. Ab-Initio spin extended calculations based on this wavefunction have been performed on a number of systems by Goddard and co-workers.²³⁻²⁵ An excellent summary of their work may be found in a recent review article by Bobrowicz and Goddard.²⁶

In the ASEHF method, the energy of the spin projected wavefunction is minimized with respect to variation in the overlap integrals between Corresponding Orbitals. The eigenvalues of the natural orbitals in the UHF wavefunction are¹¹

$$\lambda_i = 1 + d_i, \quad i \leq v \quad (47)$$

$$\lambda_{i'} = 1 - d_i \quad (48)$$

$$\lambda_t = \lambda_\mu = 1, \quad v < t, u \leq \mu, \quad t \neq u \quad (49)$$

and therefore, varying d_i shifts electron density between paired Natural Orbitals. The shifts in electron density induced by varying d_i in the wavefunction generated by Lowdin's projection operator are more difficult to interpret. The eigenvalues of the Natural Orbitals in this projected wavefunction are of the form¹¹

$$\lambda_i = 1 + d_i w(i) \quad , \quad i \leq v \quad (50)$$

$$\lambda_{i'} = 1 - d_i w(i) \quad (51)$$

$$\lambda_t = \lambda_u = 1 \quad , \quad v < t, u \leq \mu \quad , \quad t \neq u$$

where $w(i)$ is a function of all of the other overlap integrals and the Sasaki-Ohno coefficients. By varying d_i in this case, a movement of electron density is again induced between the paired Natural Orbitals ψ_i and $\psi_{i'}$, but in addition there is a smaller shift in density in all of the other pairs of Natural Orbitals. It will be shown in the section where the GVB energy expression is examined, that the eigenvalues of the Natural Orbitals resulting from a GVB wavefunction are of the form

$$\lambda_i = 1 + 2d_i / \eta_i \quad , \quad i \leq v \quad (53)$$

$$\lambda_{i'} = 1 - 2d_i / \eta_i \quad (54)$$

$$\lambda_t = \lambda_u = 1 \quad , \quad v < t, u \leq \mu \quad , \quad t \neq u \quad (55)$$

where $\eta_i = 1 + d_i^2$. Once again, the only effect of varying d_i is to shift electron density between ψ_i and $\psi_{i'}$. Only Lowdin's wavefunction and the GVB wavefunction will be employed in the ASEHF studies. The limited variational procedure of the ASEHF method can be performed very efficiently as the one and two-electron integrals occurring in equation (43) need only be calculated once. The utility of this approach depends largely on how closely the Natural Orbitals generated

in the ASEHF calculation approximate the self-consistent natural orbitals obtained from the spin extended approach. The methods used to generate the approximate Natural Orbitals are highly important and are therefore discussed in the next section.

STABILITY STUDIES OF RESTRICTED HARTREE-FOCK WAVEFUNCTIONS

One of the most interesting facets of Hartree-Fock Theory is the study of the stability of the Restricted Hartree-Fock wavefunction with respect to variations which break the spin and/or spatial symmetry of the wavefunction. This problem is of considerable importance, as unstable RHF determinants generally provide an inadequate starting wavefunction in a Configuration Interaction or Perturbation calculation. In this context, the stability of RHF solutions was considered by Thouless²⁷ who derived a set of stability equations for a single determinantal wavefunction. These equations were reformulated by Adams²⁸ and later by Cizek and Paldus,²⁹ who applied them in a number of studies of pi-electron systems.³⁰⁻³²

This problem is important to the present study because open shell single determinantal wavefunctions provide the starting point for ASEHF calculations. While open shell solutions arise as a natural consequence of a UHF treatment of a radical or an excited state, open shell UHF solutions may not exist for the ground state of nominally closed shell systems. For this reason, the stability of the RHF solutions for a number of systems was studied. If a system does indeed possess a stable RHF solution, an open shell wavefunction can often be obtained in a two-determinantal SCF calculation as recently suggested by Smeyers and Doreste-Suarez.³³ The stability equations of Cizek and Paldus will therefore be extended to account for the possibility of a low energy, two-determinantal wavefunction.

1. Single Determinantal Stability Calculations

In the Cizek and Paldus formulation of the stability problem,²⁹ each molecular orbital in a trial wavefunction is expanded as a linear combination of an occupied RHF molecular orbital plus a linear combination of virtual RHF molecular orbitals,

$$\Psi = | a_1^\alpha(1)a_2^\alpha(2)\cdots a_n^\alpha(n)b_1^\beta(n+1)\cdots b_n^\beta(2n) |, \quad (56)$$

where

$$a_i = \ell_i + \sum_j c_{i,j}^a k_j, \quad (57)$$

and

$$b_i = \ell_i + \sum_j c_{i,j}^b k_j. \quad (58)$$

The wavefunction is then expanded in the RHF molecular orbital basis and the expectation value of Q , $Q = H - E_0$, is evaluated to second order in the virtual orbital expansion coefficients,

$$E_0 \equiv \langle \psi_0 | H | \psi_0 \rangle \quad (59)$$

and

$$\Psi \cong \psi_0 + \psi_1 + \psi_2 \quad (60)$$

$$\psi_1 = C_{1i}^a | k_i^\alpha \ell_2^\alpha \cdots \ell_n^\alpha \ell_1^\beta \cdots \ell_n^\beta | + C_{1j}^a | k_j^\alpha \ell_2^\alpha \cdots \ell_n^\alpha \ell_1^\beta \cdots \ell_n^\beta | + \cdots \quad (61)$$

$$\langle \Psi | Q | \Psi \rangle \cong 2\langle \psi_0 | Q | \psi_1 \rangle + \langle \psi_1 | Q | \psi_1 \rangle + 2\langle \psi_0 | Q | \psi_2 \rangle, \quad (62)$$

Brillouin's Theorem³⁴ is used to further simplify Equation (62),

$$\langle \Psi | Q | \Psi \rangle \cong \langle \psi_1 | Q | \psi_1 \rangle + 2\langle \psi_0 | Q | \psi_2 \rangle. \quad (63)$$

A matrix representation of Q is then constructed in the orthogonal basis of one-electron excitations. If this matrix possesses a nega-

tive eigenvalue, the RHF solution is unstable and the set of virtual orbital expansion coefficients are obtained from the eigenvectors of Q .

This matrix may be block factored by transforming the alpha and beta excitations into singlet and triplet components. The transformed matrix elements of Q have been derived by Cizek and Paldus.²⁹ Since the RHF wavefunction for an even-electron system is the best single determinantal wavefunction, a Singlet instability can only arise by breaking the spatial symmetry of the RHF solution. On the other hand, if the RHF wavefunction possesses a Triplet instability, a lower energy UHF wavefunction exists which is a mixture of a triplet wavefunction and higher spin multiplicities. This wavefunction may or may not possess the required spatial symmetry. The broken symmetry wavefunctions generated by the stability calculation are used as a starting wavefunction in a UHF calculation.

The Triplet stability equations of Cizek and Paldus were introduced into a semi-empirical pi-molecular-orbital program by Schug, et al.³⁵ These equations were applied to a study of the RHF solutions of a series of linear polyacenes in the Pople-Pariser-Parr Approximation.³⁶ All of the linear polyacenes studied possessed Triplet instabilities and UHF calculations based on these instabilities were performed. The wavefunctions were subsequently spin projected using Lowdin's operator. The results are presented in Table I.

This procedure resulted in a significant lowering of the energy of each system studied. In every instance, the UHF wavefunctions were found to coincide with the Generalized Alternant Molecular Orbital

Table I

Correlation Energies (Δ , eV) Obtained from Unprojected
and Projected Open-Shell Ground States

<u>Molecule</u>	<u>Unprojected Function</u>		<u>Projected Singlet</u>	
	$\Delta_{\text{UHF}}^{(a)}$ (eV)	$\langle S^2 \rangle$ (\hbar^2)	$\Delta_{\text{PUHF}}^{(a)}$ (eV)	<u>Weight</u> ^(b)
Naphthalene	0.6453	0.9465	1.6207	0.6186
Anthracene	1.3760	1.5416	2.6270	0.4539
Naphthacene	2.2476	2.1816	3.6035	0.3605
Pentacene	1.5448	2.7599	2.9679	0.2988

(a) Δ is the lowering of energy relative to the closed-shell ground state.

(b) Weight of the projected singlet in the UHF function

(GAMO) wavefunctions generated by Koutecky.³⁷ The GAMO wavefunctions are obtained by starting a UHF calculation with a wavefunction obtained by alternately placing alpha and beta electrons in atomic pi orbitals. Each molecular orbital thus consists of only one atomic orbital in the starting wavefunction. This wavefunction is said to possess "Alternation Symmetry"³⁸ as the alpha molecular orbitals are transformed into a beta molecular orbital by an "Alternation Operator,"³⁸ B . The Alternation Operator can be identified as one of the symmetry operators in the molecular point group. It has the following properties³⁸

$$B^2 = 1 \quad (64)$$

$$F^\alpha B + BF^\beta = 2kB \quad (65)$$

where k is a scalar. In the case of linear polyacenes, B is the mirror plane perpendicular to the nuclei and containing the long axis of the molecule.

The GAMO Corresponding Orbitals are not symmetry orbitals, but are linear combinations of two symmetry orbitals,⁴

$$a_i = \sin \theta s_1 + \cos \theta s_2 \quad (66)$$

$$b_i = \sin \theta s_1 - \cos \theta s_2 \quad (67)$$

where s_1 and s_2 possess the transformation properties

$$Bs_1 = s_1 \quad (68)$$

$$Bs_2 = -s_2 \quad (69)$$

It has been noted by a number of workers that spin projection of a GAMO wavefunction also restores the spatial symmetry of the system.^{4,35}

It is quite simple to demonstrate that one need only diagonalize one of the Fock matrices in a UHF calculation employing an alternant wavefunction, as the eigenvectors of the other Fock matrix may then be obtained from symmetry considerations.³⁸ Thus, the time required to perform a GAMO calculation is equivalent to the time needed to perform an RHF calculation. This type of calculation may be employed in the study of a large number of systems as any molecule whose symmetry group contains a c_2 operation, or a mirror plane, is a candidate for a Generalized Alternant Molecular Orbital calculation.

An Ab-Initio version of this pi-program was written and a study of the ground state of C_2 and an excited state of Be_2 was undertaken. For diatomic molecules, the GAMO wavefunction may be obtained by starting the UHF calculation with localized orbitals where the unpaired electrons on different atoms possess different z-components of spin angular momentum. It was not surprising that the Ab-Initio stability calculations again found the RHF wavefunctions to be Triplet unstable and the lower energy UHF wavefunctions were found to possess Alternation Symmetry.

The Ab-Initio UHF calculations were performed by the Polyatom System of Programs obtained for the Quantum Chemistry Program Exchange at Indiana University.³⁹ The spin projection calculations were performed by a program originally written by Schug, Brewer and Lengsfeld to be compatible with Gaussian Seventy.⁴⁰ This program was modified to be compatible with Polyatom and also to perform GVB calculations.

Dunning's (9s5p/4s2p) Gaussian basis set was employed in the C_2 study and Dunning's (11s6p/4s3p) contraction scheme was used in the Be_2 calculations. The results of the C_2 calculation are summarized in Table II and the Be_2 results are presented in Table III.

The wavefunctions generated in these calculations were not minimized after spin projection. In each calculation, Lowdin's wavefunction possessed a significantly lower energy than the comparable RHF solution. The results for C_2 are particularly interesting as this procedure correctly predicts the ground state to be a singlet,⁴¹ while the RHF results predict a triplet ground state. The Be_2 results are indicative of the way spin projected UHF theory may be employed to provide an adequate description of the bond dissociation process. These results are also representative of the poor description of bond dissociation provided by RHF theory.

Molecules such as CH_2O and H_2O ,⁴² which possess the symmetry necessary to perform a GAMO calculation, were also studied at their equilibrium geometry and were found to have stable RHF solutions. Molecules such as LiH and HF ⁴² were also found to possess stable RHF solutions. The stability of H_2O and CH_2O may be attributed to the fact that symmetry adapted Hartree-Fock molecular orbitals provide a reasonable description of the bonds involving the hydrogen atom. In the case of HF and LiH we may attribute the stability of the RHF solution to the $C_{\infty v}$ symmetry of systems. In general, an unstable RHF solution results from low-lying, virtual orbitals of symmetry different than that of the highest occupied RHF molecular orbital. These low-lying orbitals are generally not present in heteronuclear diatomic

Table II
 Comparison of RHF, UHF and
 Spin Projected Energies for C_2

	<u>Spin Quantum Number</u>	<u>Symmetry</u>	<u>Energy (Hartrees)</u>	<u>Weight of the Spin State</u>
RHF	0	$1_{\Sigma_g}^+$	-90.6887	1.0
UHF	-	Σ^+	-90.8196	-
SPUHF	0	$1_{\Sigma_g}^+$	-90.8614	3.984×10^{-1}
	1	$3_{\Sigma_u}^+$	-90.8164	4.826×10^{-1}
	2	$5_{\Sigma_g}^+$	-90.7011	1.117×10^{-1}
	3	$7_{\Sigma_u}^+$	-90.5543	7.16×10^{-3}
	4	$9_{\Sigma_g}^+$	--	6.5×10^{-6}

Table III

Comparison of RHF and UHF Energies
for Be_2^* at a Number of Bond Distances

Bond Distance (A.U.)	RHF($^1\Delta_g^+ + ^1\Sigma_g^+$) (Hartrees)	UHF($\Delta^+ + \Sigma^+$) (Hartrees)
2.0	-28.6902	-28.6902
3.0	-29.0075	-29.0074
4.0	-29.0063	-29.0311
4.2	-28.9950	-29.0296
5.0	-28.9418	-29.0232
8.0	-28.7895	-29.0195
12.0	-28.7045	-29.0201

*Mixed symmetry wavefunction

molecules at the equilibrium internuclear separation. However, we desire a qualitatively acceptable description of these systems at all internuclear separations. To attain this goal, a more general wavefunction must be employed. The Half-Projected wavefunction of Smeyers suits this purpose admirably

$$\psi^{\pm} = \frac{1}{2} \{ | a_1^{\alpha} a_2^{\alpha} \dots a_n^{\alpha} b_1^{\beta} \dots b_n^{\beta} | \pm | b_1^{\alpha} b_2^{\alpha} \dots b_n^{\alpha} a_1^{\beta} \dots a_n^{\beta} | \} \quad (70)$$

Cox and Wood⁴³ have recently presented an SCF scheme based on this wavefunction which is comparable to a UHF calculation in efficiency. It may easily be shown that ψ^+ is a linear combination of even spin states and ψ^- is a linear combination of odd spin states. On the other hand, a UHF wavefunction is a mixture of both even and odd spin states. A Triplet instability is a closed shell wavefunction resulting when the energy of the singlet contribution to the UHF wavefunction is low enough to counter-balance the high energy triplet, pentet, etc. spin states. In most cases, the high energy contribution to the UHF wavefunction is dominated by the triplet term. For this reason, the Half-Projected Hartree-Fock procedure would be expected to result in an open shell wavefunction where the UHF procedure fails to do so. Recent work by Cox and Wood⁴⁴ indicate that this is indeed the case for LiH, H₂O and CO.

A study of the stability of the RHF wavefunction with respect to variations creating a Half-Projected wavefunction has not appeared in the literature. The Cizek and Paldus stability equation will now be extended to include this situation.

2. Two Determinantal Stability Calculations

First consider the possibility of a Half-Projected Hartree-Fock wavefunction consisting of even spin states giving rise to a RHF instability. Following Cizek and Paldus,²⁹ we evaluate Q to second order. By examining a four-electron example, all of the possible terms occurring in the matrix elements of Q can be generated. Let

$$\psi^+ = \frac{1}{2} \{ | a_1^\alpha a_2^\alpha b_1^\beta b_2^\beta | + | b_1^\alpha b_2^\alpha a_1^\beta a_2^\beta | \} \quad (71)$$

$$\psi_0^+ = | \ell_1^\alpha \ell_2^\alpha \ell_1^\beta \ell_2^\beta | \quad (72)$$

$$U_m^1(1,1)\psi_0^+ \equiv \frac{1}{m}\psi_1^+ = \frac{1}{2} \{ | k_1^\alpha \ell_2^\alpha \ell_1^\beta \ell_2^\beta | + | \ell_1^\alpha \ell_2^\alpha k_1^\beta \ell_2^\beta | \} \quad (73)$$

$$U_m^1(1,2)U_n^1(2,4)\psi_0^+ \equiv \frac{1}{m,n}\psi_2^+ = \frac{1}{2} \{ | k_2^\alpha k_4^\alpha \ell_1^\beta \ell_2^\beta | + | \ell_1^\beta \ell_2^\beta k_2^\alpha k_4^\alpha | \} \quad (74)$$

$$U_m^1(1,2)U_n^2(2,4)\psi_0^+ \equiv \frac{1}{m,n}\psi_2^+ = \frac{1}{2} \{ | k_2^\alpha \ell_2^\alpha \ell_1^\beta k_4^\beta | + | \ell_1^\alpha k_4^\alpha k_2^\beta \ell_2^\beta | \} \quad (75)$$

where ℓ_i and k_i again denote occupied and virtual Fock orbitals, respectively. $U_m^i(q,p)$ is defined to be the m^{th} excitation which replaces the occupied molecular orbital ℓ_q with the virtual orbital k_p . In this notation a superscript of one indicates that the specified excitation is performed on the alpha orbitals in the first determinant and the beta orbitals in the second determinant. A superscript of two indicates that the excitations are to be carried out in the reverse order.

It is convenient to represent the stability matrix, Q^+ , as a sum of two matrices,

$$Q^+ = A^+ + B^+ \quad (76)$$

$${}^{mn}A_{i,j}^+ = 2 \langle {}_i^m \psi_1^+ | Q | {}_j^n \psi_1^+ \rangle \quad (77)$$

$${}^{mn}B_{i,j}^+ = 2 \langle \psi_0 | Q | {}_{i,j}^{m,n} \psi_2^+ \rangle . \quad (78)$$

In order to derive the matrix elements of Q , we must consider four types of excitation,

- 1) $U_i(m,n) = U_j(m',n')$
- 2) $U_i(m,n) \neq U_j(m',n')$, $n = n'$ but $m \neq m'$
- 3) $U_i(m,n) \neq U_j(m',n')$, $m = m'$ but $n \neq n'$
- 4) $U_i(m,n) \neq U_j(m',n')$, $m \neq m'$ and $n \neq n'$

We need not qualify these excitations with superscripts when considering the singly excited contributions to Q as ${}^{11}A_{i,j}^+ = {}^{22}A_{i,j}^+ = {}^{12}A_{i,j}^+$. All of the matrix elements of A can then be obtained from an examination of the four excitations noted above.

Excitation 1 $U_i = U_j = U_j(m,n)$

$$A_{jj}^+ = \langle \ell_1^\alpha k_j^\alpha \ell_1^\beta \ell_j^\beta | H - E_0 | \ell_1^\alpha k_j^\alpha \ell_1^\beta \ell_j^\beta \rangle + \langle \ell_1^\alpha k_j^\alpha \ell_1^\beta \ell_j^\beta | H - E_0 | \ell_1^\alpha \ell_j^\alpha \ell_1^\beta k_j^\beta \rangle \quad (79)$$

where $\ell_j \equiv \ell_2$ and $k_j \equiv k_n$.

The orbital products appearing in these expressions are understood to be normalized, anti-symmetrized products. This matrix element

is considered to be a linear combination of three terms,

$A_{jj}^+ = a-b+c$ where

$$\begin{aligned}
 a &= \langle l_1^{\alpha} k_j^{\alpha} l_1^{\beta} l_j^{\beta} | H | l_1^{\alpha} k_j^{\alpha} l_1^{\beta} l_j^{\beta} \rangle \\
 &= \langle l_1 | h | l_1 \rangle + \langle l_j | h | l_j \rangle + \langle l_1 | F | l_1 \rangle + \\
 &\quad \langle k_j | F | k_j \rangle - \langle l_j k_j | g | l_j k_j \rangle_A, \tag{80}
 \end{aligned}$$

$$b = \langle l_1^{\alpha} k_j^{\alpha} l_1^{\beta} l_j^{\beta} | E_0 | l_1^{\alpha} k_j^{\alpha} l_1^{\beta} l_j^{\beta} \rangle = E_0$$

$$\begin{aligned}
 b = E_0 &= \langle l_1 | h | l_1 \rangle + \langle l_j | h | l_j \rangle + \langle l_1 | F | l_1 \rangle + \\
 &\quad \langle l_j | F | l_j \rangle \tag{81}
 \end{aligned}$$

and

$$\begin{aligned}
 c &= \langle l_1^{\alpha} k_j^{\alpha} l_1^{\beta} l_j^{\beta} | H-E_0 | l_1^{\alpha} l_j^{\alpha} l_1^{\beta} k_j^{\beta} \rangle \\
 &= \langle l_1^{\alpha} k_j^{\alpha} l_1^{\beta} l_j^{\beta} | H | l_1^{\alpha} l_j^{\alpha} l_1^{\beta} k_j^{\beta} \rangle \\
 &= \langle k_j l_j | g | l_j k_j \rangle. \tag{82}
 \end{aligned}$$

In these expressions F has been used to denote the closed shell

Fock Operator and

$$\langle l_m k_n | g | l_m k_n \rangle_A \equiv \langle l_m k_n | g | l_m k_n \rangle - \langle l_m k_n | g | k_n l_m \rangle. \tag{83}$$

The diagonal matrix element is seen to be

$$\begin{aligned}
 A_{jj}^+ &= a-b+c \\
 &= \langle k_j | F | k_j \rangle - \langle l_j | F | l_j \rangle + 2\langle l_j k_j | g | k_j l_j \rangle \\
 &\quad - \langle l_j k_j | g | l_j k_j \rangle
 \end{aligned} \tag{84}$$

$$A_{jj}^+ = \epsilon_n - \epsilon_m + 2 \langle l_m k_n | g | k_n l_m \rangle - \langle l_m k_n | g | l_m k_n \rangle \tag{85}$$

where ϵ_n and ϵ_m are Hartree-Fock eigenvalues.

Excitation 2 $U_i = U_i(2,n) \neq U_j = U_j(1,n)$ or $k_i = k_j, l_i \neq l_j$

$$A_{ij}^+ = \langle l_j^\alpha k_j^\alpha l_j^\beta l_i^\beta | H | k_j^\alpha l_i^\alpha l_j^\beta l_i^\beta \rangle + \langle l_j^\alpha k_i^\alpha l_j^\beta l_i^\beta | H | l_j^\alpha l_i^\alpha k_j^\beta l_i^\beta \rangle \tag{86}$$

All of the off diagonal matrix elements of A may be considered to be a sum of two terms, $A_{ij} = d + e$. In this case,

$$\begin{aligned}
 d &= \langle l_j^\alpha k_i^\alpha l_j^\beta l_i^\beta | H | k_j^\alpha l_i^\alpha l_j^\beta l_i^\beta \rangle = -\langle l_j^\alpha k_i^\alpha l_j^\beta l_i^\beta | H | l_i^\alpha k_i^\alpha l_j^\beta l_i^\beta \rangle \\
 &= \langle l_i | F | l_j \rangle - \langle k_i l_j | g | k_i l_i \rangle_A
 \end{aligned} \tag{87}$$

but $\langle l_i | F | l_j \rangle = 0$, therefore

$$d = +\langle k_j l_i | g | l_j k_i \rangle - \langle k_j l_i | g | k_i l_j \rangle. \tag{88}$$

Furthermore

$$\begin{aligned}
 e &= \langle l_j^\alpha k_i^\alpha l_j^\beta l_i^\beta | H | l_j^\alpha l_i^\alpha k_j^\beta l_i^\beta \rangle \\
 &= \langle l_j k_i | g | k_j l_i \rangle
 \end{aligned} \tag{89}$$

and

$$A_{ij}^+ = 2\langle l_j k_i | g | k_j l_i \rangle - \langle l_j k_i | g | l_i k_j \rangle. \quad (90)$$

Excitation 3 $U_i = U_i(1, n) \neq U_j(1, m) = U_j$ or $l_i = l_j$ but $k_i \neq k_j$

$$A_{ij}^+ = (d+e) = \langle k_i^\alpha l_{i2}^\alpha l_i^\beta l_{i2}^\beta | H | k_j^\alpha l_{j2}^\alpha l_i^\beta l_{j2}^\beta \rangle + \langle k_i^\alpha l_{i2}^\alpha l_i^\beta l_{i2}^\beta | H | l_i^\alpha l_{i2}^\alpha k_j^\beta l_{i2}^\beta \rangle \quad (91)$$

where

$$\begin{aligned} d &= \langle k_i^\alpha l_{i2}^\alpha l_i^\beta l_{i2}^\beta | H | k_j^\alpha l_{j2}^\alpha l_i^\beta l_{j2}^\beta \rangle \\ &= \langle k_i | F | k_j \rangle - \langle k_i l_i | g | k_j l_i \rangle A \\ &= \langle k_i l_i | g | l_j k_j \rangle A \end{aligned} \quad (92)$$

and

$$e = \langle k_i^\alpha l_{i2}^\alpha l_i^\beta l_{i2}^\beta | H | l_j^\alpha l_{j2}^\alpha k_j^\beta l_{j2}^\beta \rangle \quad (93)$$

Once again,

$$A_{ij}^+ = 2\langle k_i l_j | g | l_i k_j \rangle - \langle k_i l_j | g | k_j l_i \rangle. \quad (94)$$

Excitation 4 $U_i \neq U_j$ $k_i \neq k_j$ and $l_i \neq l_j$

$$A_{ij}^+ = \langle k_i^\alpha l_j^\alpha l_i^\beta l_j^\beta | H | l_i^\alpha k_j^\alpha l_i^\beta l_j^\beta \rangle + \quad (95)$$

$$\langle k_i^\alpha l_j^\alpha l_i^\beta l_j^\beta | H | l_i^\alpha l_j^\alpha l_i^\beta k_j^\beta \rangle$$

$$d = \langle k_i^\alpha l_j^\alpha l_i^\beta l_j^\beta | H | l_i^\alpha k_j^\alpha l_i^\beta l_j^\beta \rangle \quad (96)$$

$$= \langle k_i l_j | g | l_i k_j \rangle A$$

and

$$\begin{aligned}
 e &= \langle k_i^\alpha \ell_j^\alpha \ell_i^\beta \ell_j^\beta \mid H \mid \ell_i^\alpha \ell_j^\alpha \ell_i^\beta \ell_j^\beta \rangle \\
 &= \langle k_i \ell_j \mid g \mid \ell_i k_j \rangle.
 \end{aligned}
 \tag{97}$$

Again,

$$\begin{aligned}
 A_{ij}^+ &= d + e \\
 &= 2\langle k_i \ell_j \mid g \mid \ell_i k_j \rangle - \langle k_i \ell_j \mid g \mid k_j \ell_i \rangle.
 \end{aligned}
 \tag{98}$$

All of these equations for the off-diagonal matrix elements of A are identical. A single expression can now be obtained from any element of A,

$$\begin{aligned}
 A_{ij}^+ &= \langle k_i \mid F \mid k_j \rangle \langle \ell_i \mid \ell_j \rangle - \langle \ell_i \mid F \mid \ell_j \rangle \langle k_i \mid k_j \rangle + \\
 &2\langle \ell_i k_j \mid g \mid k_i \ell_j \rangle - \langle \ell_i k_j \mid g \mid \ell_j k_i \rangle,
 \end{aligned}
 \tag{99}$$

The expressions for the matrix elements of Q^+ generated by doubly excited configurations, are somewhat easier to obtain as they involve only two electron terms. However, in deriving the matrix elements of B, we need consider terms resulting from U_i^1 and U_i^2 , which are defined in Equations (74) and (75). The expressions for the matrix elements of B are sufficiently simple so that only the equations generated by the fourth excitation listed above need be considered.

For $U_i = U_j$, $k_i \neq k_j$ and $\ell_i \neq \ell_j$,

$$\begin{aligned}
 {}^{11}B_{i,j}^+ &= \langle \ell_i^\alpha \ell_j^\alpha \ell_i^\beta \ell_j^\beta \mid H \mid \ell_i^\alpha \ell_j^\alpha \ell_i^\beta \ell_j^\beta \rangle + \langle \ell_i^\alpha \ell_j^\alpha \ell_i^\beta \ell_j^\beta \mid H \mid k_i^\alpha k_j^\alpha \ell_i^\beta \ell_j^\beta \rangle \\
 &= 2\langle \ell_i^\alpha \ell_j^\alpha \ell_i^\beta \ell_j^\beta \mid H \mid \ell_i^\alpha \ell_j^\alpha \ell_i^\beta \ell_j^\beta \rangle
 \end{aligned}$$

$$\begin{aligned}
&= 2\langle l_i l_j | g | k_i k_j \rangle - 2\langle l_i l_j | g | k_j k_i \rangle \\
&= 2\langle l_i k_j | g | k_i l_j \rangle - 2\langle l_i l_j | g | k_j k_i \rangle
\end{aligned} \tag{100}$$

and

$$\begin{aligned}
{}^{12}_B{}_{i,j}^+ &= 2\langle l_i^{\alpha} l_j^{\alpha} l_i^{\beta} l_j^{\beta} | H | k_i^{\alpha} l_j^{\alpha} l_i^{\beta} k_j^{\beta} \rangle \\
&= 2\langle l_i l_j | g | k_i k_j \rangle = 2\langle l_i k_j | g | k_i l_j \rangle.
\end{aligned} \tag{101}$$

These expressions may easily be seen to account for all possible excitations. Note that if $l_i = l_j$ and/or $k_i = k_j$, the expression for ${}^{11}_B$ must vanish, and it does.

The matrix elements of Q can now be expressed in a simple fashion,

$$\begin{aligned}
{}^{11}_Q{}_{i,j}^+ &= {}^{11}_A{}_{i,j}^+ + {}^{11}_B{}_{i,j}^+ \\
&= \langle k_i | F | k_j \rangle \langle l_i | l_j \rangle - \langle l_i | F | l_j \rangle \langle k_i | k_j \rangle \\
&\quad + 4\langle l_i k_j | g | k_i l_j \rangle - \langle l_i k_j | g | l_j k_i \rangle \\
&\quad - 2\langle l_i l_j | g | k_j k_i \rangle
\end{aligned} \tag{102}$$

and

$$\begin{aligned}
{}^{12}_Q{}_{i,j}^+ &= \langle k_i | F | k_j \rangle \langle l_i | l_j \rangle - \langle l_i | F | l_j \rangle \langle k_i | k_j \rangle \\
&\quad + 4\langle l_i k_j | g | k_i l_j \rangle - \langle l_i k_j | g | l_j k_i \rangle.
\end{aligned} \tag{103}$$

The matrix representation of Q is then of the form,

$$Q^+ = \begin{array}{cc} & U^1 & & U^2 \\ U^1 & \left[\begin{array}{c} 11_Q^+ \\ 21_Q^+ \end{array} \right] & & \\ U^2 & & & \left[\begin{array}{c} 12_Q^+ \\ 22_Q^+ \end{array} \right] \end{array}$$

where $11_Q^+ = 22_Q^+$ and $21_Q^+ = 12_Q^+$.

The matrix elements of Q^- resulting from the Half-Projected Hartree-Fock wavefunction of odd spin states, Ψ^- , are somewhat easier to obtain. The simplicity results from the fact that only singly excited terms need be considered as $\langle \psi_0 | Q | \psi_2^- \rangle = 0$. In fact, Ψ^- can no longer be thought of as evolving from ψ_0 . However, we can still consider the problem of constructing Ψ^- with a lower energy than ψ_0 where the orbitals comprising Ψ^- are constructed via Equation (57). To construct Q^- to second order in the virtual orbital expansion coefficients, we need only consider one term, $\langle \psi_1^- | Q | \psi_1^- \rangle$. There is no distinction between the two types of excitations, 1_U and 2_U , where only singly excited wavefunctions are involved and the dimension Q is thereby halved. The matrix elements of Q^- can easily be obtained from the expressions used to define the matrix elements of A in the preceding paragraphs. The matrix elements of Q^- are constructed by subtracting rather than adding cross terms in the equations.

The diagonal matrix elements of Q are of the form

$$Q_{ii}^- = a - b - c$$

$$= \langle k_i | F | k_i \rangle - \langle l_i | F | l_i \rangle - \langle k_i l_i | g | k_i l_i \rangle \quad (104)$$

where a , b , and c are defined in equations (80), (81) and (82), respectively. The off-diagonal matrices are obtained by considering Equations (96) and (97). We find

$$Q_{ij}^- = -\langle k_i l_j | g | k_j l_i \rangle. \quad (105)$$

In general,

$$Q_{ij}^- = \langle k_i | F | k_j \rangle \langle l_i | l_j \rangle - \langle l_i | F | l_j \rangle \langle k_i | k_j \rangle$$

$$- \langle k_i l_j | g | k_j l_i \rangle \quad (106)$$

These equations were included in the Ab-Initio Stability Program and a study of Lithium Hydride was undertaken. In these calculations a STO-6G^{40,45} basis set was employed and stability calculations were performed at a number of bond distances. A summary of these calculations is presented in Table IV.

As the bond distance is decreased from 6 atomic units, the UHF and RHF results are seen to converge in the neighborhood of 3.75 atomic units. Note that the RHF and UHF results did not converge in the Be_2 calculations. The lowest eigenvalue obtained in the stability calculations are also presented in Table IV. The two-determinantal stability calculations indicate that an open shell description may be obtained over the full range of bond distances studied.

Table IV

Results of the Stability Analysis of
the Lithium Hydride RHF Wavefunction

<u>Bond Distance (A.U.)</u>	<u>RHF (h)</u>	<u>UHF (h)</u>	<u>$\lambda_{\text{T}}^{\text{a}}$</u>	<u>λ_{+}^{b}</u>
6.0	-7.7810	-7.8749	-.242	-.351
5.0	-7.8417	-7.8828	-.141	-.322
4.0	-7.9072	-7.9083	-.017	-.292
3.5	-7.9352	-7.9352	.004	-.279
3.0	-7.9522	--	.008	-.268
2.0	-7.8845	--	.118	-.262
1.0	-7.2089	--		

-
- a. Lowest eigenvalue of Cizek-Paldus Triplet Stability Matrix
- b. Lowest eigenvalue of even spin state, two-determinantal Stability Matrix, Q^{+}

3. The Alternant Molecular Orbital Approach

There is yet another procedure in which to obtain open shell starting wavefunctions for the ASEHF calculations. In this procedure, an RHF calculation is performed and then bonding and anti-bonding orbitals are mixed to define the set of Corresponding Orbitals. This is exactly the procedure followed in a traditional Alternant Molecular Orbital pi-calculation.⁴ However, the orbitals to be paired are not defined in an unambiguous manner when this method is expanded to include calculations employing more than a minimal basis set. In previous starting methods, an open shell calculation was used to define the corresponding orbitals and this problem is not encountered. Bendazzoli et al.⁴⁶ have applied this procedure to the study of a number of first row diatomic molecules, where the virtual orbitals were chosen to be eigenvectors of the Fock Operator.

It is well known from perturbation studies that these virtual orbitals are not the optimal set in which to describe the finer details of electron correlation. In fact, a close examination of the F_2 results reported by Bendazzoli⁴⁶ et al. will bear this out. Methods by which improved virtual orbitals may be obtained have been discussed by a number of authors.⁴⁷⁻⁴⁹ In fact, the stability calculations discussed in the preceding paragraphs of this thesis may be used to define appropriate virtual orbitals. These methods have not been studied in this work, but they do provide a promising topic for further research. For example, one could localize both the

occupied and virtual orbitals, as discussed by either Boys⁵⁰ or Edmiston,⁵¹ and then optimize the virtual orbitals. In this case, the ASEHF method would produce a localized electron pair description of the system.

THE GVB EXPRESSION

In this section the energy expression for a GVB wavefunction is derived in terms of the overlap integrals between Alpha and Beta Corresponding Orbitals. The final expression for the energy of the GVB singlet and triplet wavefunctions are presented in a convenient form in which to perform an ASEHF calculation. The final GVB energy expressions are compared to those obtained by Harriman¹¹ for Lowdin's spin projected UHF wavefunction. The difference in these GVB expressions from the GVB equations of Kutzelnigg⁴⁹ are pointed out.

Consider the unnormalized GVB singlet wavefunction in the Corresponding Orbital basis

$$\Psi_{\text{GVB}}^{S=0} = A(a_1(1)b_1(2) + b_1(1)a_1(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \dots \quad (107)$$

where A is an n-particle anti-symmetrizer,

$$A = \sum_P \epsilon^P P. \quad (108)$$

In this expression for A, P is a permutation of the electron coordinates appearing in equation (107) and ϵ^P is the parity of that permutation. It is convenient to transform the wavefunction to the Natural Orbital basis. The Corresponding Orbitals are expanded in the Natural Orbital basis as follows:

$$a_i = (t_i \psi_i + u_i \psi_{i'})/2, \quad b_i = (t_i \psi_i - u_i \psi_{i'})/2$$

$$t_i = (1 + d_i)^{1/2}, \quad u_i = (1 - d_i)^{1/2} \quad (109)$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} = \langle \psi_{i'} | \psi_{j'} \rangle \text{ and } \langle \psi_i | \psi_{j'} \rangle = 0,$$

then aside from a normalization constant

$$\Psi_{\text{GVB}}^{s=0} = A(t_1^2 \psi_1(1)\psi_1(2) - u_1^2 \psi_{1'}(1)\psi_{1'}(2)) (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \dots \quad (110)$$

This wavefunction can be further simplified by noting

$$(E - P_{12})(t_1^2 \psi_1(1)\psi_1(2) - u_1^2 \psi_{1'}(1)\psi_{1'}(2)) (\alpha(1)\beta(2))$$

$$= (t_1^2 \psi_1(1)\psi_1(2) - u_1^2 \psi_{1'}(1)\psi_{1'}(2)) (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \quad (111)$$

and

$$A(E - P_{12}) = 2A \quad (112)$$

where P_{12} permutes the coordinates of the two electrons and E is the identity permutation. The unnormalized wavefunction is now

$$\Psi_{\text{GVB}}^{s=0} \equiv A\psi \quad (113)$$

$$\Psi_{\text{GVB}}^{s=0} = A(t_1^2 \psi_1(1)\psi_1(2) - u_1^2 \psi_{1'}(1)\psi_{1'}(2)) \alpha(1)\beta(2) \dots \quad (114)$$

$$\dots (t_{n/2}^2 \psi_{n/2}(n-1)\psi_{n/2}(n) - u_{n/2}^2 \psi_{\hat{n}/2}(n-1)\psi_{\hat{n}/2}(n)) \alpha(n-1)\beta(n)$$

The expectation value of the energy for the wavefunction is

$$\begin{aligned}
 E &= \frac{\langle A\psi | H | A\psi \rangle}{\langle A\psi | A\psi \rangle} \\
 &= \frac{\langle \psi | H | A\psi \rangle}{\langle \psi | A\psi \rangle}
 \end{aligned}
 \tag{115}$$

The following equalities have been used to arrive at Equation (115)

$$[A, H] = 0 \tag{116}$$

$$A A = k A \tag{117}$$

where k is a scalar.

Consider the normalization integral in a six-electron test case,

$$N = \langle \psi | A\psi \rangle \tag{118}$$

First expand $\Psi_{\text{GVB}}^{S=0}$ as a linear combination of spatial products

$$\begin{aligned}
 \psi &= \{ t_1^2 t_2^2 t_3^2 \psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)\psi_3(5)\psi_3(6) \\
 &\quad - u_1^2 t_2^2 t_3^2 \psi_{1^-}(1)\psi_{1^-}(2)\psi_2(3)\psi_2(4)\psi_3(5)\psi_3(6) \\
 &\quad - t_1^2 u_2^2 t_3^2 \psi_1(1)\psi_1(2)\psi_{2^-}(3)\psi_{2^-}(4)\psi_3(5)\psi_3(6) \\
 &\quad - t_1^2 t_2^2 u_3^2 \psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)\psi_{3^-}(5)\psi_{3^-}(6) \\
 &\quad + u_1^2 u_2^2 t_3^2 \psi_{1^-}(1)\psi_{1^-}(2)\psi_{2^-}(3)\psi_{2^-}(4)\psi_3(5)\psi_3(6) \\
 &\quad + u_1^2 t_2^2 u_3^2 \psi_{1^-}(1)\psi_{1^-}(2)\psi_2(3)\psi_2(4)\psi_{3^-}(5)\psi_{3^-}(6) \\
 &\quad + t_1^2 u_2^2 u_3^2 \psi_1(1)\psi_1(2)\psi_{2^-}(3)\psi_{2^-}(4)\psi_{3^-}(5)\psi_{3^-}(6) \\
 &\quad - u_1^2 u_2^2 u_3^2 \psi_{1^-}(1)\psi_{1^-}(2)\psi_{2^-}(3)\psi_{2^-}(4)\psi_{3^-}(5)\psi_{3^-}(6) \} \times \\
 &\quad \{ \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) \}
 \end{aligned}
 \tag{119}$$

The wavefunction is now of the form

$$\begin{aligned}\Psi_{\text{GVB}}^{S=0} &= A(c_0 x_0 + c_1 x_1 + c_2 x_2 + c_3 x_3 + c_4 x_4 + c_5 x_5 + c_6 x_6 + c_7 x_7) \\ &= A \sum_{i=0}^m c_i x_i\end{aligned}\quad (120)$$

where $m = 2^{n/2} - 1$,

$$c_0 = t_1^2 t_2^2 t_3^2, \quad c_1 = u_1^2 t_2^2 t_3^2, \quad \dots, \quad (121)$$

and

$$x_0 = \psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)\psi_3(5)\psi_3(6)\alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) \quad (122)$$

etc.

This expression is extremely convenient because the expansion functions form an orthogonal set, and with our definition of the antisymmetrizer, $\langle x_i | A x_j \rangle = \delta_{ij}$. The normalization integral is now simple to evaluate;

$$N = \sum_{i=0}^m c_i^2 \quad (123)$$

The form of the GVB wavefunction shown in equation (120) was studied extensively by Kutzelnigg⁵² and later by Goddard and co-workers.²³

The expansion coefficients, c_i , appear in their final energy expressions where they are treated as variational parameters, subject to the constraint $\sum_i c_i^2 = 1$. In ASEHF calculation, these expansion coefficients are also treated as variational parameters, but are expressed as a simple function of the set of overlap integrals, d_i . We introduce the following notation

$$t_i^4 = (1+d_i)^2 = 1+2d_i+d_i^2 = \eta_i+2d_i \quad (124)$$

$$u_i^4 = (1-d_i)^2 = \eta_i-2d_i \quad (125)$$

$$\eta_i = 1+d_i^2. \quad (126)$$

In this notation the normalization integral is

$$N = c_o^2 + c_1^2 + \dots + c_7^2 \quad (127)$$

where

$$c_o^2 = t_1^4 t_2^4 t_3^4 = (\eta_1+2d_1)(\eta_2+2d_2)(\eta_3+2d_3) \quad (128)$$

$$c_1^2 = u_1^4 t_2^4 t_3^4 = (\eta_1-2d_1)(\eta_2+2d_2)(\eta_3+2d_3) \quad (129)$$

etc.

and

$$\begin{aligned} N &= (\eta_1+2d_1)(\eta_2+2d_2)(\eta_3+2d_3) + (\eta_1-2d_1)(\eta_2+2d_2)(\eta_3+2d_3) \\ &+ (\eta_1+2d_1)(\eta_2-2d_2)(\eta_3+2d_3) + (\eta_1+2d_1)(\eta_2+2d_2)(\eta_3-2d_3) \\ &+ (\eta_1-2d_1)(\eta_2-2d_2)(\eta_3+2d_3) + (\eta_1-2d_1)(\eta_2+2d_2)(\eta_3-2d_3) \\ &+ (\eta_1+2d_1)(\eta_2-2d_2)(\eta_3-2d_3) + (\eta_1-2d_1)(\eta_2-2d_2)(\eta_3-2d_3) \\ &= \{(\eta_1+2d_1)+(\eta_1-2d_1)\}\{(\eta_2+2d_2)+(\eta_2-2d_2)\}\{(\eta_3+2d_3)+(\eta_3-2d_3)\} \\ &= (2\eta_1)(2\eta_2)(2\eta_3) \\ &= 8 \eta_1 \eta_2 \eta_3. \end{aligned} \quad (130)$$

In general,

$$N = 2^{m+1} \eta_1 \dots \eta_n. \quad (131)$$

The one-electron contributions to the electronic energy may also be expressed in a convenient fashion in this notation. The expression for the one-electron energy,

$$E_1 = \langle \psi | h | A \psi \rangle / N \quad (132)$$

is particularly simple in the Natural Orbital basis. The expectation value of one-electron operators between two Slater determinants is non-zero if the determinants differ by, at most, one spin orbital. In our basis set x_i differs from x_j ($j \neq i$) by two spin orbitals and therefore, only diagonal terms contribute to the one-electron energy

$$E_1 = \sum_{j=0}^n c_j^2 \langle x_j | h | Ax_j \rangle / N \quad (133)$$

Therefore, in the expression for the one-electron energy there will be only two types of integrals to consider; $\langle \psi_i | h | \psi_i \rangle$ and $\langle \psi_{i'} | h | \psi_{i'} \rangle$. In general, one-electron integrals involving a particular Natural Orbital will appear in more than one term in equation (133). The one-electron energy expression is then of the form

$$E_1 = \sum_{i=1}^n \{ \gamma_i \langle \psi_i | h | \psi_i \rangle + \gamma_{i'} \langle \psi_{i'} | h | \psi_{i'} \rangle \} \quad (134)$$

where

$$\gamma_i = 2 \sum_{j \in \psi_i} c_j^2 \quad (135)$$

and the sum is only over the determinants which contain ψ_i . Similarly,

$$\gamma_{i'} = 2 \sum_j c_j^2 \psi_{i'} \epsilon x_j \quad (136)$$

For example,

$$\begin{aligned} \gamma_1 &= 2(c_0^2 + c_2^2 + c_3^2 + c_6^2)/N \\ &= 2(\eta_1 + 2d_1) \{(\eta_2 + 2d_2) + (\eta_2 - 2d_2)\} \{(\eta_3 + 2d_3) + (\eta_3 - 2d_3)\} \\ &= 2(\eta_1 + 2d_1)(2\eta_2)(2\eta_3)/8\eta_1\eta_2\eta_3 \end{aligned} \quad (137)$$

$$\gamma_1 = 1 + 2d_1/\eta_1.$$

Similarly,

$$\begin{aligned} \gamma_{1'} &= 2(c_1^2 + c_4^2 + c_5^2 + c_7^2)/N = (\eta_1 - 2d_1)(2\eta_2)(2\eta_3)/8\eta_1\eta_2\eta_3 \\ \gamma_{1'} &= 1 - 2d_1/\eta_1. \end{aligned} \quad (138)$$

Because of the symmetric form of $\Psi_{GVB}^{s=0}$, the general expression for the elements of the one-electron density matrix are seen to be

$$\gamma_i = 1 + 2d_i/\eta_i \quad (139)$$

$$\gamma_{i'} = 1 - 2d_i/\eta_i. \quad (140)$$

The two-electron energy is expressible in the general form

$$E_2 = \langle \psi | g | A\psi \rangle \quad (141)$$

$$= \sum_{i,j,k,l} \Gamma_{ijkl} \langle \psi_i \psi_j | g | \psi_k \psi_l \rangle \quad (142)$$

where Γ_{ijkl} is an element of the spinless two-particle density matrix.

Since the matrix elements of a two-electron operator between Slater determinants vanish if the determinants differ by more than two spin-orbitals, the number of integrals appearing in Equation (141) is greatly reduced for a GVB wavefunction. We need only consider integrals involving ψ_1, ψ_1', ψ_2 and ψ_2' to generate all of the unique two-electron terms occurring in the energy expression for the GVB singlet wavefunction. The non-zero, two-electron integrals occurring in Equation (141) for our sample GVB wavefunction involving these four Natural Orbitals are presented in Table V, where W_{ijkl} is the weighting factor for each integral. These two-electron integrals only occur once in Equation (141), but they occur P_{ijkl} times in Equation (142). With this in mind, we can obtain an expression for Γ_{ijkl} , $\Gamma_{ijkl} = W_{ijkl}/P_{ijkl}$.

To complete the energy expression, Γ_{ijkl} must be expressed in terms of d_i and η_i . From the discussion of the one-electron energy we note

$$\Gamma_{1111} = 1/2(1+2d_1/\eta_1) = (1/2)(\gamma_1) \quad (143)$$

and

$$\Gamma_{1'1'1'1'} = 1/2(1-2d_1/\eta_1) = (1/2)(\gamma_1) \quad (144)$$

The remaining two-electron terms are

$$\begin{aligned} \Gamma_{111'1'} &= -(c_0c_2+c_2c_4+c_3c_5+c_6c_7)/N & (145) \\ &= -(1+d_1)(1-d_1)(2\eta_2)(2\eta_3)/8\eta_1\eta_2\eta_3 \\ &= -(1/2)(1-d_1^2)/\eta_1, \end{aligned}$$

Table V

Two-Electron Density Matrix Elements
for a GVB Singlet Wavefunction

<u>IJKL</u> ^a	<u>W</u> _{IJKL}	<u>P</u> _{IJKL}
1 1 1 1	$(c_0^2 + c_2^2 + c_3^2 + c_6^2)/N$	1
1'1'1'1'	$(c_1^2 + c_4^2 + c_5^2 + c_7^2)/N$	1
1 1 1'1'	$2(c_0c_1 + c_2c_4 + c_3c_5 + c_6c_7)/N$	2
1 2 1 2	$4(c_0^2 + c_3^2)/N$	2
1 2 2 1	$-2(c_0^2 + c_3^2)/N$	2
1'2 1'2	$4(c_1^2 + c_5^2)/N$	2
1'2 2 1'	$-2(c_1^2 + c_5^2)/N$	2
1 2'1 2'	$4(c_2^2 + c_6^2)/N$	2
1 2'2'1	$-2(c_2^2 + c_6^2)/N$	2
1'2'1'2'	$4(c_4^2 + c_7^2)/N$	2
1'2'2'1'	$-2(c_4^2 + c_7^2)/N$	2

a. $IJKL \equiv \langle \psi_I(1)\psi_J(2) | g(1,2) | \psi_K(1)\psi_L(2) \rangle$

$$\begin{aligned}
\Gamma_{1212} &= 2(c_0^2 + c_3^2)/N = (\eta_1 + 2d_1)(\eta_2 + 2d_2)(2\eta_3)/8\eta_1\eta_2\eta_3 & (146) \\
&= (1/2)(1 + 2d_1/\eta_1)(1 + 2d_2/\eta_2) \\
&= (1/2)(\gamma_1\gamma_2)
\end{aligned}$$

$$\Gamma_{1221} = -(1/2)(\Gamma_{1212}) = -(1/4)(\gamma_1\gamma_2) \quad (147)$$

$$\begin{aligned}
\Gamma_{1'21'2} &= 2(c_1^2 + c_5^2)/N = (\eta_1 - 2d_1)(\eta_2 + 2d_2)(2\eta_3)/8\eta_1\eta_2\eta_3 & (148) \\
&= (1/2)(1 - 2d_1/\eta_1)(1 + d_2/\eta_2) \\
&= (1/2)(\gamma_1'\gamma_2)
\end{aligned}$$

$$\Gamma_{1'221'} = -(1/2)(\Gamma_{1'21'2}) = -(1/4)(\gamma_1'\gamma_2) \quad (149)$$

$$\begin{aligned}
\Gamma_{1'2'1'2'} &= 2(c_4^2 + c_7^2)/N = 2(\eta_1 - 2d_1)(\eta_2 - 2d_2)(2\eta_3)/8\eta_1\eta_2\eta_3 & (150) \\
&= (1/2)(\gamma_1'\gamma_2')
\end{aligned}$$

$$\Gamma_{1'2'2'1'} = -(1/4)(\gamma_1'\gamma_2') \quad (151)$$

Once again, these results can be seen to be perfectly general as no new terms are introduced by expanding the size of our system or by considering any other pair of Natural Orbitals.

Now consider the energy expression for the GVB triplet wavefunction ($S_z=0$), where

$$\psi_{\text{GVB}}^{S=1} = \psi_{\text{GVB}}^{S=0} (a_{n/2}^{(n-1)}b_{n/2}^{(n)} - b_{n/2}^{(n-1)}a_{n/2}^{(n)})\alpha^{(n-1)}\beta^{(n)} \quad (152)$$

Operating on this wavefunction with a raising operator S_+ ,

$$S_+ = \sum_i s_+(i) \quad , \quad s_+(k) = s_+(k) + is_y(k) \quad (153)$$

$$s_+(k)\alpha(k) = 0 \quad , \quad s_+(k)\beta(k) = \alpha(k) \quad (154)$$

$$S_+^{m=0}\psi_{\text{GVB}}^{S=1} = S_+^{m=1}\psi_{\text{GVB}}^{S=1} \quad (155)$$

where

$$\begin{aligned} \psi_{\text{GVB}}^{m=1, s=1} &= A \psi_{\text{GVB}}^{s=0} (a_{n/2}^{(n-1)} b_{n/2}^{(n)} - b_{n/2}^{(n-1)} a_{n/2}^{(n)}) \alpha^{(n-1)} \alpha^{(n)} \\ &= A \psi_{\text{GVB}}^{s=0} t_{n/2}^u \psi_{n/2}^{(n-1)} \psi_{n/2}^{(n)} \alpha^{(n-1)} \alpha^{(n)} \end{aligned}$$

The energies of $\psi_{\text{GVB}}^{m=0, s=1}$ and $\psi_{\text{GVB}}^{m=1, s=1}$ are identical and the latter wavefunction is employed to obtain the energy expressions. Consider an eight-electron test case and expand the wavefunction as a sum of Slater determinants. An eight determinantal wavefunction is again obtained. Each determinant in this expression may be obtained by multiplying the determinants in equation (120) by $t_4^u \psi_4(7) \psi_4(8)$. The quantity, t_4^u , may be ignored as it is simply a normalization factor. The new two-electron density matrix elements are;

$$\Gamma_{14'14'} = (1/2) (\gamma_1) \quad , \quad \Gamma_{14'4'1} = -(1/4) (\gamma_1) \quad (156)$$

$$\Gamma_{1'4'1'4'} = (1/2) (\gamma_1) \quad , \quad \Gamma_{1'4'4'1'} = -(1/4) (\gamma_1) \quad (157)$$

$$\Gamma_{44'44'} = (1/2) \quad , \quad \Gamma_{44'4'4'} = -(1/2) \quad (158)$$

The integral expressions found in Tables V and VI are equivalent to those obtained by Kutzelnigg.⁵²

In obtaining the integral expression for the GVB triplet, all of the terms necessary to calculate the energy of a GVB doublet,

$$\psi_{\text{GVB}}^{1/2} = A \psi_{\text{GVB}}^{s=0} a_{n+1}^{(n+1)} \alpha^{(n+1)} \quad (159)$$

or

$$\psi_{\text{GVB}}^{1/2} = A \gamma_{\text{GVB}}^{s=0} \psi_{n+1}^{(n+1)} \alpha^{(n+1)} \quad (160)$$

have also been generated.

Table VI

Additional Two-Electron Density Matrix

Elements for a GVB Triplet

<u>IJKL</u>	<u>W_{IJKL}</u>	<u>P_{IJKL}</u>
1 4 1 4	$(C_0^2 + C_2^2 + C_3^2 + C_6^2)/N$	2
1 4 4 1	$-(1/2)(C_0^2 + C_2^2 + C_3^2 + C_6^2)/N$	2
1'4 1'4	$(C_1^2 + C_4^2 + C_5^2 + C_7^2)/N$	2
1'4 4 1'	$-(1/2)(C_1^2 + C_4^2 + C_5^2 + C_7^2)/N$	2
1 4'1 4'	$(C_0^2 + C_2^2 + C_3^2 + C_6^2)/N$	2
1 4'4'1	$-(1/2)(C_0^2 + C_2^2 + C_3^2 + C_6^2)/N$	2
1'4'1'4'	$(C_1^2 + C_4^2 + C_5^2 + C_7^2)/N$	2
1'4'4'1'	$-(1/2)(C_1^2 + C_4^2 + C_5^2 + C_7^2)/N$	2
4 4'4 4'	1	2
4 4'4'4'	-1	2

Harriman's equations for the one and two-electron density matrix elements appearing in the energy expression for Lowdin's spin projected wavefunction are found in Table VII. The definitions of the auxiliary functions appearing in these equations are presented in Table VIII. If the energy expression for the GVB singlet is derived in the Corresponding Orbital basis, it is convenient to define similar sets of functions $G^m(i,j)$ and $G^n(i)$. These functions are generated by replacing the Sasaki-Ohno coefficients, $C_k^{s,m}$, by a new set of coefficients, B_k ; $B_k = (-1)^k$. By replacing Harriman's functions $D^m(i,j)$ in the energy expression of the projected wavefunction with the corresponding functions from the set of $G^m(i,j)$, one can show the following:

1) The one-electron density matrix elements appearing in the GVB energy expression are generated by this transformation and are said to transform covariantly.

2) The two-electron density matrix elements Γ_{ijij} , Γ_{itit} , $\Gamma_{i'ji'j}$, $\Gamma_{i'j'i'j}$, Γ_{iiii} , $\Gamma_{i'i'i'i}$ and $\Gamma_{i i i i'}$ are also covariant.

3) The exchange terms are not covariant, but can be conveniently partitioned as a sum of a covariant term and a term which does not occur in the GVB energy expression.

4) The two-electron density matrix elements Γ_{itti} , $\Gamma_{iji'i}$, $\Gamma_{i'i'ii}$, and $\Gamma_{ij'ji}$ do not occur in the GVB energy expression. The correspondence between the GVB density matrix elements in this notation and those obtained in the previous paragraphs can be made by noting

Table VII

Harriman's Unique Non-Zero Components
of the Second Order Density Matrix^a

<u>I J K L</u> ^b	<u>F_{IJKL}</u>	<u>V_{IJKL}</u>
t u t u	1	1/2
t u u t	-1	1/2
i t i t	$(1+d_i)/2$	$D^0(i)+d_i D^1(i)$
i t t i	$-(1+d_i)/2$	$(1/2)E(i)+d_i D^1(i)$
i' t i' t	$(1-d_i)/2$	$D^0(i)-d_i D^1(i)$
i' t t i'	$-(1-d_i)/2$	$(1/2)W(i)$
i t t i'	$-(1-d_i)^{1/2}/4$	$W(i)$
i i i i	$(1+d_i)^2/2$	$W(i)$
i' i' i' i'	$(1-d_i)^2/2$	$W(i)$
i i i' i'	$-(1-d_i)/2$	$D^0(i)$
i j i j	$(1+d_i)(1+d_j)/4$	$2[D^0(i,j)+(d_i+d_j)D^1(i,j)+d_i d_j D^2(i,j)]$
i j j i	$-(1+d_i)(1+d_j)/4$	$E(i,j)+2(d_i+d_j)D^1(i,j)-d_i d_j E^1(k,j)$
i j' i j'	$(1+d_i)(1-d_j)/4$	$2[D^0(i,j)+(d_i-d_j)D^1(i,j)-d_i d_j D^2(i,j)]$
i j' j' i	$-(1+d_i)(1-d_j)/4$	$E(i,j)+2(d_i-d_j)D^1(i,j)+d_i d_j E^1(i,j)$
i' j' i' j'	$(1-d_i)(1-d_j)/4$	$2[D^0(i,j)-d_i+d_j)D^1(i,j)+d_i d_j D^2(i,j)]$
i' j' j' i'	$-(1-d_i)(1-d_j)/4$	$E(i,j)-2(d_i+d_j)D^1(i,j)-d_i d_j E^1(i,j)$
i j j' i'	$-(1-d_i)^{1/2}(1-d_j)^{1/2}/4$	$W(i,j)+d_i d_j W^1(i,j)$
i j' j i'	$-(1-d_i)^{1/2}(1-d_j)/4$	$W(i,j)-d_i d_j W^1(i,j)$
i i' i i'	$(1-d_i)/4$	$E(i)$

a. See Ref. 15

b. $i, j \leq \nu$; $i', j' > \mu$, and $\nu < t, u \leq \mu$ where ν and μ are the number of beta and alpha electrons, respectively.

Table VIII

Auxiliary Functions Appearing in
Harriman's Density Matrix Expressions

$$\prod_{i=1}^{\nu} (1+d_i^2 x) = \sum_{j=0}^{\nu} A_j x^j$$

$$\prod_{\substack{i=1 \\ i \neq k}}^{\nu} (1+d_i^2 x) = \sum_{j=0}^{\nu} A_j(k) x^j$$

$$\prod_{\substack{i=1 \\ i \neq k, m}}^{\nu} (1+d_i^2 x) = \sum_{j=0}^{\nu-2} A_j(k, m) x^j$$

$$N = \sum_{k=0}^{\nu} C_k^{s, m} (-1)^k A_k$$

$$D^0(i) = 1/N \sum_{k=0}^{\nu-1} (-1)^k C_k^{s, m} A_k(i)$$

$$D^1(i) = 1/N \sum_{k=1}^{\nu} (-1)^k C_k^{s, m} A_{k-1}(i)$$

$$D^0(i, j) = 1/N \sum_{k=0}^{\nu-2} (-1)^k C_k^{s, m} A_k(i, j)$$

$$D^1(i, j) = 1/N \sum_{k=1}^{\nu-1} (-1)^k C_k^{s, m} A_{k-1}(i, j)$$

$$D^2(i, j) = 1/N \sum_{k=2}^{\nu} (-1)^k C_k^{s, m} A_{k-2}(i, j)$$

$$W(i) = D^0(i) + D^1(i)$$

$$W(i, j) = D^0(i, j) + D^1(i, j)$$

$$W^1(i, j) = D^1(i, j) + D^2(i, j)$$

$$E(i) = D^0(i) - D^1(i)$$

$$E(i, j) = D^0(i, j) - D^1(i, j)$$

$$E^1(i, j) = D^1(i, j) - D^2(i, j)$$

$$G^0_{(i)} = G^1_{(i)} = 1/\eta_i \quad (161)$$

$$G^0_{(i,j)} = G^1_{(i,j)} = G^2_{(i,j)} = 1/\eta_i\eta_j \quad (162)$$

where

$$N \equiv \eta_1\eta_2\cdots\eta_n$$

in these equations for $G^m_{(i)}$ and $G^m_{(i,j)}$. These relations provide a check of the density matrix elements obtained by expanding the wavefunction in the Natural Orbital basis. The relations also point out the additional two-electron integrals occurring in the energy expression for Lowdin's spin-projected wavefunction. If we consider a three-electron example,

$$\Psi_{\text{Lowdin}} = Aa_1a_2b_1(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) \quad (163)$$

$$\Psi_{\text{GVB}} = Aa_1a_2b_1(\alpha\alpha\beta - \beta\alpha\alpha). \quad (164)$$

the last term in Lowdin's wavefunction is responsible for the additional two-electron integral appearing in Harriman's energy expression. This term is obtained by interchanging spin functions between unpaired Corresponding Orbitals and is noteworthy because this type of term is needed to account for the negative spin densities observed in the spectra of molecular radicals. Negative spin densities also arise in Lowdin's wavefunction because the Sasaki-Ohno coefficients do not weigh each term in equation (163) equally. Lowdin's wavefunction therefore provides a better description of the spin properties of radicals while the GVB wavefunction yields a much simpler energy expression.

THE MODIFIED SIMPLEX ALGORITHM

Now that the means by which one may obtain open shell descriptions of nominally closed shell systems have been discussed and the energy expressions for the spin projected wavefunctions have been considered, an efficient algorithm to minimize the energy of the projected wavefunction is needed to complete the ASEHF procedure. In this minimization calculation, the Natural Orbitals are frozen and only the overlap integrals between the Corresponding Orbitals are varied. To perform this task, a Simplex algorithm⁵³ was chosen.

The Simplex algorithm is a Steepest Descent technique where the descent direction is obtained in a finite difference procedure rather than calculating derivatives of the energy functional. For this reason, the Simplex algorithm is quite simple to program and a search direction may be obtained very efficiently.

The Simplex algorithm may be easily understood with the aid of Figure 1 in which a two-dimensional problem is illustrated. Upon entry to the Simplex program, the overlap integrals have been estimated and the energy expression has been evaluated at this point, A, in the N-dimensional space. Since the overlap integrals are bounded between zero and one, we are dealing with a small portion of this space. Each of the N overlap integrals is then varied individually by a specified step length and the energy expression is evaluated at these N points. This procedure generates the points B and C in Figure 1. The N+1 sided figure defined by these points in the N-dimensional space is

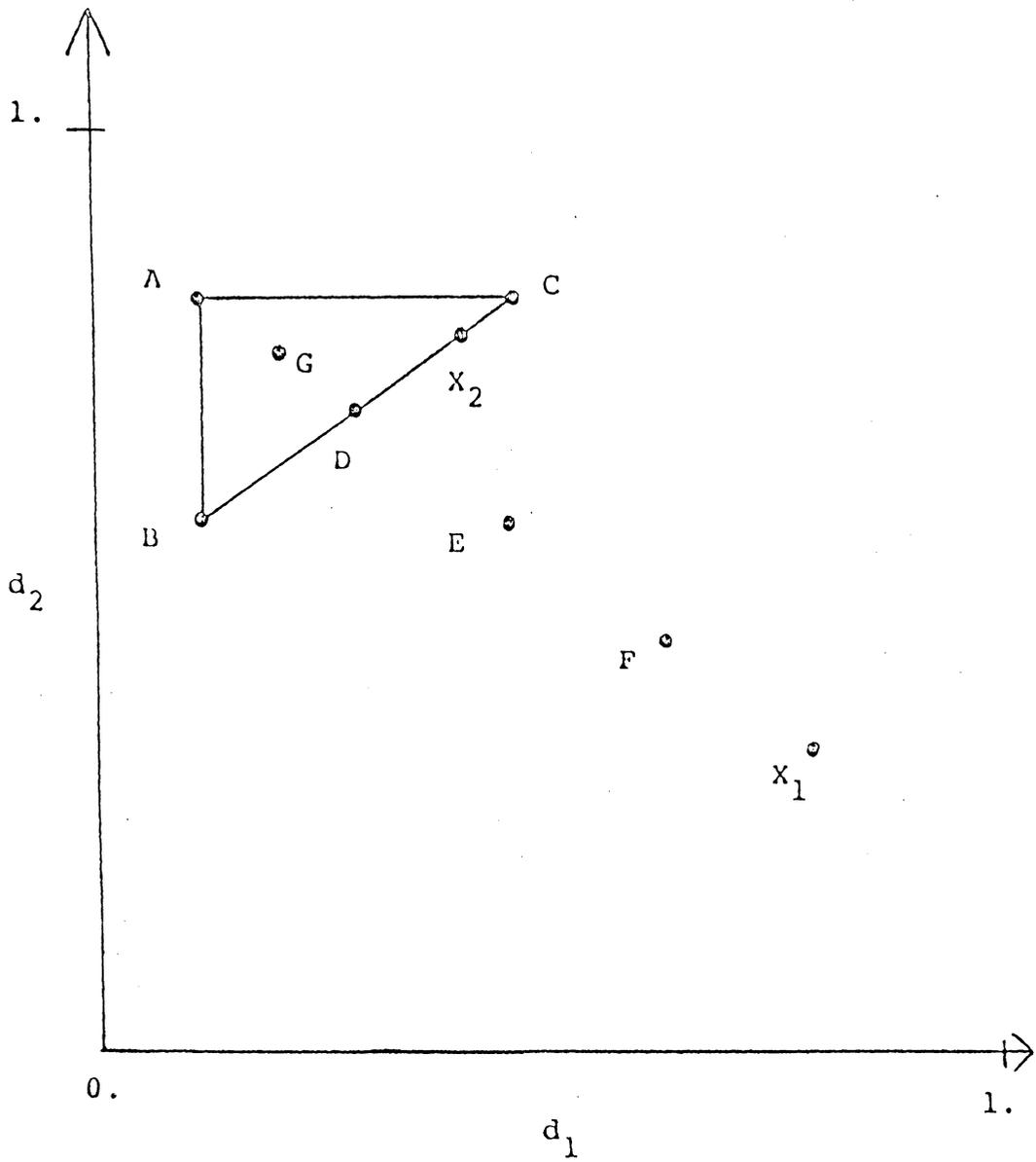


Figure 1. Modified Simplex Algorithm.

termed a Simplex. The point, at which the highest value of the energy expression was obtained, is identified. Let A represent this point. The centroid, D, of the remaining N points is then calculated. The line AD is then reflected through the centroid and point E is obtained. The energy expression is evaluated at point E and if this value is lower than the minimum obtained when the Simplex was constructed, this direction of search is extended to point F. If F yields a lower value of the energy than E, a new Simplex is constructed using B, C and F. If not, the new Simplex is defined by B, C and E and the procedure is repeated. On the other hand, if point E does not represent a lower energy state, the energy expression is evaluated at point G. A Simplex defined by B, C and G is then obtained if G represents an improved function. If not, the whole Simplex is contracted about the minimum of the original Simplex and the process of reflection or contraction is repeated until the energy converges.

As outlined above, the Simplex algorithm did not always converge to a local minimum. Very often when convergence was attained, this procedure lacked the desired efficiency. Two simple extensions of the method were then attempted. The first modification allowed for continued extensions, X_1 , in the search direction defined by AF, if point F yielded a new minimum of the energy expression. The second modification replaced the centroid D with an energy weighted centroid X_2 . These modifications improved the efficiency of the calculation and, significantly, a local minimum of the energy expression was attained by this procedure where the unmodified algorithm failed to do so.

A program was developed to perform this modified Simplex procedure. The program is capable of minimizing either Harriman's equations or the GVB energy expression obtained in the preceding chapter. A list of one and two-electron integrals between the Natural Orbitals is required as input to this program. Once this list has been generated, the efficiency of this algorithm depends only on the number of overlap integrals present and on the number of these integrals varied in the minimization procedure.

ASEHF CALCULATIONS

The three steps required to perform an ASEHF calculation have been outlined. All that remains is to test this procedure. Mayer and Kerterz⁵⁴ have published a series of spin extended pi-calculations employing Lowdin's projection operator, and the same series of compounds were studied in the ASEHF framework. The geometries of the molecules and the semi-empirical parameters were chosen to coincide with those of Mayer and Kerterz.⁵⁴ The results of these calculations are presented in Table IX. The GAMO procedure was used to obtain the Natural Orbitals in all of the calculations with the exception of the s-Triazine study. In this case, the RHF wavefunction possessed a triplet instability and the open shell wavefunction generated by the stability program was used to initiate a UHF calculation.

The variational procedure employed in the ASEHF calculations for these systems reproduce the results obtained in full variational calculations of Mayer and Kertesz⁵⁴ to within the uncertainty involved in comparing these sets of calculations. This result is not terribly surprising when one considers the limited size of the basis sets employed in these calculations. These results lead one to conclude that little is to be gained by employing the more involved procedure of Mayer and Kertesz⁵⁴ in this type of limited basis set pi-calculations.

The results of the pi-calculations were encouraging, so the ASEHF method was applied to the study of molecular Fluorine and Ozone.

Table IX

Ground State Correlation Energies (eV)

for Pi-Electron Systems

	$E_{\text{SEHF}} - E_{\text{RHF}}$		$E_{\text{SEHF}} - E_{\text{PUHF}}$	
	<u>Present</u> <u>Approximation</u>	<u>Mayer-</u> <u>Kertesz</u> ⁵⁴	<u>Present</u> <u>Approximation</u>	<u>Mayer-</u> <u>Kertesz</u> ⁵⁴
t-butadiene	-1.245	-1.245	-0.322	-0.323
hexatriene	-1.671	-1.671	-0.293	-0.294
octatetraene	-2.045	-2.040	-0.269	-0.276
benzene	-1.220	-1.219	-1.009	-1.002
s-triazine	-1.568	-1.571	-0.635	-0.647

Each of these systems cannot be adequately handled within the framework of the RHF theory. F_2 is predicted to be unbound in RHF calculations, as the minimum of the RHF potential surface lies 1.37 eV above the RHF energy of the atoms.⁵⁵⁻⁵⁸ RHF studies of Ozone predict a triplet ground state, while experimental results indicate that the ground state is actually a singlet.⁵⁹

For the Ozone calculations, Dunning's⁶⁰ (9s5p/4s2p) Gaussian basis set was employed at the equilibrium geometry ($R_{O-O} = 2.42$ AU and $\theta = 116.8^\circ$). The results of the ASEHF calculations are presented in Table X along with a set of orbital optimized GVB calculations and Configuration Interaction results obtained by Hay, Dunning and Goddard.²² The ASEHF offers significant improvement over the RHF calculations, but does not compare favorably with the full variational calculations, which in turn are not comparable to the Configuration Interaction results. However, the ASEHF results do provide a good qualitative description of the molecule as the ground state is correctly predicted to be a singlet. Moreover, GVB calculations indicate that Ozone is best described as a diradical and this character is also evident in the ASEHF results.

For systems of this size, the Simplex algorithm proved to be very time-consuming when applied to Harriman's energy expression, but the GVB energy expressions were minimized very rapidly. For Ozone, the GVB-Simplex calculation required 20 seconds of CPU time while as much as 30 minutes were required to minimize Harriman's energy expressions. This difficulty has been noted in traditional AMO calcula-

Table X

Comparison of the Energies for the Lowest 1A_1 and 3B_2 States of Ozone

Calculation	No. Conf.	Energy*		Energy*		ΔE (eV)	
		1A_1	No. Conf.	3B_2		$^1A_1 - ^3B_2$	
				$S_z=0$	$S_z=1$	$S_z=0$	$S_z=1$
RHF	1	-.2072	1	-.2867 ^a	---	-2.17	---
UHF		-.3035 ^b	1	---	-.2930	---	.28
SPUHF-L	11	-.3189	--	.2900	-.2965	.79	.61
ASEHF-L ^c	--	-.3277	--	-.2902	-.2989	1.02	.78
SPUHF-G	--	-.3110	--	---	---	---	---
ASEHF-G ^c	--	-.3215	--	---	---	---	---
GVB(1) ^a	2	-.3117	1	-.2867	---	.68	---
GVB(3-PP) ^a	8	-.3786	4	-.3539	---	.67	---
POL-CI ^a	783	-.5302	817	-.4767	---	1.46	---

*These energies must be added to -224.0(h) to obtain the total energy.

a. See ref. 22.

b. Mixed symmetry configuration.

c. Only the four smallest overlap integrals were varied.

tions by Pauncz and indicates that only the GVB wavefunction can be efficiently applied to larger systems.

Dunning's (9s5p/4s2p) contracted Gaussian basis was also employed in the F_2 calculations, and the equilibrium internuclear separation of 2.6 atomic units was employed in this study. Atomic Fluorine calculations in the ASEHF framework were also performed again using the (9s5p/4s2p) basis. The ASEHF calculations produced disappointing results as the energy of F_2 was again too high. A set of (9s5p/4s2p) orbitals was then expanded about the midpoint of the Fluorine-Fluorine bond and the ASEHF calculations were repeated. This calculation resulted in a well depth of .34 ev and .30 ev for the ASEHF-L and ASEHF-G wavefunctions respectively. The atomic ASEHF calculation was then repeated using a 9s5p uncontracted basis in order to insure that expanding a set of orbitals about the midpoint of the F_2 bond did not bias the results.

The results of the ASEHF calculations are presented in Table XI. In Table XII the depth of the F_2 potential well obtained from these and MC-SCF calculations are presented along with the experimental quantity. These results lead to the conclusion that the ASEHF method provides an acceptable description of bond dissociation, but they do not provide quantitative information. The basis set employed in the ASEHF calculations is not comparable to the extensive STO basis employed by Das and Wahl and, therefore, the ASEHF results compare quite favorably to the ODC results quoted in Table XII.

Table XI

Comparisons of the Energies* Obtained for the Ground
States of Molecular and Atomic Fluorine

	<u>F₂^a</u>	<u>F₂^b</u>	<u>F+F^a</u>	<u>F+F^c</u>
RHF	--	-.7328	--	--
UHF	-.7222	-.7429	-.7900	-.7948
SPUHF-L	-.7656	-.7823	-.7912	-.7958
ASEHF-L	-.7873	-.8110	-.7918	-.7964
SPUHF-G	--	-.7804	--	--
ASEHF-G	--	-.8075	--	--

* These energies must be added to -198 (A.U.) to obtain the total energy of the system

a. (9s5p/4s2p) atom centered basis

b. (9s5p/4s2p) atom centered basis + (9s5p/4s2p) bond centered basis

c. 9s5p uncontracted basis

Table XII

Experimental and Calculated^a Values of D_e for F_2

<u>Method</u>	<u>D_e</u>
RHF	-1.69 eV
UHF	-1.41 eV
SPUHF-G	- .41 eV
SPUHF-L	- .37 eV
ASEHF-G	.30 eV
ASEHF-L	.40 eV
ODC ^b	.54 eV
OVC ^c	.95 eV
Final ^d	1.67 eV
Exp.	1.68 eV

a) ODC, OVC, Final, and Exp. results obtained from Das and Wahl, references 52, 53, 54, and 55

b) Two configuration MC-SCF calculation

c) Six configuration MC-SCF calculation

d) 100 configuration MC-SCF calculation

Finally, it should be pointed out that ASEHF calculations may also be used to generate electron density maps in an efficient manner.

The electron density at any point in space $R_{(\bar{r})}^T$, may be obtained from the following equation for a system composed of ν beta electrons and μ alpha electrons

$$R_A^T(\bar{r}) = \sum_{i=1}^{\nu} \{ \gamma_i \psi_i(\bar{r}) \psi_i^\alpha(\bar{r}) + \gamma_i \psi_i(\bar{r}) \psi_i^*(\bar{r}) \} + \sum_{j=\nu+1}^{\mu} \psi_j(\bar{r}) \psi_j^*(\bar{r}) \quad (165)$$

where ψ_i are the Natural Orbitals and γ_i are the optimum Occupation Numbers. This facet of ASEHF theory was examined by performing both ASEHF and RHF calculations on Li_2 at an internuclear separation of 5.25 atomic units. Dunning's (9s5p/4s2p) basis was employed and the electron density maps resulting from these two calculations were compared. The RHF electron density map may also be efficiently obtained as

$$R_C^T(\bar{r}) = 2 \sum_{i=1}^{\nu} \psi_i(\bar{r}) \psi_i^*(\bar{r}) + \sum_{j=\nu+1}^{\mu} \psi_j(\bar{r}) \psi_j^*(\bar{r}). \quad (166)$$

In order to compare these two methods, a difference density was defined,

$$R_D^T = R_A^T - R_C^T \quad (167)$$

and the plot of this function is shown in Figure 2. The two peaks in Figure 2 are centered at the Lithium nuclei and are a result of the increased S electron density obtained in the ASEHF calculation. The depressed region in the figure is a result of the increased pi-electron density obtained in the RHF calculations.

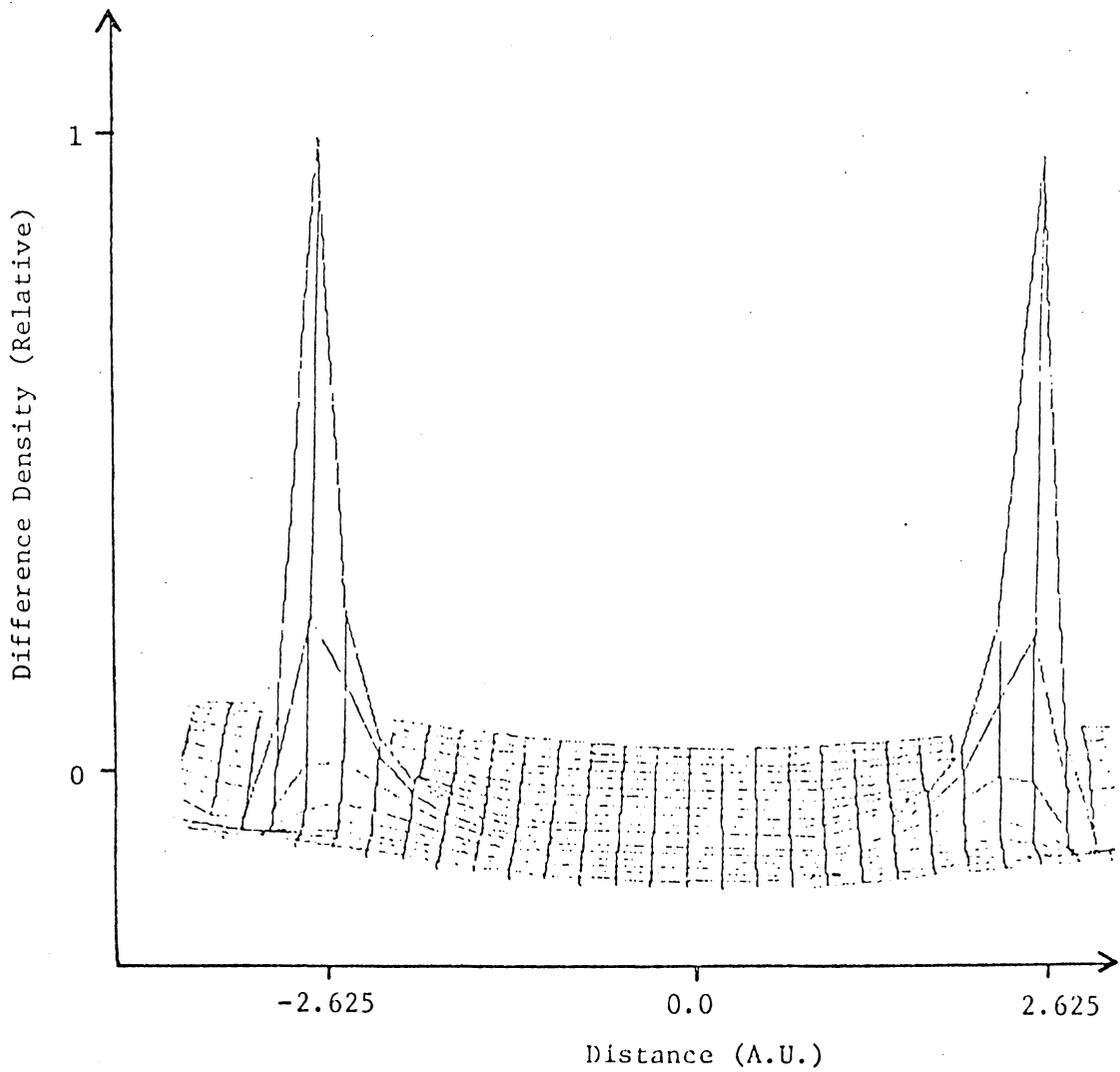


Figure 2. - Difference Density Plot of Li_2

We can make use of the fact that $R_c/2$ is a projection operator (when $v=\mu$) and define two comparative densities,

$$R_1 = (R_c/2)R_A(R_c/2) \quad (168)$$

and

$$R_2 = (1-R_c/2)R_A(1-R_c/2). \quad (169)$$

The first equation produces the electron density which results from these orbitals present in both the RHF and ASEHF wavefunction, while R_2 represents the electron density resulting from orbitals present only in the ASEHF wavefunction. A plot of R_2 generated from the Li_2 calculations is shown in Figure 3. Note that R_2 is positive everywhere, as it must be, and no pi-electron density is indicated.

These electron densities were obtained by modifying a program originally written by Schug and Lengsfeld to calculate ESR hyperfine coupling constants in conjunction with the Polyatom system of programs. The plots were produced by a program developed by Brent Lander of the Physics Department of Virginia Polytechnic Institute and State University.

In all of these calculations, the Natural Orbitals were found to be symmetry adapted. With the exception of the Ozone and the C_2 calculations, the value of the overlap integrals were very close to one. The expansion of the GVB wavefunction presented in Equation (120) may therefore be viewed as a perturbation series,

$$C_0 > C_1, C_2, C_3 > C_4, C_5, C_6 > C_7.$$

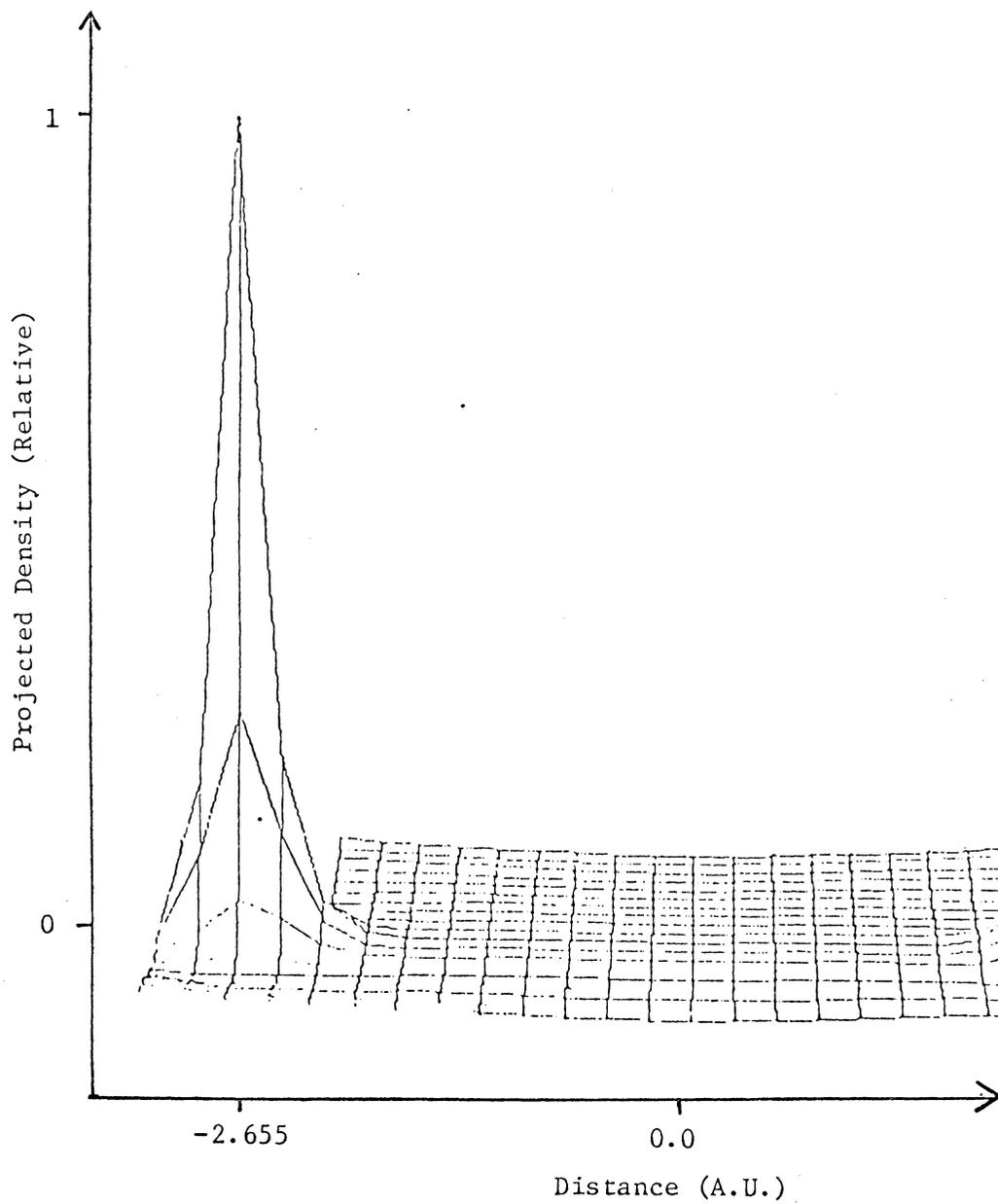


Figure 3. The Projected Density Plot of Li_2 (Symmetric).

This series may be used as a basis for understanding the success or failure of the Woodward-Hoffman Rules.⁶¹ If the first term in this series is indeed dominant, the Woodward-Hoffman Rules would be expected to provide a useful aid in the understanding of the spontaneous reactions of the system. If two or more terms in this series are of nearly equal weight, a breakdown of the Woodward-Hoffman Rules would be expected.

CONCLUSION

The ASEHF method provides an effective means of obtaining a semi-quantitative description of fundamental chemical processes such as bond dissociation and the ordering of electronic energy states. Most importantly, ASEHF theory is capable of describing the electron reorganization accompanying bond formation and bond dissociation reactions and can therefore be employed to characterize the potential energy surface of a reaction. Moreover, such seemingly diverse concepts as the Woodward-Hoffman Rules and the localized electron pair description of molecular systems may be accommodated in this method. Perhaps the most significant contribution which this method provides is the ability to efficiently handle larger systems, especially if used in conjunction with recently developed pseudo-potential methods.

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APPROXIMATE SPIN EXTENDED HARTREE-FOCK THEORY

by

Byron H. Lengsfeld III

(ABSTRACT)

An approximate spin-extended method is developed in which the Occupation Numbers of the Natural Orbitals of Charge are varied but the orbitals themselves are frozen. A number of techniques for obtaining appropriate Natural Orbitals of Charge are presented and these techniques are employed in semi-empirical and Ab-Initio studies. The molecules chosen for the Ab-Initio study, O_3 , F_2 and C_2 , are particularly interesting as Restricted Hartree-Fock (RHF) theory fails to provide an adequate description of these systems at their equilibrium geometries. The results of this work indicate that Approximate Spin-Extended Hartree-Fock (ASEHF) theory provides a qualitatively acceptable description of bond dissociation, correctly predicts the symmetry of molecular states where RHF theory fails, and provides an efficient means for obtaining a significant amount of correlation energy in molecular calculations. Moreover, when the Generalized Valence Bond form of the ASEHF wavefunction is employed, a particularly useful description of the molecule is obtained. Specifically, the success or failure of the Woodward-Hoffman becomes transparent when the system is analyzed in terms of this wavefunction.