

SPIN PROJECTION OF SEMI-EMPIRICAL AND AB INITIO
UNRESTRICTED HARTREE-FOCK WAVEFUNCTIONS

by

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V. INTRODUCTION

The accurate description of molecular orbitals and molecular interactions has been a problem confronting chemists and physicists for many years. The problem would be straightforward if the electronic Schrödinger equation could be solved exactly. However, an exact solution of this equation is possible only for the hydrogen atom. Consequently, various approximation methods have been invoked. One of the most widely used methods is the variational theorem.

The variational theorem provides approximate solutions to the electronic Schrödinger equation,

$$\mathcal{H}_e \Psi_e = E_e \Psi_e \quad (1)$$

where \mathcal{H}_e is the electronic Hamiltonian operator, Ψ_e is an antisymmetrized product of molecular spin-orbitals, and E_e is the electronic energy. The spatial part of the spin orbitals, or molecular orbitals, are constructed as normalized linear combinations of atomic orbitals, ϕ_μ ,

$$\phi_{\mu i} = \sum_{\mu} c_{\mu i} \phi_{\mu} \quad (2)$$

where the coefficients, $c_{\mu i}$, are allowed to vary in order to minimize the electronic energy of the molecule. However, because the variational theorem is an approximate technique, the expectation values of the energies derived from this method will always be

higher than the true energies of the ground state molecules.

A closed shell molecule is a system in which there is an equal number of spin up (α) and spin down (β) electrons and all orbitals are either empty or doubly occupied. The molecular orbitals for the α -electrons are the same as those for the β -electrons. Since the α - and β -wavefunctions are equal, the Hartree-Fock operator for the α -electrons is equal to the Hartree-Fock operator for the β -electrons. This is called a restricted calculation; i.e., the α - and β -wavefunctions are forced to be equal. This condition guarantees that the electronic wavefunction, Ψ , is an eigenfunction of the total spin operator, S^2 ,

$$S^2 \Psi = s(s + 1) \Psi . \quad (3)$$

An open shell molecule is a system in which either there is an unequal number of α - and β -electrons or there is an equal number of α - and β -electrons but some occupied orbitals are not doubly occupied. The treatment of such a system by a restricted calculation does not result in good approximations to the molecular energies; much closer values to the true energy are obtained when the α - and β -electrons are treated separately in an unrestricted calculation. In general, the orbitals for the α -electrons are not equal to the orbitals for the β -electrons. Unrestricted Hartree-Fock (UHF) theory or the method of different orbitals for different spins (DODS) provides much better approximations to the true energies than a restricted calculation.

Because UHF theory produces two different sets of molecular

orbitals, one set for the α - and one set for the β -electrons, the resultant single determinant wavefunction,

$$\Psi = \left| \begin{array}{cccc} \phi_1^\alpha & \phi_1^\beta & \phi_2^\alpha & \phi_2^\beta & \cdots & \phi_i^\alpha & \phi_i^\beta & \cdots \end{array} \right| \quad (4)$$

is not guaranteed to be a state of pure spin multiplicity; that is,

$$S^2 \Psi \neq s(s+1) \Psi. \quad (5)$$

Since $[\mathcal{H}, S^2] = 0$, the correct electronic states will also be eigenfunctions of S^2 . This requirement can be satisfied by projecting from the single determinant various pure spin eigenfunctions.

One method of obtaining such wavefunctions is through the application of spin projection operators. Löwdin¹ has shown that it is a relatively simple procedure to construct spin projection operators which will project pure spin wavefunctions from wavefunctions with mixed multiplicity. Two methods of applying the spin projection operators have been explored, the Harriman-type UHF and the spin-projected extended Hartree-Fock (EHF) methods. Since the following chapters deal exclusively with the former method, the latter method will be briefly outlined, and the results obtained using the two methods will be briefly compared.

In the spin projected EHF method developed by Mayer,² single determinant wavefunctions are constructed using the DODS formalism and spin projected. Such a wavefunction is used as a trial function in the variational procedure. The one-electron orbitals are then optimized to obtain a minimum energy for the resulting projected wavefunction.

The spin projected UHF calculation differs from the EHF

method in that the energy minimization procedure is performed on the unprojected DODS wavefunction. Spin projection of the unprojected wavefunction follows the minimization procedure.

First inspection of the spin-projected EHF and UHF plus spin projection methods leads one to assume that the EHF method is superior to the UHF method since the projected pure spin state is dealt with in the former method. However, Mayer and Kertesz³ have examined the results of both methods using the Pariser-Pople-Parr (PPP) π -electron approximations for polyenes with two to 38 carbon atoms with surprising results. The EHF method is superior to the UHF method for the smallest systems up to approximately 15 carbon atoms; however, as the number of atoms increases further, the energy differences between the two methods decrease rapidly. Mayer concludes that, for larger systems, it is sufficient to perform UHF calculations with subsequent spin projection. From the standpoint of computational time involved, the UHF method is far superior.

The work described below is concerned exclusively with the UHF plus spin projection method. The electronic spectra of naphthalene, anthracene, naphthacene and pentacene were calculated using the PPP approximations and both UHF and configurational interaction (CI) techniques. The results of both techniques were compared to experimentally determined spectra when data were available. There was reasonable agreement between the CI and projected UHF results. While the CI calculations generally produced lower energies for the triplet states than the UHF calculations, the spectra from the UHF

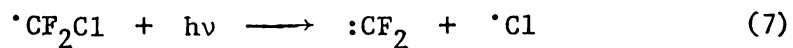
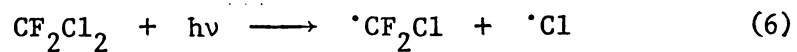
calculations were in somewhat better agreement with experiment. Anomalies encountered with degeneracies and the presence of open shell ground states are also discussed.

Monohomocyclooctatetraene anion radical (MHCOT) was studied using a DODS wavefunction with spin projection and the all-valence electron INDO approximations. The theoretical molecular geometry was varied until the experimental hyperfine coupling constants matched hyperfine constants obtained from using both projected and unprojected UHF wavefunctions. The two types of calculations resulted in slightly different energies and geometries with the projected calculations giving a higher energy for the doublet state; essentially no differences were noted in the bond orders obtained from the two types of calculations. The geometry from the projected calculations was a somewhat more strained conformation than the geometry from the unprojected calculation.

Ab initio UHF calculations with spin projection were performed on $H_2O(+)$ using the POLYATOM (Version 2)⁴ system of programs. The purpose of the study was to compare the energies of pure spin states from ab initio multi-configurational self-consistent field with CI (MCSCF/CI)⁵ with those from spin projection. The MCSCF/CI calculations are superior to the UHF plus spin projection calculations. This result will always be observed when the UHF wavefunction is very close to a pure spin state before spin projection.

The dissociation of CF_2O was studied using ab initio wavefunctions. The molecule is of possible importance in the atmos-

pheric reaction scheme since it is a possible product from the dissociation of dichlorodifluoromethane,



The energies of the unprojected wavefunctions of CF_2O were examined along with those for the dissociated CF_2 and O fragments.

VI. HARTREE-FOCK THEORY

Since the work described below deals with spin projected Hartree-Fock wavefunctions and various approximations for terms in the Hartree-Fock equations, it is advantageous to review Hartree-Fock theory at this point.⁶

The nonrelativistic Hamiltonian, in atomic units, is

$$\begin{aligned} \mathcal{H} = & -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i>j} \frac{1}{r_{ij}} - \sum_{\mu,i} \frac{Z_\mu}{r_{\mu i}} - \frac{1}{2} \sum_\mu \frac{\nabla_\mu^2}{m_\mu} \\ & + \sum_{\mu>\nu} \frac{Z_\mu Z_\nu}{r_{\mu\nu}} \end{aligned} \quad (9)$$

where i and j denote electrons and μ and ν denote nuclei. When the Born-Oppenheimer approximation⁷ is applied, the fourth term describing the translational motion of the nuclei is ignored, and the fifth term, the nuclear repulsion energy operator, V_n , becomes a constant value. In other words, electronic states are examined in the "frozen-nuclei" approximation. The electronic Hamiltonian operator then reduces to

$$\mathcal{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i>j} \frac{1}{r_{ij}} - \sum_{\mu,i} \frac{Z_\mu}{r_{\mu i}} + V_n. \quad (10)$$

The electronic energy for an unrestricted wavefunction can be expressed as

$$\begin{aligned}
E_e = & \sum_{r=1}^{B_{\text{occ}}} (T_r + V_r) + \frac{1}{2} \left(\sum_{r,s=1}^{B_{\text{occ}}} J_{rs} - \sum_{r,s=1}^{B_{\text{occ}}^{\alpha}} K_{rs}^{\alpha} \right. \\
& \left. - \sum_{r,s=1}^{B_{\text{occ}}^{\beta}} K_{rs}^{\beta} \right) \quad (11)
\end{aligned}$$

where B_{occ} is the total number of occupied orbitals, B_{occ}^{α} is the number of occupied α -molecular orbitals and B_{occ}^{β} is the number of occupied β -molecular orbitals. Letting r and s denote molecular orbitals, the first summation of one-electron terms is comprised of the kinetic and potential energy integrals, T_r and V_r , respectively,

$$T_r = \langle r(i) | -\frac{1}{2} \nabla_i^2 | r(i) \rangle \quad (12)$$

$$V_r = \langle r(i) | -\sum_{\mu} \frac{Z_{\mu}}{r_{\mu i}} | r(i) \rangle . \quad (13)$$

The two-electron integrals are described in the second term by the coulomb, J_{rs} , and the exchange integrals, K_{rs} ,

$$J_{rs} = \langle r(i) s(j) | \frac{1}{r_{ij}} | r(i) s(j) \rangle \quad (14)$$

$$K_{rs} = \langle r(i) s(j) | \frac{1}{r_{ij}} | s(i) r(j) \rangle . \quad (15)$$

The molecular orbitals are described in terms of linear combinations of atomic orbitals (LCAO) with subscripts m , n , p , and q ,

$$| r^{\alpha}(i) \rangle = \sum_m c_{mr}^{\alpha} | m(i) \rangle \quad (16)$$

$$| r^\beta(i) \rangle = \sum_m c_{mr}^\beta | m(i) \rangle . \quad (17)$$

The distribution of the α - and β -electrons in the molecule is described by the α - and β -charge density and bond order matrices, P^α and P^β , with elements,

$$P_{mn}^\alpha = \sum_r^{B_{occ}^\alpha} c_{mr}^\alpha c_{nr}^\alpha \quad (18)$$

$$P_{mn}^\beta = \sum_r^{B_{occ}^\beta} c_{mr}^\beta c_{nr}^\beta . \quad (19)$$

The total density matrix, P , is the sum of the α - and β -density matrices,

$$P_{mn} = P_{mn}^\alpha + P_{mn}^\beta \quad (20)$$

The net unpaired electron density in the molecule is described by the spin density matrix, P^Z ,

$$P_{mn}^Z = P_{mn}^\alpha - P_{mn}^\beta . \quad (21)$$

The electronic energy can now be written in terms of the density matrices and integrals over atomic orbitals,

$$E = \sum_{mn} P_{mn} (T_{mn} + V_{mn}) + \frac{1}{2} \sum_{mnpq} (P_{mn} P_{pq} - P_{mp}^\alpha P_{nq}^\alpha - P_{mp}^\beta P_{nq}^\beta) \langle m(i) p(j) | \frac{1}{r_{ij}} | n(i) q(j) \rangle . \quad (22)$$

The variational principle is applied by using Lagrange's method of undetermined multipliers to insure that the orbitals are orthonormal. An extremum is sought in

$$\delta [E - \sum_{r,s=1}^B \lambda_{rs} (S_{rs} - S_{sr})] = 0, \quad (23)$$

where S_{rs} are the overlap integrals,

$$S_{rs} = \langle r(i) | s(i) \rangle, \quad (24)$$

and λ_{rs} are the undetermined multipliers. Equation 23 contains $N(N+1)/2$ constraints; introduction of variations in the orbitals $|r(i)\rangle$ leads directly to the set of Hartree-Fock equations,

$$F^\alpha |r(i)\rangle = \sum_{s=1}^{B_{\text{occ}}^\alpha} \lambda_{rs} |s(i)\rangle \quad (25)$$

$$F^\beta |r(i)\rangle = \sum_{s=1}^{B_{\text{occ}}^\beta} \lambda_{rs} |s(i)\rangle \quad (26)$$

where F^α is the one-electron Fock operator for the α -electrons and F^β is the one-electron Fock operator for the β -electrons. The Fock operator may be expanded as

$$F^\alpha = T + V + \sum_{s=1}^{B_{\text{occ}}^\alpha} (J_s - K_s^\alpha) + \sum_{s=1}^{B_{\text{occ}}^\beta} J_s^\beta \quad (27)$$

$$F^\beta = T + V + \sum_{s=1}^{B_{\text{occ}}^\beta} (J_s - K_s^\beta) + \sum_{s=1}^{B_{\text{occ}}^\alpha} J_s^\alpha \quad (28)$$

and

$$T | r(i) \rangle = -\frac{1}{2} \nabla_i^2 | r(i) \rangle \quad (29)$$

$$V | r(i) \rangle = - \sum_{\mu} \frac{Z_{\mu}}{r_{\mu i}} | r(i) \rangle \quad (30)$$

$$J_s | r(i) \rangle = \langle s(j) | \frac{1}{r_{ij}} | s(j) r(i) \rangle \quad (31)$$

$$K_s | r(i) \rangle = \langle s(j) | \frac{1}{r_{ij}} | r(j) s(i) \rangle . \quad (32)$$

A unitary transformation of the Hartree-Fock equations can be carried out to bring the matrix of Lagrangian multipliers into diagonal form without affecting the operators F^α or F^β

$$F^\alpha | r(i) \rangle = \lambda_r^\alpha | r(i) \rangle \quad (33)$$

$$F^\beta | r(i) \rangle = \lambda_r^\beta | r(i) \rangle . \quad (34)$$

The molecular orbitals are eigenfunctions of the Fock operator, and the eigenvalues are

$$\lambda_r^\alpha = T_r^\alpha + V_r^\alpha + \sum_{s=1}^{B_{\text{occ}}^\alpha} (J_{rs} - K_{rs}^\alpha) + \sum_{s=1}^{B_{\text{occ}}^\beta} J_{rs}^\beta \quad (35)$$

$$\lambda_r^\beta = T_r^\beta + V_r^\beta + \sum_{s=1}^{B_{\text{occ}}^\beta} (J_{rs} - K_{rs}^\beta) + \sum_{s=1}^{B_{\text{occ}}^\alpha} J_{rs}^\alpha . \quad (36)$$

The electronic energy is then expressed as

$$\begin{aligned}
 E = & \sum_{r=1}^{B_{\text{occ}}^{\alpha}} \lambda_{rr}^{\alpha} + \sum_{r=1}^{B_{\text{occ}}^{\beta}} \lambda_{rr}^{\beta} - \sum_{r,s=1}^{B_{\text{occ}}^{\alpha}} (J_{rs} - K_{rs}^{\alpha}) - \\
 & \sum_{r,s=1}^{B_{\text{occ}}^{\beta}} (J_{rs} - K_{rs}^{\beta}) + \sum_{s=1}^{B_{\text{occ}}^{\alpha}} J_s^{\alpha} + \sum_{s=1}^{B_{\text{occ}}^{\beta}} J_s^{\beta} . \quad (37)
 \end{aligned}$$

When the LCAO molecular orbitals are used, two sets of coupled linear equations result,

$$\sum_{n=1}^{B_{\text{occ}}^{\alpha}} (F_{mn}^{\alpha} - \lambda_r^{\alpha} S_{mn}) c_{nk}^{\alpha} = 0 \quad (38)$$

$$\sum_{n=1}^{B_{\text{occ}}^{\beta}} (F_{mn}^{\beta} - \lambda_r^{\beta} S_{mn}) c_{nk}^{\beta} = 0 . \quad (39)$$

Equations 38 and 39 are solved iteratively to obtain the SCF molecular orbital coefficients. The two Fock Hamiltonian matrices have elements given by

$$\begin{aligned}
 F_{mn}^{\alpha} = & T_{mn} + V_{mn} + \sum_{p,q} [P_{pq} \langle m(i) p(j) | \frac{1}{r_{ij}} | n(i) q(j) \rangle \\
 & - P_{pq}^{\alpha} \langle m(i) p(j) | \frac{1}{r_{ij}} | q(i) n(j) \rangle] . \quad (40)
 \end{aligned}$$

$$F_{mn}^{\beta} = T_{mn} + V_{mn} + \sum_{p,q} [P_{pq} \langle m(i) p(j) | \frac{1}{r_{ij}} | n(i) q(j) \rangle$$

$$- P_{pq}^{\beta} \langle m(i) p(j) | \frac{1}{r_{ij}} | q(i) n(j) \rangle] . \quad (41)$$

The molecular orbital expansion coefficients are obtained by using a self-consistent field (SCF) procedure in the framework of the Hartree-Fock theory. An initial set of basis functions is assumed and the required integrals are calculated. The two Fock matrices are then constructed, one for α -electrons and one for β -electrons, and diagonalized yielding a new set of expansion coefficients. The electronic energy is then calculated using a new set of coefficients; if it differs from the energy using the previous set of coefficients by an amount greater than an accuracy threshold, the new coefficients are used to form a new Fock matrix in an iterative process. The procedure is repeated until the accuracy threshold is satisfied; i.e., self-consistency has been achieved.

VII. SPIN PROJECTION OPERATORS AND THE UNRESTRICTED HARTREE-FOCK WAVEFUNCTION

Unrestricted Hartree-Fock (UHF) theory⁸ is the simplest available method that allows the orbital rearrangement that is necessary to calculate excitation and ionization energies.⁹ However, the open-shell wavefunctions that result from application of the UHF theory are not pure spin states. It is therefore necessary to obtain pure spin states by using Löwdin's¹ spin projection operators. Harriman and coworkers¹⁰ have provided the basic equations for calculating the reduced one- and two-particle density matrices. Corrections to those expressions were later noted by Phillips and Schug.¹¹ The equations will be briefly reviewed, retaining the notation of the latter workers.

The nonrelativistic spin-free Hamiltonian can always be separated into one- and two-electron terms,

$$\mathcal{H} = \sum_i^N [T_i + V_i] + \sum_{i>j}^N \frac{1}{r_{ij}} \quad (42)$$

where N is the number of electrons in the molecule. The electronic energy can therefore be calculated from a knowledge of the first- and second-order charge density matrices. If r_i refers to spatial coordinates of the i^{th} electron, ζ_i the spin coordinates, and x_i the combined space and spin coordinates, then the second-order charge density matrix can be expressed as

$$\Gamma(r_1, r_2; r_1', r_2') = \frac{N!}{2! (N-2)!} \int \phi(x_1, x_2, \dots, x_N) \times \phi^*(x_1', x_2', \dots, x_N) d\zeta_1 d\zeta_2 dx_3 \dots dx_N \quad (43)$$

where $\phi(x_1, x_2, \dots, x_N)$ is any molecular wavefunction. If an additional integration is performed over the spatial coordinates of the second electron, the first-order charge density matrix results,

$$\gamma(r_1; r_1') = \int \frac{2}{N-1} \Gamma(r_1, r_2; r_1', r_2) dr_2. \quad (44)$$

The expressions for spin projection are simplified if the charge density matrices are expressed in terms of the natural orbitals, $\{\phi\}$, which result when the density matrices are diagonalized. Letting B denote the number of basis functions, the first-order matrix is

$$\gamma(r_1; r_1') = \sum_{r=1}^B \gamma_r \phi_r(r_1) \phi_r^*(r_1') \quad (45)$$

while the second-order matrix is

$$\Gamma(r_1, r_2; r_1', r_2') = \sum_{r,s,t,v=1}^B \Gamma_{rstv} \phi_r(r_1) \phi_s(r_2) \times \phi_t^*(r_1') \phi_v^*(r_2'). \quad (46)$$

The energy, in terms of the natural orbitals, is then expressed as

$$E = \sum_{r=1}^B \gamma_r \langle \phi_r | T_i + V_i | \phi_r \rangle + \sum_{r,s,t,v=1}^B \Gamma_{rstv} \langle \phi_r \phi_s | \frac{1}{r_{ij}} | \phi_t \phi_v \rangle. \quad (47)$$

The coefficients that describe the charge density matrices in terms of the natural orbitals are γ_r and Γ_{rstv} . More specificity of the coefficients is gained by using the superscripts u and p to denote the unprojected and projected states, respectively.

The energy expression is most conveniently written in terms of natural orbitals, because only the numerical values of the coefficients multiplying the integrals, γ_r and Γ_{rstv} , change between the projected and unprojected states. The integrals over the natural orbitals remain constant.

A set of orbitals that facilitates the calculation of the numerical values of the coefficients multiplying the one- and two-electron natural orbitals is the set of corresponding orbitals, first introduced by Amos and Hall.¹² The alpha corresponding orbitals, $\{a\}$, are the eigenvectors of the product of the alpha and beta first-order charge density matrices, $P^\alpha P^\beta P^\alpha$, while the beta corresponding orbitals, $\{b\}$, are the eigenvectors of $P^\beta P^\alpha P^\beta$. The nonzero eigenvalues of the product matrices are identical and equal to the squares of the overlap integrals of the corresponding orbitals, d_r^2 . The overlap matrix, d , between the alpha and beta corresponding orbitals, is also in diagonal form,

$$\langle a_r | b_s \rangle = \langle a_s | b_r \rangle = d_r \delta_{rs} \quad (48)$$

$$\langle a_r | a_s \rangle = \langle b_r | b_s \rangle = \delta_{rs} \quad (49)$$

where δ_{rs} is the Kronecker delta.

The coefficients describing the first- and second-order charge density matrices are defined based on the classification of

the natural orbitals of charge. For a system with N^α alpha and N^β beta electrons, where N^α is greater than or equal to N^β , and where ordering occurs such that $\gamma_r^u > \gamma_{r+1}^u$, there are D doubly occupied orbitals. In this case, the unprojected and projected coefficients are equal,

$$\gamma_p^u = 2 = 1 + d_p \quad (p = 1, 2, \dots D) \quad (50)$$

$$\gamma_p^p = 2 = 1 + d_p \quad (p = 1, 2, \dots D) \quad (51)$$

This type of orbital always occurs when the number of basis functions, B , is less than the number of electrons, N , and may also occur other times.

The second type of natural orbitals, the i and i' set, has paired members, the sum of whose occupation numbers equals two in the unprojected space,

$$\gamma_i^u + \gamma_{i'}^u = 2. \quad (52)$$

The values of the γ_i and $\gamma_{i'}$ coefficients are

$$\gamma_i^u = 1 + d_i \quad (i = D+1, D+2, \dots) \quad (53)$$

$$\gamma_i^p = 1 + d_i \omega_i \quad (54)$$

$$\gamma_{i'}^u = \gamma_{N-i+1}^u = 1 - d_i \quad (55)$$

$$\gamma_{i'}^p = \gamma_{N-i+1}^p = 1 - d_i \omega_i ; \quad (56)$$

evaluation of the ω_i has been made by Harriman.¹⁰

Another type of natural orbital occurring in the space of singly occupied orbitals has no pairing properties. The coeffi-

cients in both the projected and unprojected states are equal,

$$\gamma_{\nu+j}^u = \gamma_{\nu+j}^p = 1 \quad (j = 1, 2, \dots, 2m) \quad (57)$$

where $2m$ is equal to the difference between the number of alpha and beta electrons, $N^\alpha - N^\beta$.

The remaining orbitals, also having pairing properties, are empty; their occupation numbers are zero,

$$\gamma_{N+r}^u = \gamma_{N+r}^p = 0 \quad (r = 1, 2, \dots, B). \quad (58)$$

Relationships between the natural orbitals of charge and the corresponding orbitals are necessary in order to test the consistency of the phases of both sets of orbitals and calculate the weighting factors for the projected spin states. The two sets of orbitals are related by

$$\phi_p = a_p = b_p \quad (p = 1, 2, \dots, D) \quad (59)$$

$$\phi_i = [2(1 + d_i)]^{-1/2} (a_i + b_i) \quad (i = D+1, D+2, \dots, N^\beta) \quad (60)$$

$$\phi_{i'} = \phi_{N-i+1} = [2(1 - d_i)]^{-1/2} (a_i - b_i) \quad (61)$$

$$\phi_{\nu+j} = a_{\nu+j} \quad (j = 1, 2, \dots, 2m). \quad (62)$$

The $N+r$ orbitals ($r = 1, 2, \dots, B-N$) are undefined because no corresponding orbitals are defined in the empty space.

The inversion of equations 60 and 61 produce

$$a_i = t_i \phi_i + u_i \phi_{i'} \quad (i = D+1, D+2, \dots, N^\beta) \quad (63)$$

$$b_i = t_i \phi_i - u_i \phi_{i'} \quad (64)$$

where

$$t_i = [(1 + d_i)/2]^{1/2} \quad (65)$$

$$u_i = [(1 - d_i)/2]^{1/2} . \quad (66)$$

The coefficients Γ_{rstv} that multiply the two-electron integrals occur in twenty distinct combinations of r, s, t, and v. Further combinations are obtained through the use of the permutation relationship

$$\Gamma_{rstv} = \Gamma_{tyrs} = \Gamma_{srvt} = \Gamma_{vtsr} \quad (67)$$

Since the expressions are quite complicated, the reader is referred to the paper by Phillips and Schug¹¹ for a listing of the equations. It should be noted that two Γ_{rstv} terms were in error, the Γ_{tutu} and Γ_{tuut} terms. The correct values for the coefficients are

$$\Gamma_{tutu} = 1/2 \quad (68)$$

$$\Gamma_{tuut} = -1/2 \quad (69)$$

It is important to note that the expressions were formulated by assuming that t_i and u_i are always greater than or equal to zero.

The spin density matrix, described by the difference between the α - and β -charge density matrices,

$$P^Z = P^\alpha - P^\beta , \quad (70)$$

can also be used to obtain relationships between the projected and unprojected spin states. The natural orbitals of spin, $\{\phi^Z\}$, diagonalize this matrix,

$$P^Z(r_1; r_1') = \sum_{r=D+1}^N \lambda_r \phi_r^Z(r_1) \phi_r^{Z*}(r_1') . \quad (71)$$

The eigenvalues of the natural orbitals of spin, λ_k , are related

to the one-electron coefficients, γ_k , by

$$\lambda_i = (1 - d_i^2)^{1/2} = (\gamma_i \gamma_{i'})^{1/2} \quad (i = D+1, D+2, \dots N^\beta) \quad (72)$$

$$\lambda_{i'} = - (1 - d_i^2)^{1/2} = - (\gamma_i \gamma_{i'})^{1/2} \quad (73)$$

$$\lambda_{j+v} = 1 \quad (j = 1, 2, \dots 2m) \quad (74)$$

and the eigenfunctions are related to the natural orbitals of charge by

$$\phi_i^z = (\phi_i + \phi_{i'})/\sqrt{2} \quad (i = D+1, D+2, \dots N^\beta) \quad (75)$$

$$\phi_{i'}^z = (\phi_i - \phi_{i'})/\sqrt{2} \quad (76)$$

$$\phi_{v+j}^z = \phi_{v+j} \quad (j = 1, 2, \dots 2m) . \quad (77)$$

The UHF wavefunction is not an eigenfunction of pure spin multiplicity. However, with the use of the spin projection operators presented above, the single determinant wavefunction of mixed multiplicity can be separated into a linear combination of wavefunctions with pure spin multiplicity,

$$\Psi^u = \sum_{s=(N^\alpha-N^\beta)/2}^{(N^\alpha+N^\beta)/2} \omega_s \Psi_s^p . \quad (78)$$

The work presented below is a series of applications of the spin projection techniques at various levels of approximate wavefunctions.

VIII. EXCITED ELECTRONIC STATES OF ALTERNANT PI-ELECTRON SYSTEMS

The Pariser-Pople-Parr (PPP) pi-electron approximations,¹³ applicable only to planar molecules, have been used previously with singly excited configurational interaction (CI) to calculate electronic spectra. The basic assumption in the PPP approximations is that the σ , or those orbitals in the molecular plane, and π orbitals, those orbitals perpendicular to the molecular plane, have no Hamiltonian matrix elements in common. The validity of this assumption is shown using group theory. The σ orbitals are symmetric with respect to reflections in the molecular plane while the π orbitals are antisymmetric. Since the Hamiltonian is a symmetric operator, no matrix elements (or combinations) between σ and π orbitals exist.

A CI calculation is quite different from a spin projection calculation.¹⁴ The calculation begins with the determination of the ground state wavefunction,

$$\psi_k = A \left| \phi_1(1)\phi_1(2) \dots \phi_r(N) \right| . \quad (79)$$

A trial function for configuration interaction is then written as a linear combination of wavefunctions of the above for various configurations

$$\psi = C_1 \psi_1 + C_2 \psi_2 + \dots + C_m \psi_m \quad (80)$$

where m is the number of configurations. The coefficients of the

atomic orbitals are held constant. The energy of Ψ is minimized with respect to all C_k by solving the secular equation

$$| \mathcal{H}_{mn} - \delta_{mn} E | = 0 \quad (81)$$

where each \mathcal{H}_{mn} is a Hamiltonian matrix element between configurations. The resultant multi-determinant wavefunction has pure spin multiplicity and spatial symmetry; the eigenvalues of the wavefunction correspond to excitation energies from the ground to the excited state.

The CI method was used by Pariser¹⁵ to calculate the electronic spectra of polyacenes and alternant hydrocarbons using the PPP pi-electron approximations. It was also desirable to apply spin projection techniques to pi-electron systems to compare the results from spin projection with both experimental and CI data. The molecules chosen for study were naphthalene, anthracene, naphthalene and pentacene since the symmetries of the transitions had been previously assigned to portions of the experimental spectra.

The PPP approximations include several empirical parameters that are used as substitutes for the rigorous expressions in the Hartree-Fock equations. They are worthy of review at this time.¹⁴

The greatest simplification of the Hartree-Fock equations occurs when the total zero differential overlap (TZDO) approximation,¹⁶

$$\phi_r \phi_s = | \phi_r |^2 \delta_{rs}, \quad (82)$$

is employed. This approximation leads to

$$\langle r(i) s(j) | \frac{1}{r_{ij}} | t(i) u(j) \rangle = \gamma_{rs} \delta_{rt} \delta_{su} . \quad (83)$$

A further simplification is obtained by setting

$$\langle r(i) | T + V | s(i) \rangle = 0 \quad (84)$$

if r and s are neither on the same atom nor near-neighbor atoms.

Using this approximation, the remaining core Hamiltonian matrix elements are

$$(T + V)_{rr} = -Z_r I_r + \sum_{s \neq r} \langle r(i) | V_{si}^{Z_s^+} | r(i) \rangle \quad (85)$$

$$(T + V)_{rs} = \beta_{rs} \quad (86)$$

where the kinetic energy is approximated by a product of the core charge, Z , and the ionization potential, I . The potential energy is approximated as an integral whose operator is $V_{si}^{Z_s^+}$, the potential of an atom which has lost its pi-electrons. Using the approximation of Goeppert-Mayer and Sklar,¹⁷ the one-electron potential energy operator is

$$V_{sj}^+ = V_{sj} - Z \langle s(i) | \frac{1}{r_{ij}} | s(i) \rangle \quad (87)$$

where V_{sj} is the potential at atom j from a neutral atom s and is neglected; the integral represents the Coulomb potential due to a pi-electron on the atom s . The off-diagonal core Hamiltonian matrix elements are set equal to an empirical parameter, β_{rs} . The diagonal elements further reduce to

$$(T + V)_{rr} = -Z_r I_r - \sum_{s \neq r} Z_s \gamma_{rs} . \quad (88)$$

Using the above approximations including TZDO, the Hartree-Fock matrix elements are

$$F_{rr}^{\alpha} = -Z_r I_r - P_{rr}^{\alpha} \gamma_{rr} - \sum_{s \neq r} Z_s \gamma_{rs} + \sum_s P_{ss}^{\alpha} \gamma_{rs} + \sum_s P_{ss}^{\beta} \gamma_{rs} \quad (89)$$

$$F_{rr}^{\beta} = -Z_r I_r - P_{rr}^{\beta} \gamma_{rr} - \sum_{s \neq r} Z_s \gamma_{rs} + \sum_s P_{ss}^{\beta} \gamma_{rs} + \sum_s P_{ss}^{\alpha} \gamma_{rs} \quad (90)$$

$$F_{rs}^{\alpha} = \beta_{rs} - P_{rs}^{\alpha} \gamma_{rs} \quad (91)$$

$$F_{rs}^{\beta} = \beta_{rs} - P_{rs}^{\beta} \gamma_{rs} \quad (92)$$

The pi-electronic energy then is

$$E_{\pi} = - \sum_r P_{rr} (I_r + \sum_{s \neq r} Z_s \gamma_{rs}) + \sum_r \sum_{s \neq r} P_{rs} \beta_{rs} + \sum_r P_{rr}^{\alpha} P_{rr}^{\beta} \gamma_{rr} + \frac{1}{2} \sum_{s \neq r} (P_{rr}^{\alpha} P_{ss}^{\alpha} - P_{rs}^{\alpha} P_{rs}^{\alpha} - P_{rs}^{\beta} P_{rs}^{\beta}) \gamma_{rs} \quad (93)$$

where P_{rs} is a charge density matrix element. The two-center two-electron repulsion integrals, γ_{rs} , can be calculated using a variety of approximations, the Mataga-Nishimoto,¹⁸ the Pariser-Parr,¹⁹

the Nishimoto,²⁰ and the modified Mataga²¹ approximations. All are dependent on the distances between atoms, r_{rs} .

A wavefunction of a specific spatial symmetry can be obtained through a nonaufbau excitation. That is, the molecular orbitals are occupied so that the ground state electronic energy is not obtained, and the symmetries of the occupied alpha molecular orbitals are not equal to the symmetries of the occupied beta molecular orbitals. The occupation is reflected in the formation of the alpha and beta density matrices,

$$P_{rs}^{\alpha} = \sum_{k=1}^B c_{rk}^{\alpha} c_{sk}^{\alpha} f_k^{\alpha} \quad (94)$$

$$P_{rs}^{\beta} = \sum_{k=1}^B c_{rk}^{\beta} c_{sk}^{\beta} f_k^{\beta} \quad (95)$$

where the f_k 's are arrays of occupation numbers for the orbitals. Using the equations of Brickstock and Pople, equations 89 through 92, the molecular orbitals are iterated in an SCF procedure until the energy convergence criterion is attained. Spin projection is then performed on the UHF wavefunction using the equations outlined in the previous chapter. A computer program incorporating the semi-empirical PPP pi-electron approximations with spin projection was developed and submitted to the Quantum Chemistry Program Exchange.²²

The calculation of the electronic spectra of naphthalene, anthracene, naphthacene and pentacene employed the theory outlined

above. All fused benzene rings were taken to be regular hexagons with sides of length 1.4 Angstroms. The off-diagonal core Hamiltonian matrix elements, β_{rs} , were empirically set equal to -2.395 electron volts.²³ The one-center electron repulsion integrals, γ_{rr} , were taken to be 11.13 electron volts and the two-center repulsion integrals were evaluated by the Mataga-Nishimoto approximation,¹⁸

$$\gamma_{rs} = \frac{14.397}{\frac{28.794}{\gamma_{rr} + \gamma_{ss}} + r_{rs}} \quad (96)$$

The group theoretical notation is that suggested by IUPAC,²⁴ so that the molecules lie in the yz plane, the short molecular axis being in the z direction and the long axis, y. Since all molecules studied were members of the D_{2h} point group, no symmetry degenerate states existed. Both the spin projection and CI calculations employed the PPP approximations. The CI calculations that were done for comparison with the projected UHF calculations included all singly excited configurations.

The wavelengths for the ground to excited state transitions for naphthalene, anthracene, naphthacene and pentacene are listed in Tables I, II, III and IV, respectively. They are tabulated with the assumption that the ground state wavefunction is a closed shell. Both $m=0$ and $m=1$ calculations were performed for the purposes of comparison of the internal consistency of the spin projection technique; the $m=0$ state refers to an open shell system with an equal number of alpha and beta electrons while the $m=1$ system has two more alpha than beta electrons.

TABLE I

WAVELENGTHS (\AA) FOR THE GROUND TO EXCITED
STATE TRANSITIONS IN NAPHTHALENE

<u>System</u>	<u>Excited State</u>	<u>Calculated</u>		<u>Experimental</u>
		<u>Projected UHF</u>	<u>CI</u>	
m=0	$1B_{2u}$	3137	2991	3106 ^a
	$1B_{1u}$	2724	2765	2757 ^b
	$1B_{3g}$	2099	2115	
	$3B_{2u}$	3319	3604	3353 ^b
	$3B_{1u}$	5006	7264	4963 ^b
	$3B_{3g}$	2708	4264	
m=1	$3B_{2u}$	3148		3353 ^b
	$3B_{1u}$	6720		4963 ^b
	$3B_{3g}$	2924		

^aJ. R. Platt, J. Chem. Phys. 18, 1168 (1950).

^bR. G. Parr, "Quantum Theory of Molecular Electronic Structure", W. A. Benjamin Book Co., New York, 1964.

TABLE II

WAVELENGTHS (\AA) FOR THE GROUND TO EXCITED
STATE TRANSITIONS IN ANTHRACENE

<u>System</u>	<u>Calculated</u>			<u>Experimental</u>
	<u>Excited State</u>	<u>Projected UHF</u>	<u>CI</u>	
m=0	$1B_{2u}$	3713	3342	3745 ^a
	$1B_{1u}$	3493	3568	3649 ^b
	$1B_{3g}$	2887	2630	
	$3B_{2u}$	3711	3876	
	$3B_{1u}$	7921	11488	7298 ^b
	$3B_{3g}$	3286	5468	
m=1	$3B_{2u}$	3473		
	$3B_{1u}$	13393		7298 ^b
	$3B_{3g}$	3673		

^aJ. R. Platt, J. Chem. Phys. 18, 1168 (1950).

^bR. G. Parr, "Quantum Theory of Molecular Electronic Structure", W. A. Benjamin Book Co., New York, 1964.

TABLE III

WAVELENGTHS (\AA) FOR THE GROUND TO EXCITED
STATE TRANSITIONS IN NAPHTHACENE

<u>System</u>	<u>Excited State</u>	<u>Calculated</u>		<u>Experimental</u>
		<u>Projected UHF</u>	<u>CI</u>	
m=0	$1B_{2u}$	4163	3568	3922 ^a
	$1B_{1u}$	4239	4343	4278 ^b
	$1B_{3g}$	3402	3182	
	$3B_{2u}$	3969	3899	
	$3B_{1u}$	11802	18859	10340 ^b
	$3B_{3g}$	4121	7434	
m=1	$3B_{2u}$	3582		
	$3B_{1u}$	28788		10340 ^b
	$3B_{3g}$	4901		

^aJ. R. Platt, J. Chem. Phys. 18, 1168 (1950).

^bR. G. Parr, "Quantum Theory of Molecular Electronic Structure", W. A. Benjamin Book Co., New York, 1964.

TABLE IV

WAVELENGTHS (\AA) FOR THE GROUND TO EXCITED
STATE TRANSITIONS IN PENTACENE

<u>System</u>	<u>Excited State</u>	<u>Calculated</u>		<u>Experimental</u>
		<u>Projected UHF</u>	<u>CI</u>	
m=0	$1B_{2u}$	4471	3711	4167 ^a
	$1B_{1u}$	4915	4969	5755 ^b
	$1B_{3g}$	4086	3696	
	$3B_{2u}$	4130	3899	
	$3B_{1u}$	16934	29078	
	$3B_{3g}$	5002	8622	
m=1	$3B_{2u}$	5191		
	$3B_{1u}$	c		
	$3B_{3g}$	6303		

^aJ. R. Platt, J. Chem. Phys. 18, 1168 (1950).

^bE. Clar, "The Aromatic Sextet," Wiley Book Co., London, 1972.

^cTriplet energy was lower than ground state RHF energy.

In all cases, the unprojected states were composed of almost 50 percent singlet and 50 percent triplet character. The weights of the states with multiplicity five were about 0.3 percent for B_{1u} symmetry, about one percent for B_{3g} symmetry and about five percent for B_{2u} symmetry. Much smaller, though nonvanishing contributions were also obtained for states of multiplicity seven for the larger molecules.

In most cases, there was reasonable agreement between the CI and the projected UHF results. The CI calculation generally produced appreciably lower energies for the triplet states than did the UHF treatment. However, for those cases where experimental data were available, the UHF results were in somewhat better agreement than the CI results.

A comparison of the wavelengths for the excitation from the ground states to the triplets between the $m=0$ and $m=1$ calculations is rather interesting. For the B_{2u} triplets, the $m=0$ calculations provided lower energy states than the $m=1$ calculations with the exception of pentacene, the largest molecule. For the B_{3g} and B_{1u} triplets, lower energies were obtained in all cases from the $m=1$ calculations. The difference between the $m=0$ and $m=1$ energies increased with the size of the molecule and was much greater for B_{1u} symmetry than for B_{3g} . The result of this was that the excitation energies for the ground state to the ${}^3B_{1u}$ states obtained from the $m=1$ calculation were much too small in comparison with available experimental data. The case of pentacene is extreme in

that the ${}^3B_{1u}$ ($m=1$) state was lower in energy than the closed shell ground state. This result implies that the ground state wavefunction may be an open rather than a closed shell.

Hartree-Fock instabilities are defined as cases where the ground state wavefunction determined using the UHF equations is an open shell that gives a lower energy than the closed shell.

Koutecký³⁰ showed that Hartree-Fock instabilities occurred for molecules as small as benzene and were a consequence of the parameterization used in the PPP calculation. He cites examples of the occurrence of open shell ground states in naphthalene, anthracene and pentacene when the Mataga parameterization is employed. Koutecký's parameterization was slightly different from that employed in this work with $\beta = -2.318$ electron volts and $\gamma_{ii} = 10.84$ electron volts.

In an attempt to generate open shell ground states for the molecules under study, the SCF portion of the molecular orbital calculation was rewritten so that the alpha and beta molecular orbitals were calculated sequentially instead of concurrently. That is, in a usual SCF calculation, the alpha- and beta-electron Fock matrices are formed using the same set of starting orbitals and diagonalized to produce a new set of orbitals. Since the alpha- and beta-electron Fock matrices remain the same, the alpha and beta molecular orbitals stay the same. In the modified SCF calculation, the starting orbitals were used to form the alpha-electron Fock matrix, and the matrix was diagonalized to produce a new set

of alpha molecular orbitals; the new alpha orbitals were then used to form the beta-electron Fock matrix. By iterating back and forth to allow the alpha- and beta-electron Fock matrices to be different, it was hoped that sufficient differences would be introduced to produce open shell ground state molecular orbitals.

This procedure led to an open shell ground state for pentacene but closed shell solutions for naphthalene, anthracene and naphthacene. The projected energies and weighting factors for the open shell ground state of pentacene are listed in Table V while the electronic spectrum recalculated using the open shell ground state is presented in Table VI. The contributions to the open shell unprojected ground state energy by multiplicities greater than one are quite appreciable; also, the projected ground state energy is below the troublesome triplet energy obtained from the $m=1$ calculation.

The lack of open shell ground states in naphthalene, anthracene and naphthacene does not imply that such a solution does not exist but rather that the initial perturbation was not sufficient to produce an open shell solution.

The disparities between the $m=0$ and $m=1$ results can only be a consequence of the differences in the effective flexibility of the basis sets.²⁵ Since the $m=0$ results compared favorably with available experimental data on the whole, it must be concluded that the $m=0$ UHF basis set contained flexibility comparable to that of the closed shell calculation. The effective flexibility of the basis for the $m=1$ UHF calculations increased with molecular size

TABLE V

PROJECTED ELECTRONIC ENERGIES AND WEIGHTING
FACTORS FOR THE OPEN SHELL GROUND
STATE IN PENTACENE

<u>Multiplicity</u>	<u>Energy(eV)</u>	<u>Weight</u>
1	-932.54926	2.99489×10^{-1}
3	-931.48598	4.50627×10^{-1}
5	-929.41985	2.00174×10^{-1}
7	-926.66096	4.37340×10^{-2}
9	-923.41642	5.51858×10^{-3}
11	-919.78281	4.34172×10^{-4}
13	-915.79493	2.20764×10^{-5}
15	-911.45288	7.32055×10^{-7}
17	-906.73785	1.55937×10^{-8}
19	-901.62669	2.03853×10^{-10}
21	-896.11148	1.47624×10^{-12}

TABLE VI

WAVELENGTHS (\AA) FOR OPEN SHELL GROUND TO EXCITED
STATE TRANSITIONS IN PENTACENE

<u>System</u>	<u>Excited State</u>	<u>Calculated</u>		<u>Experimental</u>
		<u>Projected UHF</u>	<u>CI</u>	
m=0	$1B_{2u}$	2162	3711	4167 ^a
	$1B_{1u}$	2261	4969	5755 ^b
	$1B_{3g}$	2068	3696	
	$3B_{2u}$	2079	3899	
	$3B_{1u}$	3356	29078	
	$3B_{3g}$	2279	8622	
m=1	$3B_{2u}$	1963		
	$3B_{1u}$	5145		
	$3B_{3g}$	2515		

^aJ. R. Platt, J. Chem. Phys. 18, 1168 (1950).

^bE. Clar, "The Aromatic Sextet", Wiley Book Co., London, 1972.

and was different for different spatial symmetries, increasing in the order $B_{3g} < B_{2u} < B_{1u}$. This order can be rationalized by comparing the available virtual orbitals for naphthalene in the three calculations. However, all observed variations cannot be rationalized without a considerable amount of additional study.

Several unexpected problems arose in the spin projection calculations. Although the resolution of these difficulties was relatively easily accomplished, the sources of the problems are worthy of some explanation and elaboration.

The first problem arose in trying to obtain wavefunctions with symmetries other than the ground state symmetry, A_g . In general, one nonaufbau excitation on the first SCF iteration is sufficient to retain the desired spatial symmetry of the wavefunction. However, since the orbital symmetries reordered and multiple excitations in the density matrices were required to retain the desired symmetry of the total wavefunction, an orbital symmetry search pattern was established for subsequent iterations. The search pattern determined the symmetries of every alpha and beta orbital. The orbitals were occupied based on a preselected list of the number of orbitals of each symmetry type in the total wavefunction. The total density matrix was then calculated using equations 94 and 95. The search pattern was repeated until self-consistency was achieved.

Multiple problems with degeneracies occurred during the calculations and are described elsewhere.²⁶

Based on the results presented above, the projected UHF

method is a viable alternative to CI for the calculation of excited electronic states provided that the UHF and closed shell restricted Hartree-Fock (RHF) treatments employ basis sets of comparable flexibility. It is indicated that the $m=0$ UHF calculation satisfies this requirement in most cases.

IX. ALL-VALENCE ELECTRON CALCULATIONS

The semi-empirical all-valence electron calculations as set forth by Pople and Beveridge⁶ employ either the complete neglect of differential overlap (CNDO) or the intermediate neglect of differential overlap (INDO) approximations. The difference between the CNDO and INDO methods lies in the manner in which the one-center two-electron repulsion integrals are treated. The CNDO approximations were originally parameterized for the first, second and third row atoms on the periodic table, hydrogen through chlorine, while the INDO segment included hydrogen through fluorine.

Both the INDO and CNDO parameterizations have been quite useful in the past⁶ in determining molecular structure, particularly equilibrium geometries of organic molecules, and properties such as dipole moments.

The work described below consists of three distinct segments: the application of the INDO approximations to determine the equilibrium geometry of monohomocyclooctatetraene anion radical (MHCOT); the inclusion of the spin projection in the INDO computer program; and, the extension of the INDO parameterizations to include the third row atoms, sodium through chlorine.

It is advantageous to review the INDO approximations at this time.

The diagonal core Hamiltonian matrix elements,

$$(T + V)_{rr} = \langle r(i) | -\frac{1}{2} \nabla_i^2 - V_\mu | r(i) \rangle - \sum_{v \neq \mu} \langle r(i) | V_v | r(i) \rangle , \quad (97)$$

are separated into contributions due to the interaction of the orbital $\langle r(i) |$ with the nucleus μ on which it resides and interactions with the other nuclei, v , in the molecule. The first integral, which is essentially an atomic term, is approximated semi-empirically by U_{rr} , an average of the ionization potential, I_r , and the electron affinity, A_r , and a term describing the number of valence electrons on the nucleus μ ,

$$\langle r(i) | -\frac{1}{2} \nabla_i^2 - V_\mu | r(i) \rangle = U_{rr} \quad (98)$$

$$U_{rr} = -\frac{1}{2} (I_r + A_r) - (Z_\mu - \frac{1}{2}) \gamma_{\mu\mu} \quad (99)$$

where $\gamma_{\mu\mu}$ is a one-center two-electron coulomb integral of the form

$$\langle r(i) r(j) | \frac{1}{r_{ij}} | r(i) r(j) \rangle . \quad (100)$$

The second integral is approximated by

$$V_{\mu v} = \langle r(i) | V_v | r(i) \rangle = Z_v \gamma_{\mu v} . \quad (101)$$

These integrals are assumed to be the same for all orbitals $|r(i)\rangle$ on the atom μ .

The off-diagonal core Hamiltonian matrix elements are approximated by

$$(T + V)_{rs} = \beta_{\mu\nu}^0 S_{rs} \quad (102)$$

where S_{rs} is the overlap integral of equation 24 and $\beta_{\mu\nu}^0$ is composed

of empirical atomic bonding parameters of the form

$$\beta_{\mu\nu}^0 = \frac{1}{2} (\beta_{\mu}^0 + \beta_{\nu}^0) . \quad (103)$$

Orbitals r and s are required to be on different atoms, μ and ν .

The two-electron integrals are approximated using the zero differential overlap (ZDO) approximation,

$$\langle r(i) s(j) | \frac{1}{r_{ij}} | t(i) v(j) \rangle = \gamma_{rs} \delta_{rt} \delta_{sv} , \quad (104)$$

when r and s are on different atoms. When orbitals r and s are on the same atom, integrals of the form

$$\langle r(i) r(j) | \frac{1}{r_{ij}} | r(i) r(j) \rangle \quad (105)$$

$$\langle r(i) r(j) | \frac{1}{r_{ij}} | s(i) s(j) \rangle \quad (106)$$

$$\langle r(i) s(j) | \frac{1}{r_{ij}} | r(i) s(j) \rangle \quad (107)$$

have nonvanishing values and are evaluated semi-empirically using Slater-Condon parameters.³¹ Other one-center two-electron integrals vanish by symmetry; one-center integrals involving more than two orbitals are neglected.

The basis set used for the INDO calculation contains pure s and p atomic orbitals (no hybrids). They are Slater type orbitals of the form

$$\chi_i = A \exp(-\zeta_i r_i) Y_{\ell m}(\theta, \phi) \quad (108)$$

where ζ_i is the orbital exponent, r_i the distance from the nucleus on which the orbital resides, and $Y_{\ell m}(\theta, \phi)$ a spherical harmonic.

Using the above approximations, the open shell Fock matrix

elements are

$$\begin{aligned}
 F_{rr}^{\alpha} &= U_{rr} + \sum_{s \text{ on } \mu} [P_{ss} \langle r(i) s(j) | \frac{1}{r_{ij}} | r(i) s(j) \rangle \\
 &\quad - P_{ss}^{\alpha} \langle r(i) r(j) | \frac{1}{r_{ij}} | s(i) s(j) \rangle] \\
 &\quad + \sum_{v \neq \mu} (P_{vv} - Z_v) \gamma_{\mu v} \qquad (109)
 \end{aligned}$$

$$\begin{aligned}
 F_{rr}^{\beta} &= U_{rr} + \sum_{s \text{ on } \mu} [P_{ss} \langle r(i) s(j) | \frac{1}{r_{ij}} | r(i) s(j) \rangle \\
 &\quad - P_{ss}^{\beta} \langle r(i) r(j) | \frac{1}{r_{ij}} | s(i) s(j) \rangle] \\
 &\quad + \sum_{v \neq \mu} (P_{vv} - Z_v) \gamma_{\mu v} \qquad (110)
 \end{aligned}$$

$$\begin{aligned}
 F_{rs}^{\alpha} &= (2 P_{rs} - P_{rs}^{\alpha}) \langle r(i) r(j) | \frac{1}{r_{ij}} | s(i) s(j) \rangle \\
 &\quad - P_{rs}^{\alpha} \langle r(i) s(j) | \frac{1}{r_{ij}} | r(i) s(j) \rangle \qquad (111)
 \end{aligned}$$

$$\begin{aligned}
 F_{rs}^{\beta} &= (2 P_{rs} - P_{rs}^{\beta}) \langle r(i) r(j) | \frac{1}{r_{ij}} | s(i) s(j) \rangle \\
 &\quad - P_{rs}^{\beta} \langle r(i) s(j) | \frac{1}{r_{ij}} | r(i) s(j) \rangle \qquad (112)
 \end{aligned}$$

where the orbital $|r(i)\rangle$ is on atom μ .

The molecular orbital calculation is performed in an SCF procedure similar to that described in the preceding chapter.

Homoconjugation in the Monohomocyclooctatetraene
Anion Radical

The concept of homoconjugation was introduced by Winstein³² to describe the high stability of certain molecules and ions in which conjugation is interrupted in one or more places by aliphatic groups. Winstein, et. al.³³ view this phenomenon as due to delocalization across the interruption through the carbon p-orbitals which are twisted relative to the π -orbitals of the remaining system because of the inserted aliphatic group. For the specific case of methylene insertion, Hehre³⁴ has described how this picture could be rationalized by using the known valence orbitals of the cyclopropane ring.

Various homoaromatic compounds have been studied theoretically using specially-parameterized Hückel and minimum basis set ab initio calculations. The molecules studied were primarily compounds with an even number of pi-electrons including the unsubstituted and substituted cations and anions of bicyclo[3.1.0]hexene^{35,36} and homotropylium.^{36,37} The compounds were studied both for their formation and rearrangement processes. The Hückel $(4n + 2)$ rule for aromaticity can be applied to these compounds. The rule predicts aromaticity for those compounds that have an even number of pi-electrons equal to $(4n + 2)$ where n is an integer; those compounds that contain an even number of electrons not equal to $(4n + 2)$ are predicted to be antiaromatic. No prediction is made for compounds containing an odd number of pi-electrons; apparently homodelocalization through single bonds occurs in such cases.

Monohomocyclooctatetraene anion radical (MHCOT) is a system containing an odd number of pi-electrons and has not been examined theoretically by other workers. However, the formation reaction was studied and the electron spin resonance (ESR) hyperfine coupling constants for MHCOT were measured.^{38,39} No molecular geometry was available, a requirement for a bonding study. It was, therefore, necessary to determine the structure of MHCOT by systematically varying the geometry. The structure was determined by comparing the experimental hyperfine constants with those calculated by using a hypothetical geometry in an INDO calculation.

MHCOT is an eight-membered ring with a methylene group attached to two adjacent carbon atoms in the ring. Two hydrogen atoms, H1 and H8, are bonded to the carbon atoms that join the methylene group to the eight-membered ring (for example, see Figure 1). The ESR data^{38,39} indicate that the anion radical has only a single plane of symmetry which contains the entire methylene group. A number of possible geometries for the eight-membered ring were investigated including a cis-fused chair, a cis-fused boat and a planar ring with the methylene group in the perpendicular plane of symmetry. The boat and chair conformations contained alternant single and double bonds of lengths 1.54 and 1.35 Angstroms (\AA), respectively. In all possible geometries, the angles between the methylene group and the adjacent plane of the eight-membered ring, and between H1 and H8 and the adjacent plane of the ring were varied. Specific details of the INDO calculations are presented elsewhere.⁴⁰

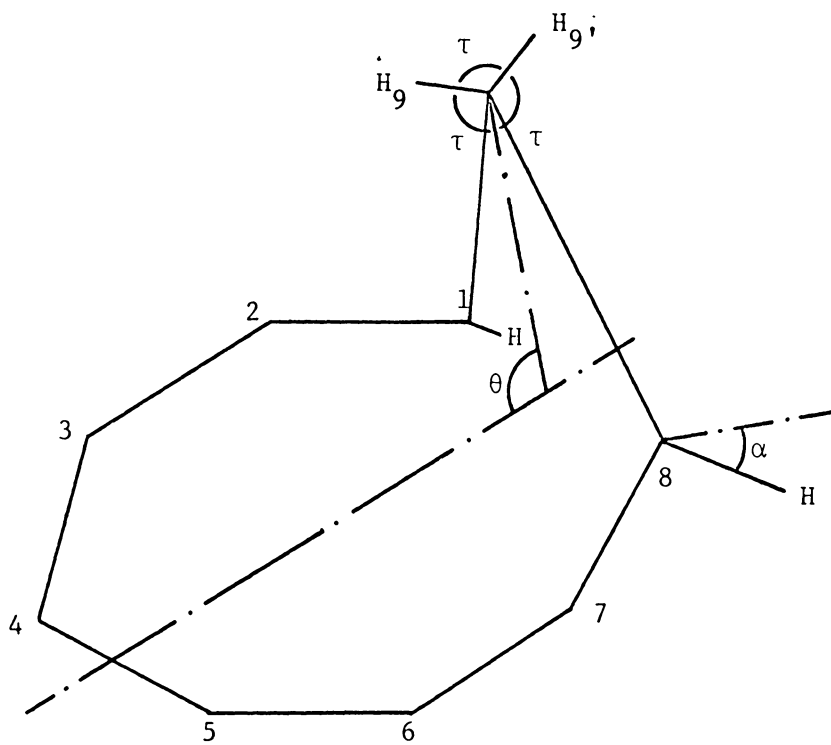


Figure 1. - Geometry of Monohomocyclooctatetraene Anion Radical

The exponents for the Slater orbitals used in both the INDO and spin projection calculations were derived from Burn's rules.⁴¹ That is, the s-orbital exponent for hydrogen was 1.2, the s-orbital exponent for carbon was 1.55, and the p-orbital exponent for carbon was 1.325.

The hyperfine coupling constants, a_H , were obtained directly from the calculated hydrogen 1s orbital spin densities, and did not involve the use of McCennell's relation⁴³ or any variation thereof.

The geometry from the INDO calculations that provided the best comparison between the calculated and experimental coupling constants was a uniform octagonal ring illustrated in Figure 1. The in-plane carbon-carbon bonds had lengths of 1.40 Å while the out-of-plane C₁-C₉ and C₈-C₉ bonds were set at 1.54 Å; all carbon-hydrogen bonds were assumed to be 1.084 Å. The carbon-hydrogen bonds at carbons two through seven were assumed to lie in the plane of the eight-membered ring, bisecting the external carbon-carbon-carbon angles. The hydrogens at carbons one and eight were similarly located, but then the carbon-hydrogen bonds were allowed to tilt below the plane by an angle α . The best comparison with experimental coupling constants was obtained when α was equal to 0° and θ , the angle between the octagonal plane and the cyclopropyl ring, was 83.5°. This angle, θ , is close to those determined by Hehre^{34,35} by ab initio calculations on the bicyclo[3.1.0]-hex-3-en-2-yl cation and the homotropylium cation. It should be noted that, in comparison to other possible geometries, this geometry did not produce the lowest binding energy, E_B , the difference between the

energy of the molecule and the energies of the atoms separated at an infinite distance.

In order to measure the amount of spin contamination in the calculated geometry of MHCOT, it was necessary to obtain a wavefunction of pure spin multiplicity. To this end, a computer program was developed to perform spin projection calculations on CNDO and INDO wavefunctions. The program has been submitted to the Quantum Chemistry Program Exchange.⁴²

Spin projection calculations were performed on the planar uniform octagonal structure of the eight-membered ring of MHCOT. Only the angle that the cyclopropyl group made with the plane of the ring, θ , and the angle that H1 and H8 tilted below the plane of the ring, α , were varied.

The best fit between the projected hyperfine coupling constants and experiment occurred when $\theta = 76.7^\circ$ and $\alpha = 0^\circ$. This geometry, too, did not produce the lowest binding energy compared to other possible geometries that were tested.

The comparisons between the unprojected hyperfine constants and experiment are presented in Table VII while the comparison between the projected hyperfine constants for the two geometries are shown in Table VIII. The unprojected hyperfine coupling constants showed better agreement with experiment than the projected hyperfine constants. In most geometries tested, the calculated hyperfine constants for H1 and H8 were greater than the hyperfine constant for H9. Since the experimental data showed the reverse situation to be true, a major requirement for the calculated

TABLE VII

PROTON HYPERFINE COUPLING CONSTANTS, a_{H} , FOR THE
 MONOHOMOCYCLOOCTATETRAENE ANION RADICAL
 OBTAINED FROM UNPROJECTED WAVEFUNCTIONS

Protons	Calculated a_{H} (Gauss)		Experimental a_{H} (Gauss) ^a
	$\theta = 83.5^\circ$ $\alpha = 0^\circ$	$\theta = 76.7^\circ$ $\alpha = 0^\circ$	
H ₁ , H ₈	4.21	1.92	±5.72
H ₂ , H ₇	-1.57	1.48	±0.87
H ₃ , H ₆	2.62	2.37	±5.12
H ₄ , H ₅	-2.03	-1.86	±1.99
H ₉	-7.55	-9.17	±12.18
H _{9'}	-3.71	-3.86	±4.54

^aS. Winstein, G. Moshuk, R. Rieke and M. A. Ogliaruso, J. Amer. Chem. Soc. 95, 2624 (1973).

TABLE VIII

PROTON HYPERFINE COUPLING CONSTANTS, a_H , FOR THE
 MONOHOMOCYCLOOCTATETRAENE ANION RADICAL
 OBTAINED FROM SPIN PROJECTED
 WAVEFUNCTIONS

Protons	Calculated a_H (Gauss)		Experimental a_H (Gauss) ^a
	$\theta = 83.5^\circ$ $\alpha = 0^\circ$	$\theta = 76.7^\circ$ $\alpha = 0^\circ$	
H ₁ , H ₈	2.72	1.15	±5.72
H ₂ , H ₇	0.78	2.84	±0.87
H ₃ , H ₆	1.34	1.17	±5.12
H ₄ , H ₅	-0.59	-0.51	±1.99
H ₉	-2.49	-3.02	±12.18
H _{9'}	-1.21	-1.26	±4.54

^aS. Winstein, G. Moshuk, R. Rieke and M. A. Ogliaruso, J. Amer. Chem. Soc. 95, 2624 (1973).

hyperfine constants was that the magnitude of H9 be greater than H1. This requirement was satisfied only within a relatively small range of change for the angle θ . It is interesting to note that a further decrease in the angle θ in the optimized projected geometry from 76.7° to 76.65° produced an increase in the hyperfine constants for H9, H9' and H1 to 184.51, 35.12 and 21.22. This sharp increase is apparently the result of H9 interfering with the conjugated π -electron cloud of the eight-membered ring.

The unprojected energies, projected energies and weighting factors for the geometries producing the best match with experiment are presented in Table IX. As is evident from Table IX, the unprojected doublet ground state had about 1.5 percent spin contamination from the quartet and sextet states. With both geometries, an energy lowering for the doublet of 0.05 atomic units was obtained upon projection.

The calculations were performed using the common convention of a uniform right-handed coordinate system. In the planar eight-membered ring, there occurs one p-orbital on each carbon atom which is oriented perpendicular to the plane of the ring. In the absence of the methylene group, these orbitals would be designated as π -orbitals and the associated bond orders as $P(\pi_r, \pi_s)$.

In order to get a more complete picture of the overall bonding, it is necessary to obtain Mulliken bond orders for the in-plane components of the carbon-carbon bonds. This was done by transforming⁴⁴ the orbitals for each carbon-carbon pair into a local coordinate system in which the p_σ -orbital of each carbon

TABLE IX

UNPROJECTED AND PROJECTED BINDING ENERGIES (A.U.)
AND WEIGHTING FACTORS FOR THE MONOHOMOCYCLO-
OCTATETRAENE ANION RADICAL

<u>Geometry</u>	<u>Unprojected Energy</u>	<u>Multiplicity</u>	<u>Weight</u>	<u>Binding Energy</u>
$\theta = 83.5^\circ,$ $\alpha = 0^\circ$	-9.710	2	9.86×10^{-1}	-9.715
		4	1.35×10^{-2}	-9.346
		6	4.27×10^{-5}	-8.036
$\theta = 76.7^\circ,$ $\alpha = 0^\circ$	-9.707	2	9.85×10^{-1}	-9.712
		4	1.44×10^{-2}	-9.353
		6	4.75×10^{-5}	-9.032

points toward the other carbon, the p_{π} -orbitals are perpendicular to the ring as described above, and the $p_{\pi'}$ -orbitals are in the plane of the ring perpendicular to the bond. For each pair, $C_r C_s$, this produces a set of bond orders, $P(\pi_i; \pi_j)$, $P(s_i; s_j)$, $P(\sigma_i; \sigma_j)$ [$P(\sigma_i; \sigma_j) + P(s_i; s_j)$], $P(\pi' i; \pi' j)$, which are invariant to the coordinate system used in the calculation and hereafter referred to as invariant bond orders. The invariant bond orders for the best geometries of MHCOT are presented in Table X. It should be noted that the projected density matrices are very close to the unprojected density matrices within the accuracies of the calculations.

As is evident from Table X, only a negligible difference in bond orders occurs between the two geometries and leads to the conclusion that the invariant bond orders are insensitive to relatively small changes in geometry.

An examination of the magnitude of the $P(\pi_i; \pi_j)$ bond orders shows close to aromatic pi-bond orders around the entire ring between carbons two and seven. The 1,2 and 7,8 pi-bond orders are understandably reduced because of the attached methylene group. The values of 0.416 and 0.422 associated with the C_1-C_8 bond are surprisingly large and imply that homoconjugation as envisioned by Winstein^{32,33} does occur.

The C_1-C_8 σ -bond order is reduced by ten to twenty percent relative to the other σ -bond orders in the ring; a similar reduction in strength occurs for the $P(s_i; s_j)$, $P(\sigma_i; \sigma_j)$ and [$P(\sigma_i; \sigma_j) + P(s_i; s_j)$] bond orders. The conclusion that must be drawn from the reduction of about twenty percent in the total C_1-C_8 bond strength is that the

TABLE X

 INVARIANT BOND ORDERS FOR CALCULATED GEOMETRIES
 OF MONOHOMOCYCLOOCTATETRAENE ANION RADICAL

Bond Order	Geometry	
	$\theta = 83.5^\circ$	$\theta = 76.7^\circ$
	$\alpha = 0^\circ$	$\alpha = 0^\circ$
P(π_1 ; π_8)	0.416	0.422
P(π_1 ; π_2)	0.384	0.388
P(π_2 ; π_3)	0.669	0.661
P(π_3 ; π_4)	0.609	0.615
P(π_4 ; π_5)	0.602	0.598
P(s1; s8)	0.270	0.270
P(s1; s2)	0.318	0.313
P(s2; s3)	0.340	0.340
P(s3; s4)	0.344	0.344
P(s4; s5)	0.344	0.344
P(σ_1 ; σ_8)	0.477	0.477
P(σ_1 ; σ_2)	0.511	0.104
P(σ_2 ; σ_3)	0.511	0.511
P(σ_3 ; σ_4)	0.510	0.510
P(σ_4 ; σ_5)	0.510	0.509
P(σ_1 ; s8) + P(s1; σ_8)	0.896	0.894
P(σ_1 ; s2) + P(s1; σ_2)	1.036	1.028
P(σ_2 ; s3) + P(s2; σ_3)	1.068	1.067
P(σ_3 ; s4) + P(s3; σ_4)	1.070	1.070
P(σ_4 ; s5) + P(s4; σ_5)	1.070	1.070
P(π' 1; π' 8)	0.246	0.249
P(π' 1; π' 2)	0.266	0.264
P(π' 2; π' 3)	0.275	0.273
P(π' 3; π' 4)	0.275	0.275
P(π' 4; π' 5)	0.275	0.275

bond has not been opened upon formation of the anion radical from cis-bicyclo[6.1.0]-nona-2,4,6-triene.

The conclusion is in good agreement with the rationalization of the cyclopropyl ring-opening process on the basis of the Woodward-Hoffman rules for the conservation of orbital symmetry.⁴⁵ When the reaction to form the nine pi-electron MHCOT is considered, both the disrotatory and conrotatory ring openings are disallowed processes since the symmetries of the starting material and product are different. However, similar considerations lead to the conclusion that the cis-bicyclo[6.1.0]-nona-2,4,6-triene dianion may undergo a symmetry allowed disrotatory cyclopropyl ring-opening process. Once obtained, the ring-opened dianion is then capable of establishing an equilibrium between the radical anion and the dianion.

Extension of INDO Calculations to Include d-Orbitals

The INDO formalism was used previously to describe the bonding in molecules comprised of the atoms hydrogen through fluorine. Kaufman and Predney⁴⁶ developed the equations necessary to extend the INDO calculations to include d-orbitals on the atoms sodium through chlorine, but a computer program to perform the INDO calculations with d-orbitals was not previously available. The program would be particularly useful in studying sulfur heterocycles and compounds containing the $-N=SF_6$ group.⁴⁷ For this reason, work was begun to extend the INDO calculation to include d-orbitals.

The Fock matrix elements that included d-orbitals were

available from the work of Kaufman and Predney⁴⁶ along with a complete set of Slater-Condon parameters, F's and G's, that were calculated from Slater-type orbitals. However, two errors in the Fock matrix elements were noted. Abbreviating the d_{z^2} , d_{xz} , d_{yz} , $d_{x^2-y^2}$ and d_{xy} orbitals by σ , π , π' , δ and δ' , the correct expressions are

$$\begin{aligned}
 F_{\delta\delta}^{\alpha} \text{ (INDO)} &= F_{\delta\delta}^{\alpha} \text{ (CNDO)} - (9 P_{\sigma\sigma}^{\alpha} + 24 P_{\pi\pi}^{\alpha} + 24 P_{\pi'\pi'}^{\alpha} \\
 &- 69 P_{\delta'\delta'}^{\alpha} - 6 P_{\sigma\alpha}^{\beta} + 4 P_{\pi\pi}^{\beta} + 4 P_{\pi'\pi'}^{\beta} - 36 P_{\delta\delta}^{\beta} + \\
 &34 P_{\delta'\delta'}^{\beta}) F^4(\text{dd})/441 - (P_{xx}^{\alpha} + P_{yy}^{\alpha}) G^1(\text{pd})/5 \\
 &- (8 P_{xx}^{\alpha} + 8 P_{yy}^{\alpha} + 5 P_{zz}^{\alpha}) 3 G^3(\text{pd})/245 - P_{ss}^{\alpha} G^2(\text{sd})/5 \\
 &- (2 P_{zz}^{\alpha} - P_{xx}^{\alpha} - P_{yy}^{\alpha} + 2 P_{zz}^{\beta} - P_{xx}^{\beta} - P_{yy}^{\beta}) 2 F^2(\text{pd})/35
 \end{aligned} \tag{113}$$

$$\begin{aligned}
 F_{x\pi'} \text{ (INDO)} &= F_{x\pi'} \text{ (CNDO)} + 4 P_{x\pi'}^{\alpha} F^2(\text{pd})/35 \\
 &+ (P_{x\pi'}^{\alpha} + 2 P_{x\pi'}^{\beta}) 3 G^3(\text{pd})/49 .
 \end{aligned} \tag{114}$$

It was also necessary to recognize the equivalence of several two-electron integrals,

$$\begin{aligned}
 \langle \pi \pi' | \frac{1}{r_{ij}} | \pi \pi' \rangle &= \langle \pi' \delta | \frac{1}{r_{ij}} | \pi' \delta \rangle = \\
 \langle \pi' \delta' | \frac{1}{r_{ij}} | \pi' \delta' \rangle &= \langle \pi \delta | \frac{1}{r_{ij}} | \pi \delta \rangle = \\
 \langle \pi \delta' | \frac{1}{r_{ij}} | \pi \delta' \rangle &
 \end{aligned} \tag{115}$$

The binding energy, E_B , is the difference between the total

energy of a molecule and the energies of the atoms separated at an infinite distance. The ground state energies of third row atoms in the INDO approximation can be calculated using

$$\begin{aligned}
 E(m,n) = & -\frac{m}{2} (I + A)_s - \frac{n}{2}(I + A)_p + \\
 & (m + n)(m + n - 1) F^0 - \frac{1}{6} m n G^1(sp) - \\
 & \frac{1}{25} n (n - 1) F^2(pp)
 \end{aligned} \tag{116}$$

where m is the number of s-orbital electrons and n is the number of p-orbital electrons in the ground state configuration $(3s)^m(3p)^n$. The atomic energies are listed in Table XI.

The computer program was transferred to Mr. John M. Fildes; results from the use of this program will be forthcoming.

TABLE XI

ATOMIC ENERGIES (A.U.) FOR THIRD ROW ATOMS
CALCULATED USING INDO APPROXIMATIONS

<u>Atom</u>	<u>Total Energy(a.u.)</u>
Na	-0.1461713
Mg	-0.6501658
Al	-1.5838907
Si	-3.1385524
P	-5.5635470
S	-9.0512034
Cl	-13.501409

X. AB INITIO UNRESTRICTED HARTREE-FOCK CALCULATIONS

Ab initio molecular orbital calculations are based on first principles and, as such, contain no empirical parameters. All one- and two-electron integrals are calculated explicitly. However, the fact that the calculations can be done with the current high speed computers does not guarantee that the predicted molecular properties will be reliable, i.e., in agreement with experiment.⁴⁹ The primary consideration in the reliability of the electronic structure calculation is the choice of a basis set.

The basis functions used in molecular calculations are usually atom-centered and either exponential or Gaussian functions. Slater⁵⁰ first suggested the use of exponential functions of the type

$$\chi_i = A r^{n-1} \exp(-\zeta_i r_i) Y_{\ell m}(\theta, \phi) \quad (117)$$

where A is a normalization factor, n is the principle quantum number and ζ_i is the orbital exponent or screening factor. The angular dependence of the orbital is introduced with a spherical harmonic, $Y_{\ell m}(\theta, \phi)$, while r is the distance from the atom on which the Slater function is centered.

Boys⁵¹ first proposed the use of Gaussian functions which, in comparison with the Slater functions, may be written as

$$\chi_i = B r^n \exp(-\alpha_i r_i^2) Y_{\ell m}(\theta, \phi) . \quad (118)$$

More frequently, however, the angular dependence of Gaussian functions is introduced by

$$\chi_i = C x^\ell y^m z^n \exp(-\alpha_i r_i^2) \quad (119)$$

where ℓ , m and n are integers. Such functions are called cartesian Gaussians. A linear combination of Gaussian-type orbitals (GTO's) can be found to match a Slater-type orbital (STO) with $\zeta_i = 1$. Then a scale factor, κ , can be introduced to relate the STO to the linear combination of GTO's. The scaled STO with $\zeta_i' = \kappa$ is represented by the same linear combination of GTO's with exponents equal to $\kappa^2 \zeta_i$.

The size of a basis set is an important factor in the reliability of molecular calculations. The work described in the previous chapter dealt with a valence orbital minimum basis set. Ab initio calculations, by their very nature, deal with both core and valence electrons. SCF energies obtained using minimum basis sets are far above the Hartree-Fock energies; for this reason, larger basis sets are usually used. A Slater basis set that receives wide use is the double zeta set, comprised of twice as many functions as the minimum basis set. For the carbon atom, the notation used to describe such a basis set is (4s2p); that is, the atom is described by two 1s and two 2s Slater functions, all with different orbital exponents. In addition, there are two sets (p_x , p_y and p_z) of 2p functions.

Extended basis sets, those larger than double zeta, are used when it is necessary to obtain SCF energies very close to the Hartree-Fock limit. Further, when molecular dissociations and properties

are studied, it is frequently necessary to employ polarization functions,⁵³ functions which have angular quantum numbers, l , greater than the highest l value generally found occupied in the ground state wavefunction. For example, the polarization functions for the carbon atom would include 3d orbitals.

As the size of the basis set increases, the amount of computational time increases accordingly. It is advantageous, then, to weigh the amount of increased accuracy obtained by increasing the size of the basis set against the increased time requirements to reach a balance between the two factors. Two portions of an ab initio molecular orbital calculation consume great quantities of time, the multi-centered two-electron integral evaluation and the diagonalization of the Hartree-Fock matrices to give the molecular orbitals.

The primary advantage of Gaussian over Slater orbitals is the speed with which integral evaluation can be accomplished. Multi-centered two-electron integrals over Gaussian functions can be evaluated in closed form while those over Slater functions cannot; thus, it has been shown⁵⁴ that integral evaluation can proceed at a rate of ten times more rapidly when Gaussian functions are used instead of Slater functions. One disadvantage of the use of Gaussian functions is that many more Gaussian than Slater functions are necessary to obtain comparable SCF energies. In a comparison of sizes of basis sets versus SCF energies obtained for oxygen and fluorine, Schaefer⁴⁹ has shown that a (10s6p) Gaussian basis set is necessary to match double zeta Slater results.

The second time consuming portion of the molecular orbital calculation, the solution of the SCF equations, requires an amount of time proportional to the fourth power of the number of basis functions. Further, large basis sets may slow convergence necessitating more iterations.⁴⁹ Therefore, the use of primitive Gaussians (equation 119) is uneconomical because of the computational time requirements.

The use of contracted Gaussian functions, linear combinations of Gaussians with fixed coefficients,^{55,56} partially alleviates the problem of large basis sets. When contracted functions are used, only the coefficients of each contracted function in an SCF orbital are determined. Whitten⁵⁶ first made effective use of contracted Gaussians by optimizing a (10s5p) basis set to a contracted [3s1p] set, where brackets denote a contracted basis set. Dunning^{57,58} continued the work in contraction schemes by optimizing various atomic basis sets and polarization functions for hydrogen through krypton. Generally, when forming a contracted basis set, the greatest number of primitives per contracted function are found in orbitals used to describe the core region of the atom. Relatively few primitives per contracted function are located in the more diffuse region of the atom; this freeing of orbitals allows a better description of the bonding region when an atom is present in a molecule than when a large number of primitives comprise a contracted function in the bonding region.

The contraction scheme thus far described does not allow the

primitive functions to have nonzero contributions in more than one contracted orbital; this type of contraction is referred to as a segmented contraction scheme. The disadvantage of this scheme is that, since atomic schemes are used in molecular calculations, they fail to adequately describe the internuclear region.

Raffenetti⁵⁹ proposed the use of a general contraction scheme to remedy this failure. In his scheme, each contracted function can have nonzero contribution from each primitive Gaussian. In addition, the most diffuse primitive Gaussian is allowed to float as a separate contracted function. Calculations on H₂O showed that 96 to 98 percent of the available energy relative to the completely uncontracted basis set was obtained.

The time required for diagonalization of the SCF matrices is dependent on the method of matrix diagonalization and roughly proportional to the fourth power of the size of the matrix. A reduction in computational time requirements can be realized when the secular determinant is symmetry-restricted. Like orbitals in other SCF calculations, each orbital must transform according to one of the irreducible representations of the molecular point group.⁶⁰ The molecular orbitals can then be grouped by symmetry; matrix elements between orbitals of different symmetry groups are zero. Using this information, the matrix diagonalization problem reduces from the diagonalization of one matrix of size B by B to the diagonalization of several smaller matrices, realizing a considerable savings in computational time.

The SCF procedure is performed using the Hartree-Fock

equations outlined in Chapter VI. One complication that is usually ignored in semi-empirical calculations and is therefore unique to ab initio calculations is the nonorthogonality of the atomic basis set.

The direct consequence of the nonorthogonality of the atomic orbitals is that one- and two-electron integrals, equations 29 through 32, are evaluated and the SCF matrices are formed in the nonorthogonal representation. The orthogonal molecular orbitals can be expressed in two forms, as a linear combination of nonorthogonal atomic functions,

$$\phi_r = \sum_{\rho} \eta_{\rho} Y_{\rho r} \quad (120)$$

or as a set of orthogonal symmetry functions,

$$\sigma_r = \sum_{\rho} \eta_{\rho} R_{\rho r} . \quad (121)$$

The former expression is preferable in relating bonding parameters to specific portions of a molecule but results in nonorthogonal density matrices.

Matrices in a nonorthogonal representation can be put into an orthogonal basis through a transformation using the symmetry blocking transformation matrix. The transformation results from the fact that the overlap matrix, \underline{S} , is in diagonal form,

$$\langle \phi_r | \phi_s \rangle = \delta_{rs} = \sum_{\rho, \tau} Y_{\rho r}^* \langle \eta_{\rho} | \eta_{\tau} \rangle Y_{\tau s} \quad (122)$$

or

$$\langle \phi_r | \phi_s \rangle = \sum_{\rho, \tau} \tilde{Y}_{r\rho} S_{\rho\tau} Y_{\tau s} \quad (123)$$

leading directly to

$$\tilde{\underline{Y}} \underline{S} \underline{Y} = \underline{1} . \quad (124)$$

Solving for $\tilde{\underline{Y}}^{-1}$ leads to

$$\tilde{\underline{Y}}^{-1} = \underline{S} \underline{Y} \quad (125)$$

Equation 124 applies for any orthogonal basis, whether the basis is the molecular orbitals from a previous iteration or other orbitals such as natural orbitals.

The Hartree-Fock problem is solved using Roothaan's equation⁶¹ which is

$$\underline{F} \underline{Y} = \underline{S} \underline{Y} \underline{E} \quad (126)$$

where the Fock matrix, \underline{F} , the matrix of eigenvectors, \underline{Y} , and the overlap matrix, \underline{S} , are in the nonorthogonal representation and \underline{E} is a diagonal matrix of orbital eigenvalues. The Fock, overlap and eigenvector matrices are transformed into the orthogonal basis by

$$\underline{F}' = \tilde{\underline{R}} \underline{F} \underline{R} \quad (127)$$

$$\underline{S}' = \tilde{\underline{R}} \underline{S} \underline{R} \quad (128)$$

$$\underline{W} = \underline{R}^{-1} \underline{Y} \quad (129)$$

giving a Fock equation of

$$\tilde{\underline{R}} \underline{F} \underline{R} \underline{R}^{-1} \underline{Y} = \tilde{\underline{R}} \underline{S} \underline{R} \underline{R}^{-1} \underline{Y} \underline{E} \quad (130)$$

which, when equation 124 is used, takes the appearance of a standard eigenvalue problem,

$$\underline{F}' \underline{W} = \underline{W} \underline{E} . \quad (131)$$

The solution of the standard Hartree-Fock equations yields molecular orbitals in the orthogonal basis; the transformation to the nonorthogonal basis is accomplished with

$$\underline{Y} = \underline{R} \underline{W} . \quad (132)$$

The POLYATOM (Version 2)⁴ system of programs is a series of programs designed to calculate ab initio molecular orbital wavefunctions using Gaussian basis functions. In order to provide maximum flexibility, the system contains a number of independent main programs. Computer memory requirements are minimized by utilizing off-line tape storage to the fullest possible extent. The main programs include PA20A and PA20B which list one- and two-electron integrals respectively, and PA30A and PA30B which evaluate those integrals. The open shell SCF calculation is performed using PA43. Several supplemental programs which perform a variety of SCF calculations and compute molecular properties are also available.

The initial set of molecular orbitals in POLYATOM can be obtained from two sources, from a set of molecular orbitals from a previous calculation or from the diagonalization of the core Hamiltonian.

Spin projection of ab initio wavefunctions requires the formation of the corresponding orbitals and the natural orbitals of charge and spin. As was stated earlier, the density matrices are expressed in a nonorthogonal basis but may be transformed to the orthogonal representation using equation 125 by

$$\underline{P}' = \underline{Y}^{-1} \underline{P} \tilde{\underline{Y}}^{-1} . \quad (133)$$

The diagonalization of \underline{P}' by

$$\underline{P}' \underline{C} = \underline{N} \underline{C} \quad (134)$$

gives the natural orbitals, $\{m_r\}$,

$$m_r = \sum_{s,\rho} \eta_\rho Y_{\rho r} \tilde{C}_{sr} = \sum_{\rho} \eta_\rho (\tilde{\underline{Y}} \underline{C})_{\rho s} . \quad (135)$$

The natural orbitals are expressed in the atomic orbital basis by the transformation

$$\underline{\chi} = \underline{Y} \underline{C} . \quad (136)$$

The alpha corresponding orbitals are formed in a manner similar to that for the natural orbitals with one noteworthy exception. The product matrix $\underline{P}^\alpha \underline{P}^\beta \underline{P}^\alpha$ cannot be transformed to the orthogonal representation as a single matrix, but rather \underline{P}^α and \underline{P}^β must be separately transformed before the product matrix is formed. The reason for the necessity of separate transformations lies in the lack of orthonormality of the orbitals. This can best be seen by examining the effect of \underline{P}^α operating on an arbitrary vector, A.

The alpha density matrix is

$$\underline{P}^\alpha = \sum_r^{B_{\text{occ}}^\alpha} |r^\alpha\rangle \langle r^\alpha| \quad (137)$$

where $|r\rangle$ is a molecular orbital. Each molecular orbital is a linear combination of atomic orbitals, $|m\rangle$,

$$| r \rangle = \sum_m c_{rm} | m \rangle . \quad (138)$$

The alpha density matrix, then, in terms of atomic orbitals, is

$$\begin{aligned} \underline{P}^\alpha &= \sum_r \sum_{m,n} c_{rm}^\alpha | m \rangle \langle n | c_{nr}^{\alpha*} \\ &= \sum_{m,n} P_{mn}^\alpha | m \rangle \langle n | \end{aligned} \quad (139)$$

where P_{mn}^α is a density matrix coefficient. When the density matrix is used as an operator operating on an arbitrary vector, \underline{A} ,

$$\underline{A} = \sum_p | p \rangle c_p , \quad (140)$$

the resultant equation is

$$\underline{P}^\alpha \underline{A} = \sum_{m,n,p} P_{mn}^\alpha | m \rangle \langle n | p \rangle c_p \quad (141)$$

where $\langle n | p \rangle$ are overlap integrals. When orthonormal orbitals are used, the overlap matrix is diagonal with elements $S_{nn} = 1$. However, the overlap matrix in the nonorthogonal representation is not diagonal but can be used to bring nonorthogonal orbitals into the orthogonal representation,

$$\underline{P}^\alpha \underline{A} = \sum_{m,n,p} P_{mn}^\alpha | m \rangle S_{np} c_p . \quad (142)$$

The overlap matrix can also be expressed, using equation 124, as

$$\underline{S} = \underline{Y}^{-1} \underline{Y} \quad (143)$$

Using these arguments, then, the matrix equation for the determination of the alpha corresponding orbitals becomes

$$\underline{Y}^{-1} \underline{P}^{\alpha} \tilde{\underline{Y}}^{-1} \underline{Y}^{-1} \underline{P}^{\beta} \tilde{\underline{Y}}^{-1} \underline{Y}^{-1} \underline{P}^{\alpha} \tilde{\underline{Y}}^{-1} \underline{A} = \underline{\Delta} \underline{A} \quad (144)$$

or

$$\underline{Y}^{-1} \underline{P}^{\alpha} \underline{S} \underline{P}^{\beta} \underline{S} \underline{P}^{\alpha} \tilde{\underline{Y}}^{-1} \underline{A} = \underline{\Delta} \underline{A} \quad (145)$$

where $\Delta_i = d_i^2$, an eigenvalue of the alpha corresponding orbital.

The spin projection calculation for ab initio wavefunctions derived from the POLYATOM (Version 2)⁴ system of programs was written to conform as closely as possible to the original system of programs and is listed in Appendix A. Documentation for the manner in which the data is input is provided in the program comments. The program utilizes an integral tape that was generated by the POLYATOM integral evaluation programs; in addition, an open shell molecular orbital wavefunction obtained from the POLYATOM UHF SCF package must be provided in either card or tape format. The desire to minimize the computer region requirements was accomplished by utilizing scratch disk to as great an extent as possible.

The program calculates the alpha corresponding orbitals and natural orbitals of charge in the manner just described. Appropriate replacements of the singly-occupied natural orbitals of charge by natural orbitals of spin are made as was described in equations 75 and 76. All orbitals are then transformed to the nonorthogonal basis in order to conform to the integral tape which is in the nonorthogonal basis; further, the orbitals are completely

reordered, breaking the symmetry blocking, so that the lowest orbital has the highest occupation number. The purpose of the reordering is to properly classify the orbitals based on occupation numbers during the spin projection calculation.

Comparison of Spin Projection and MCSCF/CI Calculations on $H_2O(+)$

The water cation was studied by several groups of workers using a variety of theoretical techniques. Dunning, Pitzer and Aung⁶² obtained near Hartree-Fock vertical ionization potentials of ground state H_2O , and Meyer,⁶³ using CI calculations, obtained vertical and adiabatic ionization potentials along with SCF equilibrium geometries for selected ion states. LeClerc, Horsley and Lorquet⁶⁴ studied the asymmetric dissociation and potential energy surfaces for the ground and excited states of $H_2O(+)$ while Smith, Jørgensen and Öhrn⁶⁵ and Fortune, Rosenberg and Wahl⁵ carried out a vibrational analysis of selected low-lying states.

The purpose of the study described below was to compare the degree of energy lowering obtained with spin projection and MCSCF/CI calculations. Spin projection has been described as a viable alternative to the time-consuming MCSCF/CI calculations. An adequate assessment of spin projection can be made only when as many parameters as possible, such as the basis set and geometry, are held constant. An evaluation of the spin projection technique was most easily made by comparing spin projection data with MCSCF/CI calculations⁵ on the X^2B_1 and \tilde{B}^2B_2 states of $H_2O(+)$.

The basis set chosen for study was one where the polarization functions were specially optimized for H_2O by Dunning.⁵⁷ It consisted of a set of (9s5p2d) orbitals contracted to [4s3p1d] for oxygen and a (4s1p) set contracted to [2s1p] for hydrogen. It is listed in Table XII.

The geometries chosen for study were equilibrium geometries obtained from the potential energy surface of Fortune, et. al.⁵ The $H_2O(+)$ molecule lies in the xz plane with oxygen at the origin (0.0, 0.0, 0.0). The equilibrium geometry of the X^2B_1 state located the hydrogens at (± 1.54499 , 0.0, 1.11224) bohrs giving an oxygen-hydrogen bond length of 1.90 bohrs and an angle, $\langle HOH \rangle$, of 47.88° ; the hydrogens were located at (± 0.99428 , 0.0, 1.91128) bohrs (an oxygen-hydrogen length of 2.15 bohrs and angle, $\langle HOH \rangle$, of 54.97°) for the equilibrium \tilde{B}^2B_2 state. The convergence criterion for the total energy for both calculations was 1.0×10^{-6} atomic units.

The unprojected and projected energies for the X^2B_1 and \tilde{B}^2B_2 states are presented in Tables XIII and XIV, respectively; a comparison of this work with MCSCF/CI and RHF calculations is available in Table XV.

An energy lowering of 0.0046 and 0.0008 atomic units for the X^2B_1 and \tilde{B}^2B_2 states, respectively, is obtained when an UHF rather than a RHF wavefunction is used. Very little additional energy lowering was obtained upon spin projection of the UHF wavefunction, 0.002 atomic units for the \tilde{B}^2B_2 and 0.003 atomic units for the X^2B_1 state. This lack of considerable energy lowering is attributed to the fact that the UHF wavefunction is so close to being a pure

TABLE XII

CONTRACTED GAUSSIAN BASIS SET FOR A (9s5p2d/4s1p)
 H₂O PRIMITIVE BASIS SET^a

<u>Atom</u>	<u>Orbital Type</u>	<u>Contracted Orbital No.</u>	<u>Exponent</u>	<u>Coefficient</u>
O	s	1	7816.5400	0.002031
O	s	1	1175.8200	0.015436
O	s	1	273.1880	0.073771
O	s	1	81.1696	0.247606
O	s	1	27.1836	0.611832
O	s	1	3.4136	0.241205
O	s	2	9.5322	1.000000
O	s	3	0.9398	1.000000
O	s	4	0.2846	1.000000
O	p	5	35.1832	0.040023
O	p	5	7.9040	0.253849
O	p	5	2.3051	0.806842
O	p	6	0.7171	1.000000
O	p	7	0.2137	1.000000
O	d	8	1.3220	0.357851
O	d	8	0.3916	0.759561
H	s	9	21.7208	0.032828
H	s	9	3.2729	0.231208
H	s	9	0.7377	0.817238
H	s	10	0.2004	1.000000
H	p	11	1.1592	1.000000

^aT. H. Dunning, J. Chem. Phys. 53, 2823 (1970); T. H. Dunning, J. Chem. Phys. 55, 3958 (1971).

TABLE XIII

UNPROJECTED AND PROJECTED ENERGIES FOR
THE X^2B_1 STATE OF $H_2O(+)$

Unprojected Energies(a.u.)

Kinetic Energy, T	75.749684
One-Electron Potential Energy, V(1)	-192.949513
Two-Electron Potential Energy, V(1,2)	33.021498
Electronic Energy, E(E)	-84.378330
Nuclear Repulsion Energy, V(N)	8.728339
Total Energy, E	-75.649992

Projected Energies(a.u.)

<u>Multiplicity</u>	<u>Weight, w_i</u>	<u>Total Energy, E_i</u>
2	9.9737×10^{-1}	-75.65323
4	2.6255×10^{-3}	-74.42535
6	1.6888×10^{-6}	-73.49101
8	2.882×10^{-10}	-72.58397

TABLE XIV

UNPROJECTED AND PROJECTED ENERGIES FOR
THE \tilde{B}^2B_2 STATE OF $H_2O(+)$

Unprojected Energies(a.u.)

Kinetic Energy, T	75.40146
One-Electron Potential Energy, V(1)	-191.25650
Two-Electron Potential Energy, V(1,2)	32.44855
Electronic Energy, E(E)	-83.40648
Nuclear Repulsion Energy, V(N)	7.92953
Total Energy, E	-75.47695

Projected Energies(a.u.)

<u>Multiplicity</u>	<u>Weight, w_i</u>	<u>Total Energy, E_i</u>
2	9.9868×10^{-1}	-75.47908
4	1.3204×10^{-3}	-73.86906
6	2.6566×10^{-7}	-72.84159
8	1.3743×10^{-11}	-71.85666

TABLE XV

COMPARISON OF MCSCF/CI^a AND SPIN PROJECTION
 ENERGIES FOR THE EQUILIBRIUM GEOMETRIES
 OF THE X^2B_1 AND \tilde{B}^2B_2 STATES OF H₂O(+)

<u>Type of Wavefunction</u>	<u>Total Energies(a.u.)</u>	
	<u>X^2B_1</u>	<u>\tilde{B}^2B_2</u>
RHF SCF	-75.64565 ^a	-75.47629 ^b
RHF Plus MCSCF/CI	-75.72328 ^a	-75.55451 ^b
UHF SCF	-75.64999	-75.47695
UHF Plus Spin Projection	-75.65323	-75.47908

^aP. J. Fortune, B. J. Rosenberg and A. C. Wahl, J. Chem. Phys. 65, 2201 (1976).

^bData from cubic fit of Fortune, et. al.

doublet state.

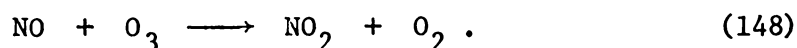
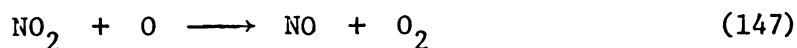
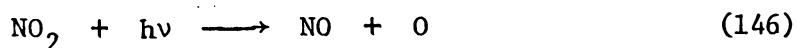
In contrast to the spin projection results, the MCSCF/CI calculations which used 20 configurations produced a much greater energy lowering of 0.078 atomic units relative to the RHF energy for both the \tilde{B}^2B_2 and X^2B_1 states. The conclusion that must be reached from this study is that the MCSCF/CI calculation is superior to spin projection when the weighting factor for the spin projected state of lowest multiplicity is very close to unity. However, studies using semi-empirical techniques^{25,26} indicated that useful results from spin projection can be obtained when the weight for the state of lowest multiplicity is much different from one. Since spin projection calculations using small basis sets are more economical in terms of computational time than MCSCF/CI calculations, further investigation into cases where weighting factors are different from unity is certainly warranted. In any case, weighting factors obtained from spin projection calculations should be examined before the more costly MCSCF/CI calculation is attempted.

The Dissociation of CF_2O

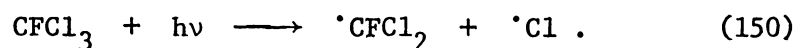
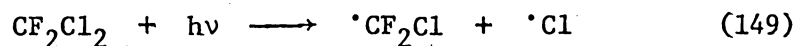
The study of the dissociation of carbonyl fluoride, CF_2O , was initiated from the desire to better understand the possible reaction pathways that could occur in the stratosphere, particularly the reactions involving chlorofluoromethanes.

Any decrease in the amount of stratospheric ozone is likely to have extreme environmental consequences.⁶⁶ The most important mode of ozone destruction at the present time is the nitrogen oxide

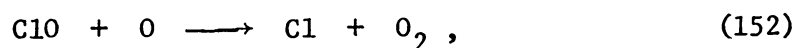
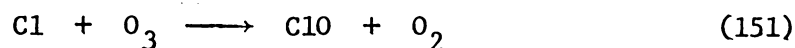
catalyzed cycle,⁶⁷



However, Rowland and Molina⁶⁸ indicate that if the use of chlorofluoromethanes, CF_2Cl_2 and CFCl_3 , continues at the present rate, the chlorine oxide catalyzed cycle will overtake the nitrogen oxide cycle in importance within several years. The chlorofluoromethanes are a starting point in the chlorine oxide cycle when they are photolytically dissociated by ultraviolet solar radiation,



The chlorine atoms then deplete the odd oxygen content by

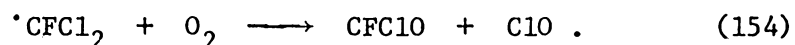
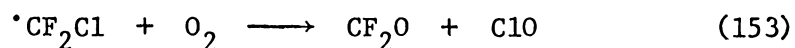


giving the same net effect as reactions 147 and 148.

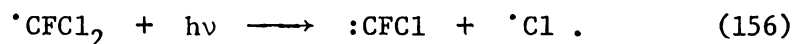
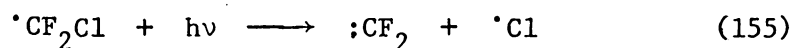
Rowland and Molina⁶⁸ point out many other reactions related to 151 and 152 that require study or are currently under study. Rowland is studying some photolytic reactions;⁶⁹ Watson is investigating the reactions of ClO with a range of atmospheric species;⁷⁰ Kaufmann's research group is studying a variety of reactions involving Cl and ClO;⁷¹ and Heicklen⁷² is researching the photodissociation of the chlorofluoromethanes.

The reactions of the chlorofluoromethyl radicals produced

in reactions 149 and 150 have been largely ignored. Rowland and Molina⁶⁸ indicate that, and some experimental data^{69,72} supports, the primary reaction of the chlorofluoromethyl radicals with oxygen is

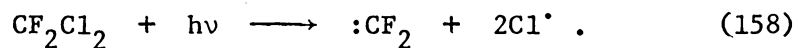
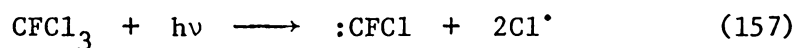


The possibility also exists that substituted methyl radicals can absorb another photon and dissociate to produce carbenes,



Either reaction 155 or 156 produces chlorine atoms which can initiate the chlorine oxide catalyzed destruction of ozone.

The possibility of direct production of carbenes from the photolysis of chlorofluoromethanes was noted at the August 1975 meeting of the American Chemical Society by Ausloos and Rebert⁷³ who found evidence to support the reactions



The focus of this work is on the reaction of difluorocarbene with oxygen to produce carbonyl fluoride,



Available thermochemical data⁷⁴ show that CF_2O is a fairly stable molecule with a standard heat of formation at 298 °K of -152.0 kcal/mole. Three possible modes of dissociation for CF_2O

can be envisioned,



with standard heats of reaction, ΔH_{298}° , of 130.6, 168.8 and 126.3 kcal/mole, respectively. The dissociation of CF_2O by reaction 161 was chosen for study.

The study of the dissociation of carbonyl fluoride was begun using two geometries, the equilibrium geometry for CF_2O determined by Laurie, Pence and Jackson⁷⁵ and illustrated in Figure 2 and the equilibrium geometry for CF_2 determined by Powell, Lide and Mathews.⁷⁶ Both molecules are members of the C_{2v} point group and were chosen to lie in the yz plane. The carbon atom was located at the origin (0.0, 0.0, 0.0) in both geometries. In the equilibrium geometry for CF_2O , the oxygen atom was located at (0.0, 0.0, -2.21858) bohrs and the fluorines at (0.0, ± 1.92806 , 1.40082) bohrs giving a carbon-fluorine bond distance of 2.38 bohrs and an angle, $\angle \text{FCF}$, of 108° . The carbon-oxygen bond length was varied in increments of 0.20000 bohrs in the z direction from 1.81858 to 2.61858 bohrs in order to obtain data on the behavior of CF_2O near the equilibrium geometry. The geometry for CF_2 located the fluorines at (0.0, ± 1.94876 , 1.52802) bohrs giving a carbon-fluorine bond distance of 2.48 bohrs and an angle, $\angle \text{FCF}$, of 103.8° ; an oxygen atom was placed at (0.0, 0.0, -18.90359) bohrs in order to approximate the dissociated CF_2O molecule.

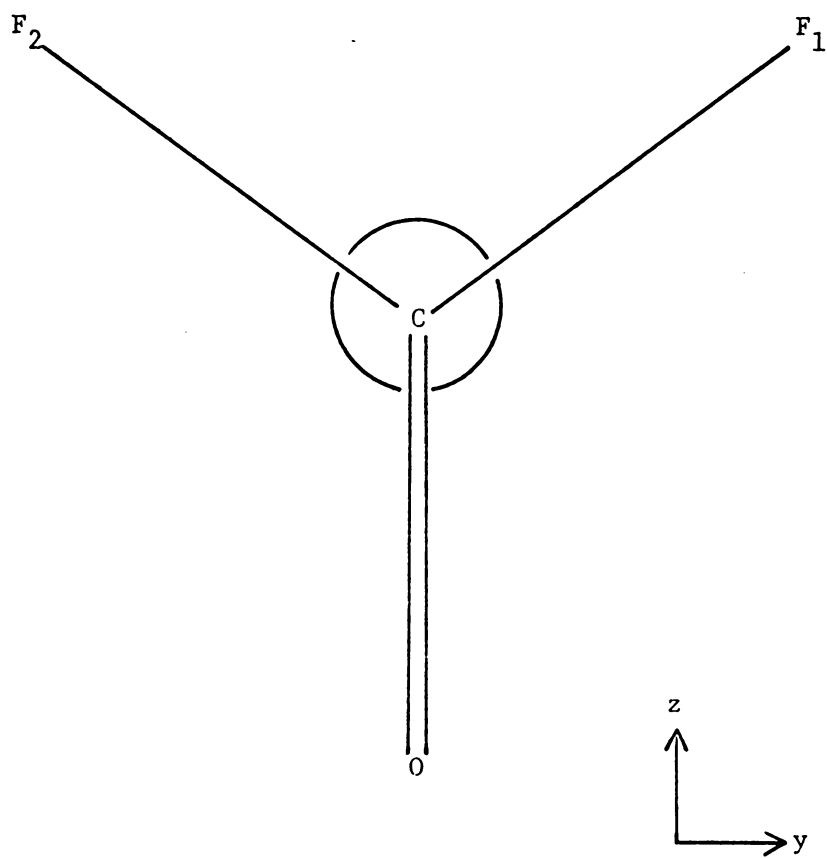


Figure 2.- Geometry of CF_2O molecule.

The POLYATOM (Version 2) system of programs⁴ discussed earlier in this chapter was used to obtain wavefunctions for all geometries of CF_2O . All two-electron integrals whose values were less than 1.0×10^{-9} atomic units were taken to be exactly zero. The criterion for energy convergence was 1.0×10^{-6} atomic units.

The basis set used in all calculations was Dunning's (9s5p) set contracted to [4s3p]⁵⁸ for each atom in CF_2O or a total of 52 contracted orbitals. Symmetry orbitals were formed to the fullest possible extent, giving 502,627 two-electron integrals, 261,910 of which were unique.

Symmetry factoring of the secular determinant in the SCF portion of the molecular orbital calculation was performed differently for the geometry where the carbon-oxygen bond distance was 18.90359 bohrs than for the remainder of the geometries. The factoring of the latter will be discussed first.

The 52 atomic orbitals of CF_2O near the equilibrium geometry can be combined into 52 symmetry orbitals, 24 a_1 , 3 a_2 , 9 b_1 and 16 b_2 which are presented in Table XVI. The atomic orbitals p_x , p_y and p_z are abbreviated x, y and z. Since all symmetry types in the point group contain orbitals, all molecular symmetry states, A_1 , A_2 , B_1 and B_2 , in the point group are accessible. A preliminary examination of the symmetry orbitals showed the $m=0$ ground state orbital occupation in the A_1 molecular symmetry state was 8 a_1 , 1 a_2 , 2 b_1 and 5 b_2 for both the alpha and beta orbitals. A RHF calculation was performed on the A_1 state of the equilibrium geometry in order to determine the lowest energy excitations and

TABLE XVI

SYMMETRY ORBITALS FOR [4s3p] BASIS SET OF CF₂O
NEAR THE EQUILIBRIUM GEOMETRY

<u>Orbital Symmetry</u>	<u>Symmetry Orbital</u>	<u>Number of Orbitals</u>
a ₁	s _O	4
a ₁	s _C	4
a ₁	s _{F1} + s _{F2}	4
a ₁	y _{F1} - y _{F2}	3
a ₁	z _O	3
a ₁	z _C	3
a ₁	z _{F1} + z _{F2}	3
a ₂	x _{F1} - x _{F2}	3
b ₁	x _O	3
b ₁	x _C	3
b ₁	x _{F1} + x _{F2}	3
b ₂	s _{F1} - s _{F2}	4
b ₂	y _O	3
b ₂	y _C	3
b ₂	y _{F1} + y _{F2}	3
b ₂	z _{F1} - z _{F2}	3

thus the occupation of symmetry orbitals necessary to form the A_2 , B_1 and B_2 states. The lowest energy excitations were obtained when the following alpha-electron symmetry orbitals were occupied: 8 a_1^α , 1 a_2^α , 3 b_1^α , and 4 b_2^α for the A_2 state; 9 a_1^α , 1 a_2^α , 1 b_1^α and 5 b_2^α for the B_1 state; and 9 a_1^α , 1 a_2^α , 2 b_1^α and 4 b_2^α for the B_2 state. In all cases, the occupation of the beta symmetry orbitals was equal to that for the A_1 state.

An attempt was made to treat all geometries in the same manner with respect to symmetry factoring. However, the geometry where the carbon-oxygen distance equalled 18.90359 bohrs produced wide oscillations in the total energy when an SCF calculation was attempted. In addition, the orbitals attributed to the oxygen atom showed very little interaction with those orbitals associated with the CF_2 fragment. In order to obtain SCF convergence, it was necessary to separate by symmetry factoring the oxygen orbitals from the difluorocarbene orbitals. The symmetry factoring for this geometry is shown in Table XVII. By using such symmetry factoring, this geometry approached CF_2O dissociated into CF_2 and O at an infinite separation.

Eight molecular symmetry states were considered for the dissociated $CF_2 + O$, four symmetries in the C_{2v} point group for CF_2 , A_1 , A_2 , B_1 and B_2 and two atomic states for oxygen, 3P and 1D . The occupation of symmetry orbitals for CF_2 was determined using $CF_2(A_1) + O(^3P)$ in a manner similar to that described previously for the CF_2O geometries near equilibrium. The occupation of the beta-electron symmetry orbitals for all states was set equal

TABLE XVII

SYMMETRY ORBITALS FOR THE [4s3p] BASIS
SET OF $\text{CF}_2 + \text{O}$

<u>Orbital Symmetry</u>	<u>Symmetry Orbital</u>	<u>Number of Orbitals</u>
a_1	s_C	4
a_1	$s_{F1} + s_{F2}$	4
a_1	$y_{F1} - y_{F2}$	3
a_1	z_C	3
a_1	$z_{F1} + z_{F2}$	3
a_2	$x_{F1} - x_{F2}$	3
b_1	x_C	3
b_1	$x_{F1} + x_{F2}$	3
b_2	y_C	3
b_2	$y_{F1} + y_{F2}$	3
b_2	$z_{F1} - z_{F2}$	3
b_2	$s_{F1} - s_{F2}$	4
a_1'	s_O	4
a_1'	z_O	3
b_1'	x_O	3
b_2'	y_O	3

to that for the A_1 alpha-electron orbitals in all molecular symmetries considered; the alpha orbital occupations for CF_2 were: 6 a_1^α , 1 a_2^α , 1 b_1^α and 4 b_2^α for the A_1 state; 6 a_1^α , 1 a_2^α , 2 b_1^α and 3 b_2^α for the A_2 state; 5 a_1^α , 1 a_2^α , 2 b_1^α and 4 b_2^α for the B_1 state; and 5 a_1^α , 1 a_2^α , 1 b_1^α and 5 b_2^α for the B_2 state. The 3P state of oxygen was generated by occupying 3 $a_1^{\alpha'}$, 1 $b_1^{\alpha'}$, and 1 $b_2^{\alpha'}$ while the occupation for the $O(^1D)$ was 3 a_1' and 1 b_2' .

The existence of an open shell ground state in pentacene was discussed previously. In order to allow for the possibility of open shell ground states in CF_2O , the B_1 states were obtained, and the open shell orbitals from the B_1 state were used as starting orbitals for the generation of the A_1 states; the A_1 orbitals were used as starting points for the A_2 states and orbitals from the A_2 state used as starting points for the B_2 states. This procedure not only allowed for the possibility of open shell ground states but had the added advantage of saving the computational time that would have been required had the starting point for each state been the core Hamiltonian.

The total energies with respect to carbon-oxygen bond distances for the A_1 , A_2 , B_1 and B_2 states are listed in Tables XVIII, XIX, XX and XXI, respectively, and presented graphically in Figure 3. First inspection leads to the conclusion that the A_2 , B_1 and B_2 states are dissociative; that is, no possibility of bonding occurs in any of those states. However, upon viewing these data together with those for the dissociated $CF_2 + O$ presented in Table XXII, only one state is truly dissociative, the B_1 state.

TABLE XVIII

TOTAL ENERGIES (A.U.) FOR THE A_1 STATE OF CF_2O
AS A FUNCTION OF THE CARBON-OXYGEN
BOND DISTANCE

<u>Carbon-Oxygen Bond Distance (bohrs)</u>	<u>Total Energy(a.u.)</u>
1.81858	-311.422091
2.01858	-311.533835
2.21858	-311.560185
2.41858	-311.543846
2.61858	-311.508605

TABLE XIX

TOTAL ENERGIES (A.U.) FOR THE A_2 STATE OF CF_2O
AS A FUNCTION OF THE CARBON-OXYGEN
BOND DISTANCE

<u>Carbon-Oxygen Bond Distance (bohrs)</u>	<u>Total Energy(a.u.)</u>
1.81858	-311.076288
2.01858	-311.270210
2.21858	-311.366903
2.41858	-311.409140
2.61858	-311.421066

TABLE XX

TOTAL ENERGIES (A.U.) FOR THE B_1 STATE OF CF_2O
AS A FUNCTION OF THE CARBON-OXYGEN
BOND DISTANCE

<u>Carbon-Oxygen Bond Distance (bohrs)</u>	<u>Total Energy(a.u.)</u>
1.81858	-310.882854
2.01858	-311.043688
2.21858	-311.123940
2.41858	-311.166386
2.61858	-311.202223

TABLE XXI

TOTAL ENERGIES(A.U.) FOR THE B₂ STATE OF CF₂O
AS A FUNCTION OF THE CARBON-OXYGEN
BOND DISTANCE

<u>Carbon-Oxygen Bond Distance (bohrs)</u>	<u>Total Energy(a.u.)</u>
1.81858	-310.941836
2.01858	-311.091515
2.21858	-311.160894
2.41858	-311.195404
2.61858	-311.226302

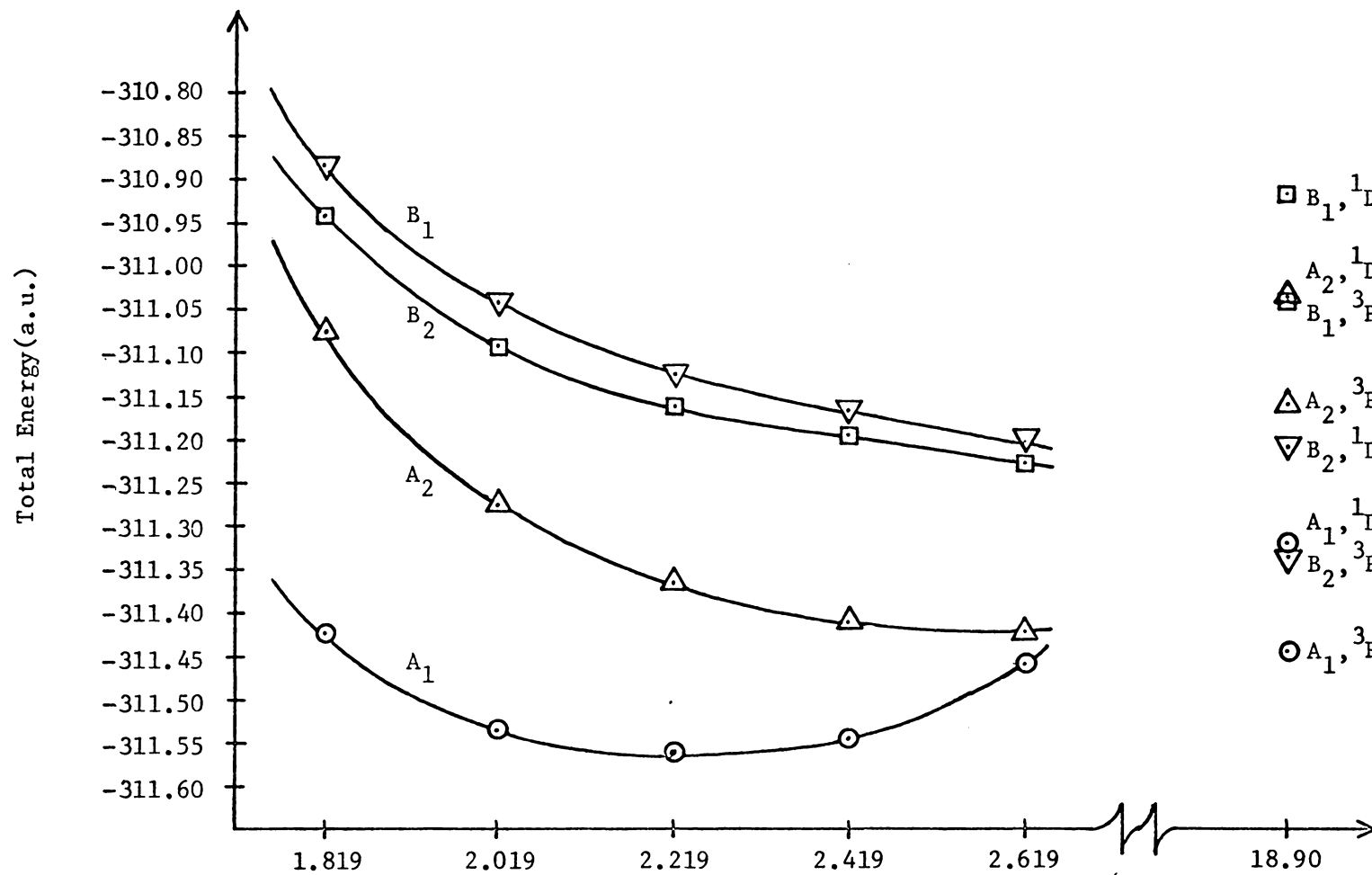


Figure 3.- Total Energy(a.u.) as a Function of Carbon-Oxygen Bond Distance(bohrs) in CF_2O

TABLE XXII

TOTAL ENERGIES (A.U.) AS FUNCTIONS OF MOLECULAR
SYMMETRY FOR THE DISSOCIATED $\text{CF}_2 + \text{O}$

<u>Molecular Symmetry</u> <u>State of CF_2</u>	<u>Atomic Symmetry</u> <u>of O</u>	<u>Total Energy</u> <u>(a.u.)</u>
A ₁	3P	-311.443844
A ₁	1D	-311.319693
A ₂	3P	-311.160710
A ₂	1D	-311.036568
B ₁	3P	-311.332431
B ₁	1D	-311.208280
B ₂	3P	-311.039037
B ₂	1D	-310.914880

The energy minima for the A_2 and B_2 states were not reached with the geometries considered; it is necessary to calculate wavefunctions at additional carbon-oxygen bond distances, but the lack of computer time prevented these additional calculations. Also additional curves should be calculated to correspond to every state for the dissociated $CF_2 + O$ geometry.

The attempts to generate the A_1 open shell ground states for the near equilibrium geometries produced surprising results. Closed shell wavefunctions resulted for all geometries with the exception of the case where the carbon-oxygen bond distance equalled 2.21858 bohrs, the equilibrium geometry. Exactly the reverse situation was anticipated since, as the carbon-oxygen bond was stretched or contracted from its equilibrium position, the electrons forming the bond should begin to take on some atomic nature, producing open shell wavefunctions. The fact that an open shell wavefunction was produced at equilibrium leads to the conclusions that open shell ground states for the A_1 symmetry should certainly exist and that an alternate procedure must be used to produce such wavefunctions. Such a procedure might be to begin a calculation using the orbitals from $CF_2 + O$ as a starting point.

Koopman's theorem⁷⁸ can be used to compare the observed ionization potentials of Thomas and Thompson³² and those calculated for the closed shell A_1 state of the equilibrium geometry. Koopman's theorem states that orbital energies or eigenvalues can be associated with the vertical ionization potentials of a molecule for which the SCF wavefunction has been obtained. The association

is made by using the highest occupied eigenvalue of the positive ion, or, alternately, multiplying the highest doubly occupied orbital eigenvalue of a given symmetry by 0.92⁷⁹ to account for the correlation energy⁸⁰ obtained on forming the positive ion. Correlation energy is the energy difference between the RHF energy and the exact nonrelativistic energy of a particular system. In the Hartree-Fock approximation scheme, the motion of each electron is solved in the presence of the average rather than the instantaneous motion of the remaining electrons. The factor of 0.92 is an attempt to empirically compensate for the lack of correlation energy in the Hartree-Fock orbitals.

Table XXIII provides a comparison between the experimental and calculated vertical ionization potentials together with the symmetries of the orbitals used to approximate the positive ion; experimental and calculated data show good agreement both numerically and in the assignments of orbital symmetries to the ionizations. However, some disagreement exists in the assignments of specific orbitals to the ionizations. The discrepancies arise because molecular orbital calculations, by their very nature, produce eigenvectors that are linear combinations of several atomic orbitals; the calculations do not restrict an eigenvector to a specific atom.

Thomas and Thompson⁷⁷ assigned the lowest experimental ionization at 13.62 electron volts (eV) to an oxygen lone pair orbital; the calculations showed this orbital was a combination of a p_y orbital on oxygen and p_z orbitals on the fluorines, $z_1 - z_2$.

TABLE XXIII

COMPARISON OF EXPERIMENTAL AND CALCULATED
VERTICAL IONIZATION POTENTIALS FOR CF_2O

<u>Experimental Ionization Potential^a(eV)</u>	<u>Orbital Eigenvalue (eV)</u>	<u>Calculated Ionization Potential (eV)</u>	<u>Symmetry of Orbital</u>
13.62	-15.40	14.17	b ₂
14.62	-15.67	14.42	b ₁
16.6	-19.10	17.57	a ₁
17.0	-20.21	18.59	a ₂

^aR. K. Thomas and H. Thompson, Proc. Royal Soc. (London)
A327, 13 (1972).

The ionization at 14.62 electron volts, attributed to a carbon-oxygen π bonding orbital, was shown to be a combination of carbon and oxygen p_x orbitals, $x_C + x_O$, and p_x orbitals on the fluorines, $x_1 + x_2$. The assignment of an ionization from an a_1 orbital to a nonbonding orbital on fluorine also disagreed; the calculations point to combinations of p_z orbitals on carbon and oxygen, $z_C - z_O$, and p_z orbitals on fluorine, $z_1 + z_2$. The ionization at 17.0 electron volts and attributed to a b_1 π orbital on fluorine agrees with the calculated combination of p_x orbitals on fluorine, $x_1 - x_2$.

Relatively few calculations have been carried out on difluorocarbene. The starting point for our calculations of the dissociated CF_2O , $CF_2 + O$, was the core Hamiltonian. The first state generated was $CF_2(A_1) + O(^3P)$. Since all occupied orbitals comprising the A_1 state of CF_2 contained two electrons, no opportunity existed for the solution of an open shell ground state. An attempt was made to begin the $CF_2(A_1)$ calculation with the B_1 orbitals from the CF_2O calculation at 2.21858 bohrs; however, this attempt failed for the lack of proper symmetry blocking of the dissociated CF_2O molecule that was discussed earlier.

The initial purpose of this work was to study the dissociation of CF_2O using spin projection of the ab initio wavefunctions. When the use of the computer program for spin projection was attempted, however, it was estimated that the spin projection calculation would take ten hours for each wavefunction on the IBM 370/158 JES2/YM machine. In comparison, the spin projection calculations for the $H_2O(+)$ wavefunctions required 5.5 minutes. Clearly the

large time requirements were unacceptable.

The computer program was then modified to provide more efficient calculation of the two-electron integrals over natural orbitals; those modifications are included in the computer program listed in Appendix A. Lack of sufficient computer time made it impossible to complete the examination of the dissociation of CF_2O at this time.

The completed study of the dissociation of CF_2O will provide electronic spectra for CF_2 and CF_2O , the dissociation energy for carbonyl fluoride and, hopefully, a reasonable picture of the potential energy surface for CF_2O . Additional curves corresponding to all states of $\text{CF}_2 + \text{O}$ are expected. The potential energy surface will further provide a good test of the utility of the spin projection technique.

XI. LITERATURE CITED

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XII. APPENDIX A

C		DAN00010
C	PA90 - SPIN PROJECTION OF UNRESTRICTED AB INITIO WAVEFUNCTIONS	DAN00020
C	WRITTEN FOR AN IBM 370/158 JES2/VM (VIRTUAL MACHINE)	DAN00030
C	COMPUTER BY DANA A. BREWER, JOHN C. SCHUG AND BYRON H.	DAN00040
C	LENGSFIELD AT VIRGINIA POLYTECHNIC INSTITUTE AND STATE	DAN00050
C	UNIVERSITY.	DAN00060
C		DAN00070
C	THIS PROGRAM CONTAINS EFFICIENCY MODIFICATIONS THAT HAVE	DAN00080
C	BEEN TESTED FOR A MOLECULE WITH C2V SYMMETRY.	DAN00090
C		DAN00100
C	THIS SPIN PROJECTION PACKAGE IS DESIGNED TO BE COMPATIBLE	DAN00110
C	WITH THE POLYATOM SYSTEM OF PROGRAMS. IT REQUIRES THAT AN	DAN00120
C	INTEGRAL TAPE BE PROVIDED IN THE FORMAT GENERATED BY THE	DAN00130
C	POLYATOM INTEGRAL EVALUATION PROGRAMS.	DAN00140
C		DAN00150
C	THE OPEN SHELL MOLECULAR ORBITALS GENERATED FROM PA43 ARE ALSO	DAN00160
C	REQUIRED. THESE MUST BE AVAILABLE IN ONE OF THREE FORMS:	DAN00170
C	1) AS CARD INPUT; 2) ON FILE 5 OF THE INTEGRAL TAPE (THE	DAN00180
C	INTEGRAL TAPE IS NOT FILE PROTECTED IN PA43); 3) ON A SEPARATE	DAN00190
C	FILE (THE INTEGRAL FILE WAS FILE PROTECTED IN PA43).	DAN00200
C		DAN00210
C	THE FINAL OUTPUT OF THE PROGRAM CONSISTS OF THE WEIGHTING	DAN00220
C	FACTORS FOR THE PROJECTED STATES, THE ALPHA CORRESPONDING	DAN00230
C	ORBITALS, THE NATURAL ORBITALS OF CHARGE AND SPIN, THE	DAN00240
C	PROJECTED ATOMIC SPIN DENSITIES, THE DIAGONAL COMPONENTS OF	DAN00250
C	THE SECOND ORDER PROJECTED CHARGE DENSITY MATRIX, AND THE	DAN00260
C	PROJECTED STATE ENERGIES.	DAN00270
C		DAN00280
C	THE PROGRAM MAKES USE OF A MINIMUM OF TWO TAPES. IF THE	DAN00290
C	INTEGRAL TAPE IS FILE PROTECTED, ONE ADDITIONAL FILE (TAPE OR	DAN00300
C	DISK) IS NEEDED.	DAN00310
C		DAN00320

C	THE SUBROUTINES USED ARE -	DAN00330
C	PURELY FOR THE SPIN PROJECTION...	DAN00340
C	PA90, WATE, F, CK, SWITCH, NOINTS	DAN00350
C	MATRIX MANIPULATION...	DAN00360
C	MTBSYM, MBTSYM, MMBAT2, MULT2, MMOVE, MMATB1, MCLEAR, MCLRT,	DAN00370
C	MABAT	DAN00380
C	MATRIX OUTPUT...	DAN00390
C	MWRITT, MWRITE, MWRITB, MPRY1, MPRY2	DAN00400
C	FILE HANDLING...	DAN00410
C	LAB, SEC, FILE, FOLLOW, EFSKIP, ABT, TEST2, ADDT	DAN00420
C	ADDITIONAL MATRIX MANIPULATION...	DAN00430
C	HDIAG, FMFUHF, FMJUHF, FMEXTB, REORD, FMDMB, FMDTB, MODBLK,	DAN00440
C	ORDREI	DAN00450
C		DAN00460
C		DAN00470
C	THE CARD INPUT IS AS FOLLOWS:	DAN00480
C		DAN00490
C	(1) ONE CARD (12A6) WITH THE LABEL OF THE PROBLEM	DAN00500
C		DAN00510
C	(2) ONE CARD (24I3) WITH THE INPUT/OUTPUT OPTIONS, ICON(1-24).	DAN00520
C	ICON(3) .LT. 0 READ MOLECULAR ORBITALS FROM CARDS	DAN00530
C	.EQ. 0 READ MOLECULAR ORBITALS FROM INTEGRAL TAPE	DAN00540
C	.GT. 0 READ MOLECULAR ORBITALS FROM FILE 12 (INTEGRAL	DAN00550
C	TAPE IS FILE PROTECTED)	DAN00560
C	ICON(4) .EQ. 0 CALCULATES A GROUND STATE WAVEFUNCTION	DAN00570
C	ICON(9) .NE. 0 PRINT CHECKSUMS FROM READING TWO-ELECTRON	DAN00580
C	INTEGRALS	DAN00590
C	ICON(10) .NE. 0 PRINTS FILE HANDLING INFORMATION	DAN00600
C		DAN00610
C	(3) ONE CARD (A6) WITH THE NAME OF THE INTEGRAL TAPE	DAN00620
C		DAN00630
C	(4) ONE CARD (D15.7) WITH CUT. TWO ELECTRON INTEGRALS WHOSE	DAN00640

C	ABSOLUTE VALUE IS LESS THAN CUT ARE IGNORED IN FORMING THE	DAN00650
C	FOCK AND NATURAL ORBITAL INTEGRAL MATRICES.	DAN00660
C		DAN00670
C	IF ICON(3) .LT. 0 GO TO 8	DAN00680
C		DAN00690
C	(5) ONE OR MORE CARDS (26I3) WITH ISYM, (NS(I), I=1,ISYM). ISYM	DAN00700
C	IS THE NUMBER OF SYMMETRY BLOCKS IN THE MOLECULAR ORBITAL	DAN00710
C	MATRIX. NS IS THE NUMBER OF MOLECULAR ORBITALS IN EACH	DAN00720
C	SYMMETRY BLOCK.	DAN00730
C		DAN00740
C	(6) AS MANY CARDS AS NEEDED (8F10.5) TO GIVE THE OCCUPATION	DAN00750
C	NUMBERS OF THE ALPHA MOLECULAR ORBITALS. FULL OCCUPANCY OF AN	DAN00760
C	ORBITAL IS 0.5. FRACTIONAL OCCUPANCY OTHER THAN 0.5 AND 0.0	DAN00770
C	IS ALLOWED.	DAN00780
C		DAN00790
C	(7) AS MANY CARDS AS NEEDED (8F10.5) TO GIVE THE OCCUPATION	DAN00800
C	NUMBERS OF THE BETA MOLECULAR ORBITALS. FULL OCCUPANCY	DAN00810
C	OF AN ORBITAL IS 0.5. FRACTIONAL OCCUPANCY OTHER THAN 0.5 AND	DAN00820
C	0.0 IS ALLOWED.	DAN00830
C		DAN00840
C	GO TO STEP 13.	DAN00850
C		DAN00860
C	(8) ONE CARD (2I3) WITH THE TOTAL NUMBER OF SYMMETRY ORBITALS, NR,	DAN00870
C	AND THE NUMBER OF BASIS FUNCTIONS, NC.	DAN00880
C		DAN00890
C	CARDS (9) AND (10) ARE REPEATED FOR EACH ITH ALPHA MOLECULAR	DAN00900
C	ORBITAL.	DAN00910
C		DAN00920
C	(9) ONE CARD (4X,I4,I2X,D15.8,F15.8) WITH IS, EA, FR. IS IS THE	DAN00930
C	NUMBER OF THE ORBITAL IN THE SYMMETRY BLOCK. EA IS THE EIGEN-	DAN00940
C	VALUE OF THE ORBITAL AND FR IS THE OCCUPATION NUMBER OF THE	DAN00950
C	ORBITAL. FRACTIONAL OCCUPANCY OTHER THAN 0.5 AND 0.0 IS	DAN00960

C	ALLOWED.	DAN00970
C		DAN00980
C	(10) AS MANY AC RDS AS NEEDED (4D15.8) TO SPECIFY THE COEFFICIENTS	DAN00990
C	OF THE ITH MOLECULAR ORBITAL. (THESE ARE COEFFICIENTS OF A	DAN01000
C	NORMALIZED BASIS FUNCTION). THE EIGENVECTORS ARE READ IN AS	DAN01010
C	ROWS.	DAN01020
C		DAN01030
C	CARDS (11) AND (12) ARE REPEATED FOR EACH JTH BETA MOLECULAR	DAN01040
C	ORBITAL.	DAN01050
C		DAN01060
C	(11) ONE CARD (20X,D15.8,F15.8) WITH EB AND FR. EB IS THE EIGEN-	DAN01070
C	VALUE OF THE JTH BETA ORBITAL. FR IS THE OCCUPANCY OF THAT	DAN01080
C	ORBITAL. FULL OCCUPANCY IS 0.5. FRACTIONAL OCCUPANCY OTHER	DAN01090
C	THAN 0.5 AND 0.0 IS ALLOWED.	DAN01100
C		DAN01110
C	(12) AS MANY CARDS AS NEEDED (4D15.8) TO SPECIFY THE COEFFICIENTS	DAN01120
C	OF THE JTH BETA MOLECULAR ORBITAL. (THESE ARE COEFFICIENTS	DAN01130
C	OF A NORMALIZED BASIS FUNCTION.) THE MOLECULAR ORBITAL	DAN01140
C	COEFFICIENTS ARE READ IN AS ROWS.	DAN01150
C		DAN01160
C	(13) ONE CARD (3I5) WITH KIKMAX, THE MAXIMUM NUMBER OF PROJECTED	DAN01170
C	STATES THAT WILL BE CALCULATED.	DAN01180
C		DAN01190
C	(14) ONE CARD (2I3) WITH THE ORBITAL NUMBERS FOR THE SINGLY	DAN01200
C	OCCUPIED ORBITALS, ASSUMING THAT THE FIRST ORBITAL OCCUPIED	DAN01210
C	IS NUMBERED ONE.	DAN01220
C		DAN01230
C	DIMENSION STATEMENTS	DAN01240
C		DAN01250
C	IMPLICIT REAL*8(A-H,O-Z)	DAN01260
C	REAL*8 ILBL,ILAB,INTNAM,INAME(6),ILABL(12)	DAN01270
C		DAN01280

C	LABELLED COMMON	DAN01290
C		DAN01300
	COMMON/ZEIT/LAPSE,LAPST	DAN01310
	COMMON/LABELS/ILBL(12),ILAB(12)	DAN01320
	COMMON/IOIND/ICON(24)	DAN01330
C		DAN01340
C	DIMENSION STATEMENTS	DAN01350
C		DAN01360
	DIMENSION R(60,60),S(60,60),T(60,60),TT(60,60)	DAN01370
	DIMENSION PKD(636),VAL(636)	DAN01380
	DIMENSION FR(60)	DAN01390
	DIMENSION RR(60,60),SS(60,60)	DAN01400
	DIMENSION TENO(3000)	DAN01410
	DIMENSION NS(60),IS(60)	DAN01420
	DIMENSION EA(60),EB(60)	DAN01430
	INTEGER D2TAPE	DAN01440
	DATA NTAPE, D2TAPE, ITAPE/10,11,12/	DAN01450
	DATA INAME/6HETA+VL,6HG-INTS,6HT-INTS,6HV-INTS,6HVYMATX,6HM-INTS/	DAN01460
C		DAN01470
C	SET MISCELLANEOUS PARAMETERS	DAN01480
C		DAN01490
	CALL ERRSET(208,500,-1,1)	DAN01500
	NRX=60	DAN01510
	NIN=636	DAN01520
	NTOP=3000	DAN01530
	AD=1.00/DSQRT(2.00)	DAN01540
	ITR=1	DAN01550
	XNA=0.00	DAN01560
	XNB=0.00	DAN01570
C		DAN01580
C	READ LABEL OF PROBLEM AND INPUT/OUTPUT OPTIONS	DAN01590
C		DAN01600

	CALL LAB	DAN01610
	READ(5,189)INTNAM	DAN01620
	CALL TEST2(NTAPE,INTNAM)	DAN01630
	IF(ICON(3).EQ.0)ITAPE=NTAPE	DAN01640
	READ(5,49)CUT	DAN01650
	WRITE(6,59)CUT	DAN01660
	IPTI=ICON(9)	DAN01670
C		DAN01680
C	DA=R DB=S DT=T NC=NBFS	DAN01690
C		DAN01700
C		DAN01710
C	READ MOLECULAR ORBITALS	DAN01720
C		DAN01730
	IF(ICON(3))5,15,25	DAN01740
25	REWIND ITAPE	DAN01750
	GO TO 35	DAN01760
15	CALL FILE(INAME(5),NTAPE,ILABL)	DAN01770
35	READ(ITAPE)	DAN01780
	READ(ITAPE)	DAN01790
	READ(ITAPE)NR,(EA(I),I=1,NR)	DAN01800
	READ(ITAPE)NRR,NC,((S(I,J),J=1,NC),I=1,NRR)	DAN01810
	READ(ITAPE)NRR,(EB(I),I=1,NRR)	DAN01820
	READ(ITAPE)NRR,NCC,((TT(I,J),J=1,NCC),I=1,NRR)	DAN01830
	READ(5,199)ISYM,(NS(I),I=1,ISYM)	DAN01840
	READ(5,179)(FR(I),I=1,NR)	DAN01850
	DO 70 I=1,NR	DAN01860
70	XNA=XNA+2.DO*FR(I)	DAN01870
	NA=XNA+0.01	DAN01880
	GO TO 45	DAN01890
5	READ(5,199)NR,NC	DAN01900
	DO 10 I=2,NRX	DAN01910
10	NS(I)=0	DAN01920

DO 60 I=1, NR	DAN01930
READ(5,249) IS(I), EA(I), FR(I)	DAN01940
60 READ(5,219) (S(I,J), J=1, NC)	DAN01950
WRITE(D2TAPE) ((S(I,J), J=1, NC), I=1, NR)	DAN01960
ISYM=1	DAN01970
NS(1)=1	DAN01980
DO 40 I=1, NR	DAN01990
40 XNA=XNA+2.DO*FR(I)	DAN02000
NA=XNA+0.01	DAN02010
DO 50 I=2, NR	DAN02020
IM=I-1	DAN02030
IF(IS(I).LE.IS(IM)) GO TO 55	DAN02040
NS(ISYM)=NS(ISYM)+1	DAN02050
GO TO 50	DAN02060
55 ISYM=ISYM+1	DAN02070
NS(ISYM)=NS(ISYM)+1	DAN02080
50 CONTINUE	DAN02090
45 CALL MPRY1(S, EA, FR, 6HALPHA, 6HORBITA, 6HLS, 1, NC, NR, NRX)	DAN02100
C	DAN02110
C FORM ALPHA DENSITY MATRIX, DA	DAN02120
C	DAN02130
CALL FMDMB(S, R, FR, 2.0, NR, NC, NRX)	DAN02140
CALL MCLEAR(T, NC, NC, NRX)	DAN02150
C	DAN02160
C FORM SYMMETRY BLOCKING TRANSFORMATION MATRIX	DAN02170
C	DAN02180
CALL ADDT(INAME(2), NTAPE, ILABL, T, NRX, PKD, VAL, NIN)	DAN02190
CALL MTBSYM(T, NC, NRX)	DAN02200
CALL MMBAT2(T, S, NC, NC, NR, EA, NRX)	DAN02210
WRITE(D2TAPE) NR, NC, ((S(I,J), J=1, NC), I=1, NR)	DAN02220
C	DAN02230
C READ BETA MOLECULAR ORBITALS	DAN02240

C		DAN02250
	IF(ICON(3))85,95,95	DAN02260
85	DO 90 I=1,NR	DAN02270
	READ(5,209)EA(I),FR(I)	DAN02280
90	READ(5,219)(T(I,J),J=1,NC)	DAN02290
	GO TO 105	DAN02300
95	DO 100 I=1,NR	DAN02310
	EA(I)=EB(I)	DAN02320
	DO 100 J=1,NC	DAN02330
100	T(I,J)=TT(I,J)	DAN02340
	READ(5,179)(FR(I),I=1,NR)	DAN02350
105	DO 75 I=1,NR	DAN02360
75	XNB=XNB+2.DO*FR(I)	DAN02370
	NB=XNB+0.01	DAN02380
C		DAN02390
C	FORM BETA DENSITY MATRIX, DB	DAN02400
C		DAN02410
	CALL MPRY1(T,EA,FR,6HBETA ,6HORBITA,6HLS ,1,NC,NR,NRX)	DAN02420
	CALL FMDMB(T,S,FR,2.0,NR,NC,NRX)	DAN02430
	CALL FMDTB(R,S,T,1.0,NC,NRX)	DAN02440
	WRITE(D2TAPE)NC,((R(I,J),J=1,I),I=1,NC)	DAN02450
	WRITE(D2TAPE)NC,((S(I,J),J=1,I),I=1,NC)	DAN02460
	WRITE(D2TAPE)NC,((T(I,J),J=1,I),I=1,NC)	DAN02470
	DO 30 I=1,NRX	DAN02480
30	FR(I)=1.DO	DAN02490
	CALL MBTSYM(R,NC,NRX)	DAN02500
	CALL MBTSYM(S,NC,NRX)	DAN02510
	CALL MBTSYM(T,NC,NRX)	DAN02520
	CALL MWRTB(R,6HALPHA ,6HDENSIT,6HY MATX,0,NC,NRX)	DAN02530
	CALL MWRTB(S,6HBETA D,6HENSITY,6H MATRX,0,NC,NRX)	DAN02540
	CALL MWRTB(T,6HTOTAL ,6HDENSIT,6HY MATX,0,NC,NRX)	DAN02550
	CALL SEC(6HREAD D,6HENSITY,6H MATRX)	DAN02560

C		DAN02570
C	FORM KINETIC ENERGY MATRIX IN TT	DAN02580
C		DAN02590
	CALL MCLRT(TT,NC,NRX)	DAN02600
	CALL ADDT(INAME(3),NTAPE,ILABL,TT,NRX,PKD,VAL,NIN)	DAN02610
C		DAN02620
C	CALCULATE EXPECTATION VALUE OF T WITH DT;	DAN02630
C	EXPECTATION VALUE STORED IN XK	DAN02640
C		DAN02650
	CALL FMEXTB(TT,T,NC,NRX,1.0,XK)	DAN02660
C		DAN02670
C	ADD POTENTIAL ENERGY TO KINETIC ENERGY	DAN02680
C		DAN02690
	CALL ADDT(INAME(4),NTAPE,ILABL,TT,NRX,PKD,VAL,NIN)	DAN02700
C		DAN02710
C	CALCULATE EXPECTATION VALUE OF T+V WITH DT	DAN02720
C	STORE THIS VALUE IN XH	DAN02730
C		DAN02740
	CALL FMEXTB(TT,T,NC,NRX,1.0,XH)	DAN02750
	CALL SEC(6HREAD 1,6H-ELEC ,6HINTS)	DAN02760
	XKE=XH-XK	DAN02770
C		DAN02780
C	READ (FROM INTEGRAL TAPE) THE NUCLEAR REPULSION ENERGY	DAN02790
C	STORED IN EN	DAN02800
C		DAN02810
	CALL FILE(INAME(1),NTAPE,ILABL)	DAN02820
	READ(NTAPE)	DAN02830
	READ(NTAPE)	DAN02840
	READ(NTAPE)	DAN02850
	READ(NTAPE)EN	DAN02860
C		DAN02870
C	FORM MATRIX FT IN TT BY FORMING AND ADDING JT TO H ALREADY IN	DAN02880

C	TT. ALSO FORM KA IN RR AND KB IN SS.	DAN02890
C	FT=H+JT	DAN02900
C	JT(I,J)=SUM(OVER K,L) DT(K,L) * (IJ,KL)	DAN02910
C	KA(I,J)=SUM(OVER K,L) DA(K,L) * (IK,JL)	DAN02920
C	KB(I,J)=SUM(OVER K,L) DB(K,L) * (IK,JL)	DAN02930
C	FIRST RETAIN THE CORE HAMILTONIAN	DAN02940
C		DAN02950
C	WRITE(D2TAPE)NC,((TT(I,J),I=1,J),J=1,NC)	DAN02960
C	CALL MCLRT(RR,NC,NRX)	DAN02970
C	CALL MCLRT(SS,NC,NRX)	DAN02980
C	CALL FMJUHF(TT,RR,SS,T,R,S,NC,NRX,INAME(6),NTAPE,ILABL,PKD,VAL,NINDAN02990	
C	1,IPTI,CUT,IX)	DAN03000
C	CALL SEC(6HREAD 2,6H-ELEC ,6HINTS)	DAN03010
C	CALL MWRITT(TT,6H JT+H,6H FT MA,6HTRIX ,ITR,NC,NRX)	DAN03020
C	CALL MWRITT(RR,6H KALPHA,6H KA MA,6HTRIX ,ITR,NC,NRX)	DAN03030
C	CALL MWRITT(SS,6H KBETA,6H KB MA,6HTRIX ,ITR,NC,NRX)	DAN03040
C		DAN03050
C	FORM ALPHA AND BETA UHF HAMILTONIAN MATRICES, FA AND FB,	DAN03060
C	IN RR AND SS RESPECTIVELY	DAN03070
C	FA = FT - KA = H + JT - KA	DAN03080
C	FB = FT - KB = H + JT - KB	DAN03090
C		DAN03100
C	CALL FMFUHF(RR,SS,TT,NC,NRX)	DAN03110
C		DAN03120
C	COMPUTE EXPECTATION VALUES OF FA WITH DA AND FB WITH DB	DAN03130
C		DAN03140
C	CALL FMEXTB(RR,R,NC,NRX,1.0,XFA)	DAN03150
C	CALL FMEXTB(SS,S,NC,NRX,1.0,XFB)	DAN03160
C	XF=XFA+XFB	DAN03170
C	WRITE(6,9)XK	DAN03180
C	WRITE(6,29)XKE	DAN03190
C	WRITE(6,19)XH	DAN03200

	EPI2=0.5D0*(XF-XH)	DAN03210
	WVE33=XKE+EPI2	DAN03220
	WE33=XH+EPI2	DAN03230
	WV33=XKE+EPI2+EN	DAN03240
	W33=WE33+EN	DAN03250
	WRITE(6,69)EPI2	DAN03260
	WRITE(6,79)WVE33	DAN03270
	WRITE(6,89)WE33	DAN03280
	WRITE(6,39)EN	DAN03290
	WRITE(6,129)WV33	DAN03300
	WRITE(6,149)W33	DAN03310
C		DAN03320
C	OBTAIN SYMMETRY BLOCKING TRANSFORMATION MATRIX.	DAN03330
C	STORE IN RR	DAN03340
C		DAN03350
	REWIND D2TAPE	DAN03360
	IF(ICON(3))165,175,175	DAN03370
165	READ(D2TAPE)	DAN03380
175	READ(D2TAPE)NRR,NCC,((RR(I,J),J=1,NCC),I=1,NRR)	DAN03390
	READ(D2TAPE)NCC,((R(J,I),J=1,I),I=1,NCC)	DAN03400
C		DAN03410
C	SYMMETRY BLOCK DA AND DB	DAN03420
C		DAN03430
	READ(D2TAPE)NCC,((S(J,I),J=1,I),I=1,NCC)	DAN03440
	CALL MABAT(RR,R,NR,NC,TT,NRX)	DAN03450
	CALL MABAT(RR,S,NR,NC,TT,NRX)	DAN03460
	CALL MTBSYM(R,NR,NRX)	DAN03470
	CALL MTBSYM(S,NR,NRX)	DAN03480
C		DAN03490
C	FORM DA*DB*DA IN ORTHOGONAL BASIS REPRESENTATION.	DAN03500
C		DAN03510
	CALL MULT2(S,R,TT,NR,NRX)	DAN03520

	CALL MULT2(R,TT,SS,NR,NRX)	DAN03530
C		DAN03540
C	FORM SPIN DENSITY MATRIX IN ORTHOGONAL BASIS	DAN03550
C		DAN03560
	DO 80 I=1,NR	DAN03570
	DO 80 J=1,NR	DAN03580
	80 T(I,J)=R(I,J)-S(I,J)	DAN03590
	IF(ICON(3))115,125,135	DAN03600
135	REWIND ITAPE	DAN03610
	GO TO 145	DAN03620
125	CALL FILE(INAME(5),NTAPE,ILABL)	DAN03630
145	READ(ITAPE)	DAN03640
	READ(ITAPE)	DAN03650
	READ(ITAPE)	DAN03660
	READ(ITAPE)NRR,NCC,((S(I,J),J=1,NCC),I=1,NRR)	DAN03670
	GO TO 155	DAN03680
115	REWIND D2TAPE	DAN03690
	READ(D2TAPE)((S(I,J),J=1,NC),I=1,NR)	DAN03700
	READ(D2TAPE)	DAN03710
	READ(D2TAPE)	DAN03720
	READ(D2TAPE)	DAN03730
155	CONTINUE	DAN03740
C		DAN03750
C	FORM ALPHA CORRESPONDING ORBITALS	DAN03760
C		DAN03770
	CALL MODBLK(RR,SS,TT,NS,EA,EB,S,NR,NC,NRX,6HA.C.D.,0,0)	DAN03780
	CALL REORD(SS,TT,EB,EA,NR,NC,NRX)	DAN03790
	CALL MMOVE(SS,TT,NR,NC,NRX)	DAN03800
	CALL MPRY1(TT,EB,FR,6HALPHA,6H CORR.,6HORBS.,0,NC,NR,NRX)	DAN03810
	CALL SEC(6H CALC A,6HLFA CC,6HRR ORB)	DAN03820
C		DAN03830
C	FORM NATURAL ORBITALS OF SPIN AND STORE IN TENO	DAN03840

C		DAN03850
	CALL MODBLK(RR,T,R,NS,FR,EA,S,NR,NC,NRX,6HN.D.S.,0,0)	DAN03860
	CALL REORD(T,R,EA,FR,NR,NC,NRX)	DAN03870
	CALL MPRY1(T,EA,FR,6HNATL 0,6HRBS OF,6H SPIN ,0,NC,NR,NRX)	DAN03880
	CALL SEC(6HCALC N,6HATL OR,6HB SPIN)	DAN03890
	AD=1.00/DSQRT(2.00)	DAN03900
	DO 20 I=1,NC	DAN03910
	TENO(I)=AD*(T(NC,I)+T(1,I))	DAN03920
	20 TENO(NC+I)=AD*(T(NC,I)-T(1,I))	DAN03930
C		DAN03940
C	FORM NATURAL ORBITALS OF CHARGE	DAN03950
C		DAN03960
	READ(D2TAPE)NCC,((T(J,I),J=1,I),I=1,NCC)	DAN03970
	CALL MABAT(RR,T,NR,NC,SS,NRX)	DAN03980
	CALL MODBLK(RR,T,R,NS,FR,EA,S,NR,NC,NRX,6HN.U.C.,0,0)	DAN03990
	CALL REORD(T,R,EA,FR,NR,NC,NRX)	DAN04000
	CALL MMOVE(T,R,NR,NC,NRX)	DAN04010
	CALL MPRY1(R,EA,FR,6HNATL 0,6HRBS OF,6H CHG ,0,NC,NR,NRX)	DAN04020
	CALL SEC(6HCALC N,6HATL OR,6HBS CHG)	DAN04030
C		DAN04040
C	SWITCH ROWS AND COLUMNS.	DAN04050
C	THE SPIN PROJECTION IS PERFORMED WITH THE ORBITALS AS	DAN04060
C	COLUMNS.	DAN04070
C		DAN04080
	CALL SWITCH(TT,T,NR,NC,NRX)	DAN04090
	CALL SWITCH(R,T,NR,NC,NRX)	DAN04100
	CALL MCLEAR(S,NRX,NRX,NRX)	DAN04110
	CALL MCLEAR(T,NRX,NRX,NRX)	DAN04120
	CALL MCLEAR(SS,NRX,NRX,NRX)	DAN04130
	READ(D2TAPE)NCC,((RR(I,J),J=1,I),I=1,NCC)	DAN04140
	CALL MWRITB(RR,6HCORE H,6HAMILTO,6HNIAN ,1,NC,NRX)	DAN04150
	CALL MBTSYM(RR,NC,NRX)	DAN04160


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REWIND D2TAPE
C
C          READY TO PERFORM SPIN PROJECTION
C          MATRIX OCCUPATION (IN ATOMIC BASIS):
C          TT = A.C.D. EIGENVECTORS
C          EB = A.C.D. EIGENVALUES
C          R = N.O.C. EIGENVECTORS
C          EA = N.O.C. EIGENVALUES
C          T = EMPTY
C          X = EMPTY
C          S = EMPTY
C          RR = CORE HAMILTONIAN
C          SS = EMPTY
C          XI = EMPTY
C
          CALL WATE(S,SS,R,TT,RR,TENO,EB,T(1,1),T(1,2),T(1,3),T(1,4),EA,T(1,
          15),T(1,6),T(1,7),T(1,8),T(1,9),T(1,10),PKD,VAL,CUT,EN,INAME,NTAPE,
          INRX,NTOP,NIN,NC,NA,NB,NR)
          CALL FOLLOW
          9 FORMAT(' ', ' KINETIC ENERGY, T = ', 30X, 1PD20.10)
          19 FORMAT(' ', ' ONE ELECTRON ENERGY, H = T+V(1) = ', 16X, 1PD20.10)
          29 FORMAT(' ', ' ONE ELECTRON POTENTIAL ENERGY, V(1) = ', 12X, 1PD20.10)
          39 FORMAT(' ', ' NUCLEAR REPULSION ENERGY, V(N) = ', 17X, 1PD20.10)
          49 FORMAT(D15.7)
          59 FORMAT('0', 'TWO-ELECTRON INTEGRAL CUTOFF = ', 1PD12.4)
          69 FORMAT(' ', ' TWO ELECTRON POTENTIAL ENERGY, V(1,2) = ', 10X,
          11PD20.10)
          79 FORMAT(' ', ' ELECTRONIC POTENTIAL ENERGY, V(E) = V(1)+V(1,2) = ',
          11PD20.10)
          89 FORMAT(' ', ' ELECTRONIC ENERGY, E(E) = H+V(1,2) = ', 13X, 1PD20.10)
          129 FORMAT(' ', ' POTENTIAL ENERGY, V = V(E)+V(N) = ', 16X, 1PD20.10)
          149 FORMAT(' ', ' TOTAL ENERGY, E = E(E)+V(N) = ', 20X, 1PD20.10)

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DAN04170
DAN04180
DAN04190
DAN04200
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DAN04400
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DAN04440
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DAN04460
DAN04470
DAN04480

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169	FORMAT('0','READ ERROR ON D2TAPE')	DAN04490
179	FORMAT(8F10.5)	DAN04500
189	FORMAT(A6)	DAN04510
199	FORMAT(26I3)	DAN04520
209	FORMAT(20X,D15.8,F15.8)	DAN04530
219	FORMAT(4D15.8)	DAN04540
229	FORMAT('0','NUMBER OF ROWS IN BETA MOLECULAR ORBITALS .NE. NUMBER	DAN04550
	1 OF ROWS IN ALPHA MOLECULAR ORBITALS')	DAN04560
239	FORMAT('0','NUMBER OF COLUMNS IN BETA MOLECULAR ORBITALS .NE. NO	DAN04570
	1 F COLUMNS IN ALPHA MOLECULAR ORBITALS')	DAN04580
249	FORMAT(4X,14,12X,D15.8,F15.8)	DAN04590
	STOP	DAN04600
	END	DAN04610
	BLOCK DATA	DAN04620
	REAL*8 ILAB,ILBL	DAN04630
	COMMON/LABELS/ILBL(12),ILAB(12)	DAN04640
	DATA ILAB/6H PA90 ,6H UNRE,6HSTRICT,6HED HAR,6HTREE-F,6HOCK SP,6HDAN04650	
	1 IN PRO,6HJECTIO,6HN METH,6HOD L.C,6H.A.O. ,6HTEST /	DAN04660
	END	DAN04670
CNGINTS	SUBROUTINE NOINTS	DAN04680
	SUBROUTINE NOINTS(EA,PKLABL,VALUEM,C,T,CUTLO,INAME,NB,MNM,MO,M,NINDAN04690	
	ITS,NINMAX,NRX,NTOP,NTAPE)	DAN04700
	IMPLICIT REAL *8(A-H,O-Z)	DAN04710
	DIMENSION PKLABL(NINMAX),VALUEM(NINMAX),C(NRX,NRX),T(NTOP)	DAN04720
	DIMENSION EA(NRX)	DAN04730
	DIMENSION IPRT(36)	DAN04740
	REAL *8 INTNAM,INAME,ILAB,ILABL(12)	DAN04750
	COMMON/IOIND/ICON(24)	DAN04760
	COMMON/LABELS/ILBL(12),ILAB(12)	DAN04770
	DIMENSION INAME(6)	DAN04780
	NRENT=0	DAN04790
	NMINNW=0	DAN04800

	IRC=1	DAN04810
	IFLAG=0	DAN04820
	IPTI=ICON(9)	DAN04830
C		DAN04840
C	PRINT HEADER IF CHECK SUM FLAG IS ON	DAN04850
C		DAN04860
	IF(IPTI.EQ.0)GO TO 70	DAN04870
	WRITE(6,19)	DAN04880
70	CONTINUE	DAN04890
	READ(5,59)NSING1,NSING2	DAN04900
59	FORMAT(2I3)	DAN04910
	DD 40 I=1,NTOP	DAN04920
40	T(I)=0.D0	DAN04930
C		DAN04940
C	POSITION TAPE TO READ TWO-ELECTRON INTEGRALS	DAN04950
C		DAN04960
	CALL FILE(INAME(6),NTAPE,ILABL)	DAN04970
20	IF(IFLAG)21,21,76	DAN04980
21	READ(NTAPE)NINTS,LSTRCD,PKLABL,VALUEM	DAN04990
	IF(LSTRCD.NE.0)IFLAG=1	DAN05000
	NRECNT=NRECNT+1	DAN05010
	NMINNW=NMINNW+NINTS	DAN05020
	IF(IPTI.EQ.0)GO TO 75	DAN05030
	IF(IRC.EQ.1)IPRT(1)=NRECNT	DAN05040
	CALL UNPACK(PKLABL(1),IA,JA,KA,LA,IZ,ITA)	DAN05050
	CALL UNPACK(PKLABL(NINTS),IB,JB,KB,LB,IZ,ITB)	DAN05060
	IPRT(IRC+1)=JA	DAN05070
	IPRT(IRC+2)=LA	DAN05080
	IPRT(IRC+3)=NINTS	DAN05090
	IPRT(IRC+4)=JB	DAN05100
	IPRT(IRC+5)=LB	DAN05110
	IRC=IRC+5	DAN05120

IF(IRC.LT.36)GO TO 75	DAN05130
WRITE(6,29)(IPRT(MN),MN=1,IRC)	DAN05140
IRC=1	DAN05150
75 IF(NINTS.GT.NINMAX.OR.NINTS.LE.0)GO TO 30	DAN05160
MN1=1	DAN05170
55 XI=VALUEM(MN1)	DAN05180
JCTR=1	DAN05190
CALL UNPACK(PKLABL(MN1),I1,J1,K1,L1,MU,IZ)	DAN05200
52 IF(MN1.EQ.NINTS)GO TO 50	DAN05210
53 IF(MN1.GE.NINTS)GO TO 50	DAN05220
CALL UNPACK(PKLABL(MN1+1),I2,J2,K2,L2,MU2,IZ2)	DAN05230
IF(IZ2)51,50,51	DAN05240
51 JCTR=JCTR+1	DAN05250
MN1=MN1+1	DAN05260
GO TO 53	DAN05270
50 IF(DABS(XI).LT.CUTLG)GO TO 10	DAN05280
XI=XI*JCTR	DAN05290
C	DAN05300
C	DAN05310
C	DAN05320
SKIP THE INTEGRAL IF ITS VALUE IS SMALL	DAN05330
X2=2.D0*X1	DAN05340
X4=4.D0*X1	DAN05350
X8=8.D0*X1	DAN05360
GO TO (1100,200,300,400,500,700,600,600,100,100,100,100,100,100),	DAN05370
1MU	DAN05380
100 J=0	DAN05390
DO 140 K=1,NB	DAN05400
KP=M-K+1	DAN05410
A1=C(I1,K)	DAN05420
A2=C(J1,K)	DAN05430
A3=C(K1,K)	DAN05440
A4=C(L1,K)	

118	IF(DABS(A1).LE.1.D-08.OR.DABS(A2).LE.1.D-08.AND.K.NE.NSING1)	DAN05450
	1GO TO 116	DAN05460
	IF(DABS(A1).LE.1.D-08.OR.DABS(A2).LE.1.D-08.AND.K.NE.NSING2)	DAN05470
	1GO TO 116	DAN05480
	IF(DABS(A3).LE.1.D-08.OR.DABS(A4).LE.1.D-08.AND.K.NE.NSING2)	DAN05490
	1GO TO 115	DAN05500
	IF(DABS(A3).LE.1.D-08.OR.DABS(A4).LE.1.D-08.AND.K.NE.NSING1)	DAN05510
	1GO TO 115	DAN05520
	GO TO 117	DAN05530
116	J=J+1	DAN05540
	P1=0.D0	DAN05550
	P2=A3*A4	DAN05560
	IF(K.LT.MNM)GO TO 110	DAN05570
	IF(EA(K).GT.1.999999)GO TO 110	DAN05580
	J=J+3	DAN05590
	A5=C(I1,KP)	DAN05600
	A6=C(J1,KP)	DAN05610
	A7=C(K1,KP)	DAN05620
	A8=C(L1,KP)	DAN05630
	P3=0.D0	DAN05640
	P4=A7*A8	DAN05650
	P31=0.D0	DAN05660
	P32=0.D0	DAN05670
	P33=A3*A8	DAN05680
	P34=A4*A7	DAN05690
	GO TO 110	DAN05700
115	J=J+1	DAN05710
	P1=A1*A2	DAN05720
	P2=0.D0	DAN05730
	IF(K.LT.MNM)GO TO 110	DAN05740
	IF(EA(K).GT.1.999999)GO TO 110	DAN05750
	J=J+3	DAN05760

```

A5=C(I1,KP)
A6=C(J1,KP)
A7=C(K1,KP)
A8=C(L1,KP)
P3=A5*A6
P4=0.00
P31=A1*A6
P32=A2*A5
P33=0.00
P34=0.00
GO TO 110
117 P1=A1*A2
P2=A3*A4
J=J+1
T(J)=T(J)+X8*P1*P2
IF(K.LT.MNM)GO TO 110
IF(EA(K).GT.1.999999)GO TO 110
A5=C(I1,KP)
A6=C(J1,KP)
A7=C(K1,KP)
A8=C(L1,KP)
P3=A5*A6
P4=A7*A8
P31=A1*A6
P32=A2*A5
P33=A3*A8
P34=A4*A7
Q=(P31+P32)*(P33+P34)
J=J+1
T(J)=X8*P3*P4+T(J)
J=J+1
T(J)=T(J)+X4*Q

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DAN05770
DAN05780
DAN05790
DAN05800
DAN05810
DAN05820
DAN05830
DAN05840
DAN05850
DAN05860
DAN05870
DAN05880
DAN05890
DAN05900
DAN05910
DAN05920
DAN05930
DAN05940
DAN05950
DAN05960
DAN05970
DAN05980
DAN05990
DAN06000
DAN06010
DAN06020
DAN06030
DAN06040
DAN06050
DAN06060
DAN06070
DAN06080

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      J=J+1
      T(J)=T(J)+X8*(P1*P4+P2*P3)
110  KAND=K+1
      IF(K.EQ.NB)GO TO 130
      DO 120 LN=KAND,NB
      LP=M-LN+1
      A9=C(I1,LN)
      A10=C(J1,LN)
      A11=C(K1,LN)
      A12=C(L1,LN)
      P7=A11*A12
      P8=A9*A10
      P13=A1*A10
      P14=A2*A9
      P15=A11*A4
      P16=A12*A3
      J=J+1
      T(J)=T(J)+X8*(P1*P7+P2*P8)
      J=J+1
      T(J)=T(J)+X4*(P13+P14)*(P15+P16)
      IF(LN.LT.MNM)GO TO 120
      IF(EA(LN).GT.1.999999)GO TO 120
      A13=C(I1,LP)
      A14=C(J1,LP)
      A15=C(K1,LP)
      A16=C(L1,LP)
      P5=A15*A16
      P6=A13*A14
      P9=A1*A14
      P10=A13*A2
      P11=A15*A4
      P12=A16*A3

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DAN06090
DAN06100
DAN06110
DAN06120
DAN06130
DAN06140
DAN06150
DAN06160
DAN06170
DAN06180
DAN06190
DAN06200
DAN06210
DAN06220
DAN06230
DAN06240
DAN06250
DAN06260
DAN06270
DAN06280
DAN06290
DAN06300
DAN06310
DAN06320
DAN06330
DAN06340
DAN06350
DAN06360
DAN06370
DAN06380
DAN06390
DAN06400

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P17=A7*A16	DAN06410
P18=A8*A15	DAN06420
P19=A13*A6	DAN06430
P20=A5*A14	DAN06440
J=J+1	DAN06450
T(J)=T(J)+X8*(P1*P5+P2*P6)	DAN06460
J=J+1	DAN06470
T(J)=T(J)+X4*(P9+P10)*(P11+P12)	DAN06480
IF(K.LT.MNM)GO TO 120	DAN06490
IF(EA(K).GT.1.999999)GO TO 120	DAN06500
P35=A9*A6	DAN06510
P36=A5*A10	DAN06520
P37=A7*A12	DAN06530
P38=A8*A11	DAN06540
J=J+1	DAN06550
T(J)=T(J)+X8*(P3*P4+P7*P3)	DAN06560
J=J+1	DAN06570
T(J)=T(J)+X4*(P35+P36)*(P37+P38)	DAN06580
J=J+1	DAN06590
T(J)=T(J)+X8*(P3*P5+P4*P6)	DAN06600
J=J+1	DAN06610
T(J)=T(J)+X4*(P19+P20)*(P17+P18)	DAN06620
J=J+1	DAN06630
T(J)=T(J)+X4*((P9+P10)*(P37+P38)+(P12+P11)*(P35+P36))	DAN06640
J=J+1	DAN06650
T(J)=T(J)+X4*((P13+P14)*(P17+P18)+(P15+P16)*(P19+P20))	DAN06660
120 CONTINUE	DAN06670
130 IF(MO.LE.0)GO TO 140	DAN06680
DO 135 LQ=1,MO	DAN06690
LN=LQ+NB	DAN06700
A9=C(I1,LN)	DAN06710
A10=C(J1,LN)	DAN06720

A11=C(K1, LN)	DAN06730
A12=C(L1, LN)	DAN06740
P21=A11*A12	DAN06750
P22=A9*A10	DAN06760
P23=A1*A10	DAN06770
P24=A9*A2	DAN06780
P27=A11*A4	DAN06790
P28=A12*A3	DAN06800
J=J+1	DAN06810
T(J)=T(J)+X8*(P1*P21+P2*P22)	DAN06820
J=J+1	DAN06830
T(J)=T(J)+X4*(P23+P24)*(P27+P28)	DAN06840
IF(K.LT.MNM)GO TO 135	DAN06850
IF(EA(K).GT.1.999999)GO TO 135	DAN06860
P25=A11*A8	DAN06870
P26=A7*A12	DAN06880
P29=A5*A10	DAN06890
P30=A6*A9	DAN06900
J=J+1	DAN06910
T(J)=T(J)+X8*(P3*P21+P4*P22)	DAN06920
J=J+1	DAN06930
T(J)=T(J)+X4*(P29+P30)*(P25+P26)	DAN06940
J=J+1	DAN06950
T(J)=T(J)+X4*((P23+P24)*(P25+P26)+(P27+P28)*(P29+P30))	DAN06960
135 CONTINUE	DAN06970
140 CONTINUE	DAN06980
IF(MO.LE.1)GO TO 160	DAN06990
DO 150 KQ=1,MO	DAN07000
K=KQ+NB	DAN07010
IF(KQ.EQ.MO)GO TO 150	DAN07020
KQ1=KQ+1	DAN07030
DO 145 LQ=KQ1,MO	DAN07040

LN=LQ+NB	DAN07050
A1=C(I1,K)	DAN07060
A2=C(J1,K)	DAN07070
A3=C(K1,K)	DAN07080
A4=C(L1,K)	DAN07090
A9=C(I1,LN)	DAN07100
A10=C(J1,LN)	DAN07110
A11=C(K1,LN)	DAN07120
A12=C(L1,LN)	DAN07130
J=J+1	DAN07140
T(J)=T(J)+X8*(A1*A2*A11*A12+A3*A4*A9*A10)	DAN07150
J=J+1	DAN07160
145 T(J)=T(J)+X4*(A1*A10+A9*A2)*(A11*A4+A12*A3)	DAN07170
150 CONTINUE	DAN07180
160 GO TO 6000	DAN07190
200 J=0	DAN07200
DO 240 K=1,NB	DAN07210
KP=M-K+1	DAN07220
A1=C(I1,K)	DAN07230
A2=C(J1,K)	DAN07240
218 IF(DABS(A1).LE.1.D-08.OR.DABS(A2).LE.1.D-08.AND.K.NE.NSING1)	DAN07250
1GO TO 216	DAN07260
IF(DABS(A1).LE.1.D-08.OR.DABS(A2).LE.1.D-08.AND.K.NE.NSING2)	DAN07270
1GO TO 216	DAN07280
GO TO 217	DAN07290
216 J=J+1	DAN07300
P1=0.D0	DAN07310
IF(K.LT.MNM)GO TO 210	DAN07320
IF(EA(K).GT.1.999999)GO TO 210	DAN07330
J=J+3	DAN07340
A5=C(I1,KP)	DAN07350
A6=C(J1,KP)	DAN07360

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P3=0.D0
P31=0.D0
P32=0.D0
GO TO 210
217 P1=A1*A2
J=J+1
T(J)=T(J)+X4*P1*P1
IF(K.LT.MNM)GO TO 210
IF(EA(K).GT.1.999999)GO TO 210
A5=C(I1,KP)
A6=C(J1,KP)
P3=A5*A6
P31=A1*A6
P32=A2*A5
Q=(P31+P32)**2
J=J+1
T(J)=T(J)+X4*P3*P3
J=J+1
T(J)=T(J)+X2*Q
J=J+1
T(J)=T(J)+X8*P1*P3
210 KAND=K+1
IF(K.EQ.NB)GO TO 230
DO 220 LN=KAND,NB
LP=M-LN+1
A9=C(I1,LN)
A10=C(J1,LN)
P7=A9*A10
P13=A1*A10
P14=A2*A9
J=J+1
T(J)=T(J)+X8*P1*P7

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DAN07370
DAN07380
DAN07390
DAN07400
DAN07410
DAN07420
DAN07430
DAN07440
DAN07450
DAN07460
DAN07470
DAN07480
DAN07490
DAN07500
DAN07510
DAN07520
DAN07530
DAN07540
DAN07540
DAN07550
DAN07560
DAN07570
DAN07580
DAN07590
DAN07600
DAN07610
DAN07620
DAN07630
DAN07640
DAN07650
DAN07660
DAN07670
DAN07680

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J=J+1
T(J)=T(J)+X2*(P13+P14)**2
IF(LN.LT.MNM)GO TO 220
IF(EA(LN).GT.1.999999)GO TO 220
A13=C(I1,LP)
A14=C(J1,LP)
P5=A13*A14
P9=A1*A14
P10=A13*A2
P17=A5*A14
P18=A6*A13
J=J+1
T(J)=T(J)+X8*P1*P5
J=J+1
T(J)=T(J)+X2*(P9+P10)**2
IF(K.LT.MNM)GO TO 220
IF(EA(K).GT.1.999999)GO TO 220
P35=A9*A6
P36=A5*A10
J=J+1
T(J)=T(J)+X8*P3*P7
J=J+1
T(J)=T(J)+X2*(P35+P36)**2
J=J+1
T(J)=T(J)+X8*P3*P5
J=J+1
T(J)=T(J)+X2*(P17+P18)**2
J=J+1
T(J)=T(J)+X4*(P9+P10)*(P35+P36)
J=J+1
T(J)=T(J)+X4*(P13+P14)*(P17+P18)

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220

CONTINUE

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DAN07690
DAN07700
DAN07710
DAN07720
DAN07730
DAN07740
DAN07750
DAN07760
DAN07770
DAN07780
DAN07790
DAN07800
DAN07810
DAN07820
DAN07830
DAN07840
DAN07850
DAN07860
DAN07870
DAN07880
DAN07890
DAN07900
DAN07910
DAN07920
DAN07930
DAN07940
DAN07950
DAN07960
DAN07970
DAN07980
DAN07990
DAN08000

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230	IF(MO.LE.0)GO TO 240	DAN08010
	DO 235 LQ=1,MO	DAN08020
	LN=LQ+NB	DAN08030
	A9=C(I1,LN)	DAN08040
	A10=C(J1,LN)	DAN08050
	P21=A10*A9	DAN08060
	P23=A1*A10	DAN08070
	P24=A9*A2	DAN08080
	J=J+1	DAN08090
	T(J)=T(J)+X8*P1*P21	DAN08100
	J=J+1	DAN08110
	T(J)=T(J)+X2*(P23+P24)**2	DAN08120
	IF(K.LT.MNM)GO TO 235	DAN08130
	IF(EA(K).GT.1.999999)GO TO 235	DAN08140
	P25=A9*A6	DAN08150
	P26=A5*A10	DAN08160
	J=J+1	DAN08170
	T(J)=T(J)+X8*P3*P21	DAN08180
	J=J+1	DAN08190
	T(J)=T(J)+X2*(P25+P26)**2	DAN08200
	J=J+1	DAN08210
	T(J)=T(J)+X4*(P23+P24)*(P25+P26)	DAN08220
235	CONTINUE	DAN08230
240	CONTINUE	DAN08240
	IF(MO.LE.1)GO TO 260	DAN08250
	DO 250 KQ=1,MO	DAN08260
	K=KQ+NB	DAN08270
	IF(KQ.EQ.MO)GO TO 250	DAN08280
	KQ1=KQ+1	DAN08290
	DO 245 LQ=KQ1,MO	DAN08300
	LN=LQ+NB	DAN08310
	A1=C(I1,K)	DAN08320

A2=C(J1,K)	DAN08330
A9=C(I1,LN)	DAN08340
A10=C(J1,LN)	DAN08350
J=J+1	DAN08360
T(J)=T(J)+X8*A1*A2*A9*A10	DAN08370
J=J+1	DAN08380
245 T(J)=T(J)+X2*(A1*A10+A2*A9)**2	DAN08390
250 CONTINUE	DAN08400
260 GO TO 6000	DAN08410
1100 J=0	DAN08420
DO 1140 K=1,NB	DAN08430
KP=M-K+1	DAN08440
A1=C(I1,K)	DAN08450
1118 IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING1)GO TO 1116	DAN08460
IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING2)GO TO 1116	DAN08470
GO TO 1117	DAN08480
1116 J=J+1	DAN08490
P1=0.D0	DAN08500
IF(K.LT.MNM)GO TO 1110	DAN08510
IF(EA(K).GT.1.999999)GO TO 1110	DAN08520
J=J+3	DAN08530
A5=0.D0	DAN08540
P3=0.D0	DAN08550
P31=0.D0	DAN08560
GO TO 1110	DAN08570
1117 P1=A1*A1	DAN08580
J=J+1	DAN08590
T(J)=T(J)+X1*P1*P1	DAN08600
IF(K.LT.MNM)GO TO 1110	DAN08610
IF(EA(K).GT.1.999999)GO TO 1110	DAN08620
A5=C(I1,KP)	DAN08630
P3=A5*A5	DAN08640

P31=A1*A5	DAN08650
J=J+1	DAN08660
T(J)=T(J)+X1*P3*P3	DAN08670
J=J+1	DAN08680
T(J)=T(J)+X2*P31*P31	DAN08690
J=J+1	DAN08700
T(J)=T(J)+X2*P1*P3	DAN08710
1110 KAND=K+1	DAN08720
IF(K.EQ.NB)GO TO 1130	DAN08730
DO 1120 LN=KAND,NB	DAN08740
LP=M-LN+1	DAN08750
A9=C(I1, LN)	DAN08760
P7=A9*A9	DAN08770
P13=A1*A9	DAN08780
J=J+1	DAN08790
T(J)=T(J)+X2*P1*P7	DAN08800
J=J+1	DAN08810
T(J)=T(J)+X2*P13**2	DAN08820
IF(LN.LT.MNM)GO TO 1120	DAN08830
IF(EA(LN).GT.1.999999)GO TO 1120	DAN08840
A13=C(I1, LP)	DAN08850
P5=A13*A13	DAN08860
P9=A1*A13	DAN08870
P17=A5*A13	DAN08880
J=J+1	DAN08890
T(J)=T(J)+X2*P1*P5	DAN08900
J=J+1	DAN08910
T(J)=T(J)+X2*P9**2	DAN08920
IF(K.LT.MNM)GO TO 1120	DAN08930
IF(EA(K).GT.1.999999)GO TO 1120	DAN08940
P35=A9*A5	DAN08950
J=J+1	DAN08960

T(J)=T(J)+X2*P3*P7	DAN08970
J=J+1	DAN08980
T(J)=T(J)+X2*P35**2	DAN08990
J=J+1	DAN09000
T(J)=T(J)+X2*P3*P5	DAN09010
J=J+1	DAN09020
T(J)=T(J)+X2*P17**2	DAN09030
J=J+1	DAN09040
T(J)=T(J)+X4*P9*P35	DAN09050
J=J+1	DAN09060
T(J)=T(J)+X4*P13*P17	DAN09070
1120 CONTINUE	DAN09080
1130 IF(MD.LE.0)GO TO 1140	DAN09090
DO 1135 LQ=1,MD	DAN09100
LN=LQ+NB	DAN09110
A9=C(I1,LN)	DAN09120
P21=A9*A9	DAN09130
P23=A1*A9	DAN09140
J=J+1	DAN09150
T(J)=T(J)+X2*P1*P21	DAN09160
J=J+1	DAN09170
T(J)=T(J)+X2*P23**2	DAN09180
IF(K.LT.MNM)GO TO 1135	DAN09190
IF(EA(K).GT.1.999999)GO TO 1135	DAN09200
P25=A9*A5	DAN09210
J=J+1	DAN09220
T(J)=T(J)+X2*P3*P21	DAN09230
J=J+1	DAN09240
T(J)=T(J)+X2*P25**2	DAN09250
J=J+1	DAN09260
T(J)=T(J)+X4*P23*P25	DAN09270
1135 CONTINUE	DAN09280

1140	CONTINUE	DAN09290
	IF(MD.LE.1)GO TO 1160	DAN09300
	DO 1150 KQ=1,MD	DAN09310
	K=KQ+NB	DAN09320
	IF(KQ.EQ.MD)GO TO 1150	DAN09330
	KQ1=KQ+1	DAN09340
	DO 1145 LQ=KQ1,MD	DAN09350
	LN=LQ+NB	DAN09360
	A1=C(I1,K)	DAN09370
	A9=C(I1,LN)	DAN09380
	J=J+1	DAN09390
	T(J)=T(J)+X2*(A1**2)*(A9**2)	DAN09400
	J=J+1	DAN09410
1145	T(J)=T(J)+X2*(A1**2)*(A9**2)	DAN09420
1150	CONTINUE	DAN09430
1160	GO TO 6000	DAN09440
300	J=0	DAN09450
	DO 340 K=1,NB	DAN09460
	KP=M-K+1	DAN09470
	A1=C(I1,K)	DAN09480
	A3=C(K1,K)	DAN09490
318	IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING1)GO TO 316	DAN09500
	IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING2)GO TO 316	DAN09510
	IF(DABS(A3).LE.1.D-08.AND.K.NE.NSING1)GO TO 315	DAN09520
	IF(DABS(A3).LE.1.D-08.AND.K.NE.NSING2)GO TO 315	DAN09530
	GO TO 317	DAN09540
316	J=J+1	DAN09550
	P1=0.DO	DAN09560
	P2=A3*A3	DAN09570
	IF(K.LT.MNM)GO TO 310	DAN09580
	IF(EA(K).GT.1.999999)GO TO 310	DAN09590
	J=J+3	DAN09600

```

A5=0.D0
A7=C(K1,KP)
P3=0.D0
P4=A7*A7
P31=0.D0
P33=A3*A7
GO TO 310
315 J=J+1
P1=A1*A1
P2=0.D0
IF(K.LT.MNM)GO TO 310
IF(EA(K).GT.1.999999)GO TO 310
J=J+3
A5=C(I1,KP)
A7=0.D0
P3=A5*A5
P4=0.D0
P31=A1*A5
P33=0.D0
GO TO 310
317 P1=A1*A1
P2=A3*A3
J=J+1
T(J)=T(J)+X2*P1*P2
IF(K.LT.MNM)GO TO 310
IF(EA(K).GT.1.999999)GO TO 310
A5=C(I1,KP)
A7=C(K1,KP)
P3=A5*A5
P4=A7*A7
P31=A1*A5
P33=A3*A7

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DAN09610
DAN09620
DAN09630
DAN09640
DAN09650
DAN09660
DAN09670
DAN09680
DAN09690
DAN09700
DAN09710
DAN09720
DAN09730
DAN09740
DAN09750
DAN09760
DAN09770
DAN09780
DAN09790
DAN09800
DAN09810
DAN09820
DAN09830
DAN09840
DAN09850
DAN09860
DAN09870
DAN09880
DAN09890
DAN09900
DAN09910
DAN09920

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```

J=J+1
T(J)=X2*P3*P4+T(J)
J=J+1
T(J)=T(J)+X4*P31*P33
J=J+1
T(J)=T(J)+X2*(P1*P4+P2*P3)
310 KAND=K+1
IF(K.EQ.NB)GO TO 330
DO 320 LN=KAND,NB
LP=M-LN+1
A9=C(I1, LN)
A11=C(K1, LN)
P7=A11*A11
P8=A9*A9
P13=A1*A9
P15=A11*A3
J=J+1
T(J)=T(J)+X2*(P1*P7+P2*P8)
J=J+1
T(J)=T(J)+X4*P13*P15
IF(LN.LT.MNM)GO TO 320
IF(EA(LN).GT.1.999999)GO TO 320
A13=C(I1, LP)
A15=C(K1, LP)
P5=A15*A15
P6=A13*A13
P9=A1*A13
P11=A15*A3
P17=A7*A15
P19=A13*A5
J=J+1
T(J)=T(J)+X2*(P1*P5+P2*P6)

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DAN09930
DAN09940
DAN09950
DAN09960
DAN09970
DAN09980
DAN09990
DAN10000
DAN10010
DAN10020
DAN10030
DAN10040
DAN10050
DAN10060
DAN10070
DAN10080
DAN10090
DAN10100
DAN10110
DAN10120
DAN10130
DAN10140
DAN10150
DAN10160
DAN10170
DAN10180
DAN10190
DAN10200
DAN10210
DAN10220
DAN10230
DAN10240

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```

J=J+1
T(J)=T(J)+X4*P9*P11
IF(K.LT.MNM)GO TO 320
IF(EA(K).GT.1.999999)GO TO 320
P35=A9*A5
P37=A7*A11
J=J+1
T(J)=T(J)+X2*(P8*P4+P7*P3)
J=J+1
T(J)=T(J)+X4*P35*P37
J=J+1
T(J)=T(J)+X2*(P3*P5+P4*P6)
J=J+1
T(J)=T(J)+X4*P19*P17
J=J+1
T(J)=T(J)+X4*(P9*P37+P11*P35)
J=J+1
T(J)=T(J)+X4*(P13*P17+P15*P19)
320 CONTINUE
330 IF(MO.LE.0)GO TO 340
DO 335 LQ=1,MO
LN=LQ+NB
A9=C(I1,LN)
A11=C(K1,LN)
P21=A11*A11
P22=A9*A9
P23=A1*A9
P27=A11*A3
J=J+1
T(J)=T(J)+X2*(P1*P21+P2*P22)
J=J+1
T(J)=T(J)+X4*P23*P27

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DAN10250
DAN10260
DAN10270
DAN10280
DAN10290
DAN10300
DAN10310
DAN10320
DAN10330
DAN10340
DAN10350
DAN10360
DAN10370
DAN10380
DAN10390
DAN10400
DAN10410
DAN10420
DAN10430
DAN10440
DAN10450
DAN10460
DAN10470
DAN10480
DAN10490
DAN10500
DAN10510
DAN10520
DAN10530
DAN10540
DAN10550
DAN10560

```

IF(K.LT.MNM)GO TO 335	DAN10570
IF(EA(K).GT.1.999999)GO TO 335	DAN10580
P25=A11*A7	DAN10590
P29=A5*A9	DAN10600
J=J+1	DAN10610
T(J)=T(J)+X2*(P3*P21+P4*P22)	DAN10620
J=J+1	DAN10630
T(J)=T(J)+X4*P25*P29	DAN10640
J=J+1	DAN10650
T(J)=T(J)+X4*(P23*P25+P27*P29)	DAN10660
335 CONTINUE	DAN10670
340 CONTINUE	DAN10680
IF(MO.LE.1)GO TO 360	DAN10690
DO 350 KQ=1,MO	DAN10700
K=KQ+NB	DAN10710
IF(KQ.EQ.MO)GO TO 350	DAN10720
KQ1=KQ+1	DAN10730
DO 345 LQ=KQ1,MO	DAN10740
LN=LQ+NB	DAN10750
A1=C(I1,K)	DAN10760
A3=C(K1,K)	DAN10770
A9=C(I1,LN)	DAN10780
A11=C(K1,LN)	DAN10790
J=J+1	DAN10800
T(J)=T(J)+X2*(A1*A1*A11*A11+A3*A3*A9*A9)	DAN10810
J=J+1	DAN10820
345 T(J)=T(J)+X4*A1*A9*A3*A11	DAN10830
350 CONTINUE	DAN10840
360 GO TO 6000	DAN10850
400 J=0	DAN10860
DO 440 K=1,NB	DAN10870
KP=M-K+1	DAN10880

	A1=C(I1,K)	DAN10890
	A4=C(L1,K)	DAN10900
418	IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING1)GO TO 416	DAN10910
	IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING2)GO TO 416	DAN10920
	IF(DABS(A4).LE.1.D-08.AND.K.NE.NSING1)GO TO 415	DAN10930
	IF(DABS(A4).LE.1.D-08.AND.K.NE.NSING2)GO TO 415	DAN10940
	GO TO 417	DAN10950
416	J=J+1	DAN10960
	P1=0.D0	DAN10970
	P2=0.D0	DAN10980
	IF(K.LT.MNM)GO TO 410	DAN10990
	IF(EA(K).GT.1.999999)GO TO 410	DAN11000
	J=J+3	DAN11010
	A5=0.D0	DAN11020
	A3=C(L1,KP)	DAN11030
	P3=0.D0	DAN11040
	P4=0.D0	DAN11050
	P31=0.D0	DAN11060
	P33=0.D0	DAN11070
	P34=0.D0	DAN11080
	GO TO 410	DAN11090
415	J=J+1	DAN11100
	P1=A1*A1	DAN11110
	P2=0.D0	DAN11120
	IF(K.LT.MNM)GO TO 410	DAN11130
	IF(EA(K).GT.1.999999)GO TO 410	DAN11140
	J=J+3	DAN11150
	A5=C(I1,KP)	DAN11160
	A8=0.D0	DAN11170
	P3=A5*A5	DAN11180
	P4=0.D0	DAN11190
	P31=A1*A5	DAN11200

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P33=0.D0
P34=0.D0
GO TO 410
417 P1=A1*A1
P2=A1*A4
J=J+1
T(J)=T(J)+X4*P1*P2
IF(K.LT.MNM)GO TO 410
IF(EA(K).GT.1.999999)GO TO 410
A5=C(I1,KP)
A8=C(L1,KP)
P3=A5*A5
P4=A5*A8
P31=A1*A5
P33=A1*A8
P34=A4*A5
Q=2.D0*P31*(P33+P34)
J=J+1
T(J)=X4*P3*P4+T(J)
J=J+1
T(J)=T(J)+X2*Q
J=J+1
T(J)=T(J)+X4*(P1*P4+P2*P3)
410 KAND=K+1
IF(K.EQ.NB)GO TO 430
DO 420 LN=KAND,NB
LP=M-LN+1
A9=C(I1,LN)
A12=C(L1,LN)
P7=A9*A12
P8=A9*A9
P13=A1*A9

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DAN11210
DAN11220
DAN11230
DAN11240
DAN11250
DAN11260
DAN11270
DAN11280
DAN11290
DAN11300
DAN11310
DAN11320
DAN11330
DAN11340
DAN11350
DAN11360
DAN11370
DAN11380
DAN11390
DAN11400
DAN11410
DAN11420
DAN11430
DAN11440
DAN11450
DAN11460
DAN11470
DAN11480
DAN11490
DAN11500
DAN11510
DAN11520

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P15=A9*A4
P16=A12*A1
J=J+1
T(J)=T(J)+X4*(P1*P7+P2*P8)
J=J+1
T(J)=T(J)+X4*P13*(P15+P16)
IF(LN.LT.MNM)GO TO 420
IF(EA(LN).GT.1.999999)GO TO 420
A13=C(I1,LP)
A16=C(L1,LP)
P5=A13*A16
P6=A13*A13
P9=A1*A13
P11=A13*A4
P12=A16*A1
P17=A5*A16
P18=A8*A13
P19=A13*A5
J=J+1
T(J)=T(J)+X4*(P1*P5+P2*P6)
J=J+1
T(J)=T(J)+X4*P9*(P11+P12)
IF(K.LT.MNM)GO TO 420
IF(EA(K).GT.1.999999)GO TO 420
P35=A9*A5
P38=A8*A9
P37=A5*A12
J=J+1
T(J)=T(J)+X4*(P3*P4+P7*P3)
J=J+1
T(J)=T(J)+X4*P35*(P37+P38)
J=J+1

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DAN11530
DAN11540
DAN11550
DAN11560
DAN11570
DAN11580
DAN11590
DAN11600
DAN11610
DAN11620
DAN11630
DAN11640
DAN11650
DAN11660
DAN11670
DAN11680
DAN11690
DAN11700
DAN11710
DAN11720
DAN11730
DAN11740
DAN11750
DAN11760
DAN11770
DAN11780
DAN11790
DAN11800
DAN11810
DAN11820
DAN11830
DAN11840

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T(J)=T(J)+X4*(P3*P5+P4*P6)	DAN11850
J=J+1	DAN11860
T(J)=T(J)+X4*P19*(P17+P18)	DAN11870
J=J+1	DAN11880
T(J)=T(J)+X4*(P9*(P37+P38)+P35*(P11+P12))	DAN11890
J=J+1	DAN11900
T(J)=T(J)+X4*(P13*(P17+P18)+P19*(P15+P16))	DAN11910
420 CONTINUE	DAN11920
430 IF(MO.LE.0)GO TO 440	DAN11930
DO 435 LQ=1,MO	DAN11940
LN=LQ+NB	DAN11950
A9=C(I1,LN)	DAN11960
A12=C(L1,LN)	DAN11970
P21=A9*A12	DAN11980
P22=A9*A9	DAN11990
P23=A1*A9	DAN12000
P27=A9*A4	DAN12010
P28=A12*A1	DAN12020
J=J+1	DAN12030
T(J)=T(J)+X4*(P1*P21+P2*P22)	DAN12040
J=J+1	DAN12050
T(J)=T(J)+X4*P23*(P27+P28)	DAN12060
IF(K.LT.MNM)GO TO 435	DAN12070
IF(EA(K).GT.1.999999)GO TO 435	DAN12080
P25=A9*A8	DAN12090
P26=A5*A12	DAN12100
P29=A5*A9	DAN12110
J=J+1	DAN12120
T(J)=T(J)+X4*(P3*P21+P4*P22)	DAN12130
J=J+1	DAN12140
T(J)=T(J)+X4*P29*(P25+P26)	DAN12150
J=J+1	DAN12160

T(J)=T(J)+X4*(P23*(P25+P26)+P29*(P27+P28))	DAN12170
435 CONTINUE	DAN12180
440 CONTINUE	DAN12190
IF(MO.LE.1)GO TO 460	DAN12200
DO 450 KQ=1,MO	DAN12210
K=KQ+NB	DAN12220
IF(KQ.EQ.MO)GO TO 450	DAN12230
KQ1=KQ+1	DAN12240
DO 445 LQ=KQ1,MO	DAN12250
LN=LQ+NB	DAN12260
A1=C(I1,K)	DAN12270
A4=C(L1,K)	DAN12280
A9=C(I1,LN)	DAN12290
A12=C(L1,LN)	DAN12300
J=J+1	DAN12310
T(J)=T(J)+X4*A1*A9*(A1*A12+A4*A9)	DAN12320
J=J+1	DAN12330
445 T(J)=T(J)+X4*A1*A9*(A4*A9+A1*A12)	DAN12340
450 CONTINUE	DAN12350
460 GO TO 6000	DAN12360
500 J=0	DAN12370
DO 540 K=1,NB	DAN12380
KP=M-K+1	DAN12390
A1=C(I1,K)	DAN12400
A3=C(K1,K)	DAN12410
A4=C(L1,K)	DAN12420
518 IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING1)GO TO 516	DAN12430
IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING2)GO TO 516	DAN12440
IF(DABS(A3).LE.1.D-08.OR.DABS(A4).LE.1.D-08.AND.K.NE.NSING1)	DAN12450
1GO TO 515	DAN12460
IF(DABS(A3).LE.1.D-08.OR.DABS(A4).LE.1.D-08.AND.K.NE.NSING2)	DAN12470
1GO TO 515	DAN12480

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GO TO 517
516 J=J+1
P1=0.00
P2=A3*A4
IF(K.LT.MNM)GO TO 510
IF(EA(K).GT.1.999999)GO TO 510
J=J+3
A5=0.00
A7=C(K1,KP)
A8=C(L1,KP)
P3=0.00
P4=A7*A8
P31=0.00
P33=A3*A8
P34=A4*A7
GO TO 510
515 J=J+1
P1=A1*A1
P2=0.00
IF(K.LT.MNM) GO TO 510
IF(EA(K).GT.1.999999)GO TO 510
J=J+3
A5=C(I1,KP)
A7=C(K1,KP)
A8=C(L1,KP)
P3=A5*A5
P4=0.00
P31=A1*A5
P33=0.00
P34=0.00
GO TO 510
517 P1=A1*A1

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DAN12490
DAN12500
DAN12510
DAN12520
DAN12530
DAN12540
DAN12550
DAN12560
DAN12570
DAN12580
DAN12590
DAN12600
DAN12610
DAN12620
DAN12630
DAN12640
DAN12650
DAN12660
DAN12670
DAN12680
DAN12690
DAN12700
DAN12710
DAN12720
DAN12730
DAN12740
DAN12750
DAN12760
DAN12770
DAN12780
DAN12790
DAN12800

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```

P2=A3*A4
J=J+1
T(J)=T(J)+X4*P1*P2
IF(K.LT.MNM)GO TO 510
IF(EA(K).GT.1.999999)GO TO 510
A5=C(I1,KP)
A7=C(K1,KP)
A8=C(L1,KP)
P3=A5*A5
P4=A7*A8
P31=A1*A5
P33=A3*A8
P34=A4*A7
Q=2.D0*(P33+P34)*P31
J=J+1
T(J)=X4*P3*P4+T(J)
J=J+1
T(J)=T(J)+X2*Q
J=J+1
T(J)=T(J)+X4*(P1*P4+P2*P3)
510 KAND=K+1
IF(K.EQ.NB)GO TO 530
DO 520 LN=KAND,NB
LP=M-LN+1
A9=C(I1,LN)
A11=C(K1,LN)
A12=C(L1,LN)
P7=A11*A12
P8=A9*A9
P13=A1*A9
P15=A11*A4
P16=A12*A3

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DAN12810
DAN12820
DAN12830
DAN12840
DAN12850
DAN12860
DAN12870
DAN12880
DAN12890
DAN12900
DAN12910
DAN12920
DAN12930
DAN12940
DAN12950
DAN12960
DAN12970
DAN12980
DAN12990
DAN13000
DAN13010
DAN13020
DAN13030
DAN13040
DAN13050
DAN13060
DAN13070
DAN13080
DAN13090
DAN13100
DAN13110
DAN13120

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J=J+1
T(J)=T(J)+X4*(P1*P7+P2*P8)
J=J+1
T(J)=T(J)+X4*P13*(P15+P16)
IF(LN.LT.MNM)GO TO 520
IF(EA(LN).GT.1.999999)GO TO 520
A13=C(I1,LP)
A15=C(K1,LP)
A16=C(L1,LP)
P5=A15*A16
P6=A13*A13
P9=A1*A13
P11=A15*A4
P12=A16*A3
P17=A7*A16
P18=A8*A15
P19=A13*A5
J=J+1
T(J)=T(J)+X4*(P1*P5+P2*P6)
J=J+1
T(J)=T(J)+X4*P9*(P11+P12)
IF(K.LT.MNM)GO TO 520
IF(EA(K).GT.1.999999)GO TO 520
P35=A9*A5
P37=A7*A12
P38=A8*A11
J=J+1
T(J)=T(J)+X4*(P8*P4+P7*P3)
J=J+1
T(J)=T(J)+X4*P35*(P37+P38)
J=J+1
T(J)=T(J)+X4*(P3*P5+P4*P6)

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DAN13130
DAN13140
DAN13150
DAN13160
DAN13170
DAN13180
DAN13190
DAN13200
DAN13210
DAN13220
DAN13230
DAN13240
DAN13250
DAN13260
DAN13270
DAN13280
DAN13290
DAN13300
DAN13310
DAN13320
DAN13330
DAN13340
DAN13350
DAN13360
DAN13370
DAN13380
DAN13390
DAN13400
DAN13410
DAN13420
DAN13430
DAN13440

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J=J+1	DAN13450
T(J)=T(J)+X4*P19*(P17+P18)	DAN13460
J=J+1	DAN13470
T(J)=T(J)+X4*(P9*(P37+P38)+P35*(P11+P12))	DAN13480
J=J+1	DAN13490
T(J)=T(J)+X4*(P13*(P17+P18)+P19*(P15+P16))	DAN13500
520 CONTINUE	DAN13510
530 IF(MO.LE.0)GO TO 540	DAN13520
DO 535 LQ=1,MO	DAN13530
LN=LQ+N8	DAN13540
A9=C(I1,LN)	DAN13550
A11=C(K1,LN)	DAN13560
A12=C(L1,LN)	DAN13570
P21=A11*A12	DAN13580
P22=A9*A9	DAN13590
P23=A1*A9	DAN13600
P27=A11*A4	DAN13610
P28=A12*A3	DAN13620
J=J+1	DAN13630
T(J)=T(J)+X4*(P1*P21+P2*P22)	DAN13640
J=J+1	DAN13650
T(J)=T(J)+X4*P23*(P27+P28)	DAN13660
IF(K.LT.MNM)GO TO 535	DAN13670
IF(EA(K).GT.1.999999)GO TO 535	DAN13680
P25=A11*A8	DAN13690
P26=A7*A12	DAN13700
P29=A5*A9	DAN13710
J=J+1	DAN13720
T(J)=T(J)+X4*(P3*P21+P4*P22)	DAN13730
J=J+1	DAN13740
T(J)=T(J)+X4*P29*(P25+P26)	DAN13750
J=J+1	DAN13760

	T(J)=T(J)+X4*(P23*(P25+P26)+P29*(P27+P28))	DAN13770
535	CONTINUE	DAN13780
540	CONTINUE	DAN13790
	IF(MO.LE.1)GO TO 560	DAN13800
	DO 550 KQ=1,MO	DAN13810
	K=KQ+NB	DAN13820
	IF(KQ.EQ.MO)GO TO 550	DAN13830
	KQ1=KQ+1	DAN13840
	DO 545 LQ=KQ1,MC	DAN13850
	LN=LQ+NB	DAN13860
	A1=C(I1,K)	DAN13870
	A3=C(K1,K)	DAN13880
	A4=C(L1,K)	DAN13890
	A9=C(I1,LN)	DAN13900
	A11=C(K1,LN)	DAN13910
	A12=C(L1,LN)	DAN13920
	J=J+1	DAN13930
	T(J)=T(J)+X4*(A1*A1*A11*A12+A3*A4*A9*A9)	DAN13940
	J=J+1	DAN13950
545	T(J)=T(J)+X4*A1*A9*(A4*A11+A3*A12)	DAN13960
550	CONTINUE	DAN13970
560	GO TO 6000	DAN13980
700	J=0	DAN13990
	DO 740 K=1,NB	DAN14000
	KP=M-K+1	DAN14010
	A1=C(I1,K)	DAN14020
	A2=C(J1,K)	DAN14030
718	IF(DABS(A2).LE.1.D-08.AND.K.NE.NSING1)GO TO 715	DAN14040
	IF(DABS(A2).LE.1.D-08.AND.K.NE.NSING2)GO TO 715	DAN14050
	IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING1)GO TO 716	DAN14060
	IF(DABS(A1).LE.1.D-08.AND.K.NE.NSING2)GO TO 716	DAN14070
	GO TO 717	DAN14080

```

716 P1=0.00
    P2=A2*A2
    J=J+1
    IF(K.LT.MNM)GO TO 710
    IF(EA(K).GT.1.999999)GO TO 710
    J=J+3
    A5=0.00
    A6=C(J1,KP)
    P3=0.00
    P4=A6*A6
    P31=0.00
    P32=0.00
    P33=A2*A6
    GO TO 710

715 J=J+1
    P1=0.00
    P2=0.00
    IF(K.LT.MNM)GO TO 710
    IF(EA(K).GT.1.999999)GO TO 710
    J=J+3
    A5=C(I1,KP)
    A6=0.00
    P3=0.00
    P4=0.00
    P31=0.00
    P32=0.00
    P33=0.00
    GO TO 710

717 P1=A1*A2
    P2=A2*A2
    J=J+1
    T(J)=T(J)+X4*P1*P2

```

```

DAN14090
DAN14100
DAN14110
DAN14120
DAN14130
DAN14140
DAN14150
DAN14160
DAN14170
DAN14180
DAN14190
DAN14200
DAN14210
DAN14220
DAN14230
DAN14240
DAN14250
DAN14260
DAN14270
DAN14280
DAN14290
DAN14300
DAN14310
DAN14320
DAN14330
DAN14340
DAN14350
DAN14360
DAN14370
DAN14380
DAN14390
DAN14400

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```

IF(K.LT.MNM)GO TO 710
IF(EA(K).GT.1.999999)GO TO 710
A5=C(I1,KP)
A6=C(J1,KP)
P3=A5*A6
P4=A6*A6
P31=A1*A6
P32=A2*A5
P33=A2*A6
Q=2.D0*P33*(P31+P32)
J=J+1
T(J)=X4*P3*P4+T(J)
J=J+1
T(J)=T(J)+X2*Q
J=J+1
T(J)=T(J)+X4*(P1*P4+P2*P3)
710 KAND=K+1
IF(K.EQ.NB)GO TO 730
DO 720 LN=KAND,NB
LP=M-LN+1
A9=C(I1,LN)
A10=C(J1,LN)
P7=A10*A10
P8=A9*A10
P13=A1*A10
P14=A2*A9
P15=A10*A2
J=J+1
T(J)=T(J)+X4*(P1*P7+P2*P8)
J=J+1
T(J)=T(J)+X4*P15*(P13+P14)
IF(LN.LT.MNM)GO TO 720

```

```

DAN14410
DAN14420
DAN14430
DAN14440
DAN14450
DAN14460
DAN14470
DAN14480
DAN14490
DAN14500
DAN14510
DAN14520
DAN14530
DAN14540
DAN14550
DAN14560
DAN14570
DAN14580
DAN14590
DAN14600
DAN14610
DAN14620
DAN14630
DAN14640
DAN14650
DAN14660
DAN14670
DAN14680
DAN14690
DAN14700
DAN14710
DAN14720

```

```

IF(EA(LN).GT.1.999999)GO TO 720
A13=C(I1,LP)
A14=C(J1,LP)
P5=A14*A14
P6=A13*A14
P9=A1*A14
P10=A13*A2
P11=A14*A2
P17=A6*A14
P19=A13*A6
P20=A5*A14
J=J+1
T(J)=T(J)+X4*(P1*P5+P2*P6)
J=J+1
T(J)=T(J)+X4*P11*(P9+P10)
IF(K.LT.MNM)GO TO 720
IF(EA(K).GT.1.999999)GO TO 720
P35=A9*A6
P36=A5*A10
P37=A6*A10
J=J+1
T(J)=T(J)+X4*(P8*P4+P7*P3)
J=J+1
T(J)=T(J)+X4*P37*(P35+P36)
J=J+1
T(J)=T(J)+X4*(P3*P5+P4*P6)
J=J+1
T(J)=T(J)+X4*P17*(P19+P20)
J=J+1
T(J)=T(J)+X4*(P37*(P9+P10)+P11*(P35+P36))
J=J+1
T(J)=T(J)+X4*(P17*(P13+P14)+P15*(P19+P20))

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```

DAN14730
DAN14740
DAN14750
DAN14760
DAN14770
DAN14780
DAN14790
DAN14800
DAN14810
DAN14820
DAN14830
DAN14840
DAN14850
DAN14860
DAN14870
DAN14880
DAN14890
DAN14900
DAN14910
DAN14920
DAN14930
DAN14940
DAN14950
DAN14960
DAN14970
DAN14980
DAN14990
DAN15000
DAN15010
DAN15020
DAN15030
DAN15040

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```

720 CONTINUE
730 IF(MO.LE.0)GO TO 740
DO 735 LQ=1,MO
LN=LQ+NB
A9=C(I1,LN)
A10=C(J1,LN)
P21=A10*A10
P22=A9*A10
P23=A1*A10
P24=A9*A2
P27=A10*A2
J=J+1
T(J)=T(J)+X4*(P1*P21+P2*P22)
J=J+1
T(J)=T(J)+X4*P27*(P23+P24)
IF(K.LT.MNM)GO TO 735
IF(EA(K).GT.1.999999)GO TO 735
P25=A10*A6
P29=A5*A10
P30=A6*A9
J=J+1
T(J)=T(J)+X4*(P3*P21+P4*P22)
J=J+1
T(J)=T(J)+X4*P25*(P29+P30)
J=J+1
T(J)=T(J)+X4*(P25*(P23+P24)+P27*(P29+P30))
735 CONTINUE
740 CONTINUE
IF(MO.LE.1)GO TO 760
DO 750 KQ=1,MO
K=KQ+NB
IF(KQ.EQ.MO)GO TO 750

```

```

DAN15050
DAN15060
DAN15070
DAN15080
DAN15090
DAN15100
DAN15110
DAN15120
DAN15130
DAN15140
DAN15150
DAN15160
DAN15170
DAN15180
DAN15190
DAN15200
DAN15210
DAN15220
DAN15230
DAN15240
DAN15250
DAN15260
DAN15270
DAN15280
DAN15290
DAN15300
DAN15310
DAN15320
DAN15330
DAN15340
DAN15350
DAN15360

```

KQ1=KQ+1	DAN15370
DO 745 LQ=KQ1,MO	DAN15380
LN=LQ+NB	DAN15390
A1=C(I1,K)	DAN15400
A2=C(J1,K)	DAN15410
A9=C(I1,LN)	DAN15420
A10=C(J1,LN)	DAN15430
J=J+1	DAN15440
T(J)=T(J)+X4*A2*A10*(A1*A10+A2*A9)	DAN15450
J=J+1	DAN15460
745 T(J)=T(J)+X4*A2*A10*(A1*A10+A2*A9)	DAN15470
750 CONTINUE	DAN15480
760 GO TO 6000	DAN15490
600 J=0	DAN15500
DO 640 K=1,NB	DAN15510
KP=M-K+1	DAN15520
A1=C(I1,K)	DAN15530
A2=C(J1,K)	DAN15540
A3=C(K1,K)	DAN15550
618 IF(DABS(A1).LE.1.D-08.OR.DABS(A2).LE.1.D-08.AND.K.NE.NSING1)	DAN15560
1GO TO 616	DAN15570
IF(DABS(A1).LE.1.D-08.OR.DABS(A2).LE.1.D-08.AND.K.NE.NSING2)	DAN15580
1GO TO 616	DAN15590
IF(DABS(A3).LE.1.D-08.AND.K.NE.NSING1)GO TO 615	DAN15600
IF(DABS(A3).LE.1.D-08.AND.K.NE.NSING2)GO TO 615	DAN15610
GO TO 617	DAN15620
616 J=J+1	DAN15630
P1=0.DO	DAN15640
P2=A3*A3	DAN15650
IF(K.LT.MNM)GO TO 610	DAN15660
IF(EA(K).GT.1.999999)GO TO 610	DAN15670
J=J+3	DAN15680

```

A5=C(I1,KP)
A6=C(J1,KP)
A7=C(K1,KP)
P3=0.D0
P4=A7*A7
P31=0.D0
P32=0.D0
P33=A3*A7
GO TO 610
615 J=J+1
P1=A1*A2
P2=0.D0
IF(K.LT.MNM)GO TO 610
IF(EA(K).GT.1.999999)GO TO 610
J=J+3
A5=C(I1,KP)
A6=C(J1,KP)
A7=0.D0
P3=A5*A6
P4=0.D0
P31=A6*A1
P32=A2*A5
P33=0.D0
GO TO 610
617 P1=A1*A2
P2=A3*A3
J=J+1
T(J)=T(J)+X4*P1*P2
IF(K.LT.MNM)GO TO 610
IF(EA(K).GT.1.999999)GO TO 610
A5=C(I1,KP)
A6=C(J1,KP)

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```

DAN15690
DAN15700
DAN15710
DAN15720
DAN15730
DAN15740
DAN15750
DAN15760
DAN15770
DAN15780
DAN15790
DAN15800
DAN15810
DAN15820
DAN15830
DAN15840
DAN15850
DAN15860
DAN15870
DAN15880
DAN15890
DAN15900
DAN15910
DAN15920
DAN15930
DAN15940
DAN15950
DAN15960
DAN15970
DAN15980
DAN15990
DAN16000

```

```

A7=C(K1,KP)
P3=A5*A6
P4=A7*A7
P31=A1*A6
P32=A2*A5
P33=A3*A7
Q=2.D0*P33*(P31+P32)
J=J+1
T(J)=X4*P3*P4+T(J)
J=J+1
T(J)=T(J)+X2*Q
J=J+1
T(J)=T(J)+X4*(P1*P4+P2*P3)
610 KAND=K+1
IF(K.EQ.NB)GO TO 630
DO 620 LN=KAND,NB
LP=M-LN+1
A9=C(I1, LN)
A10=C(J1, LN)
A11=C(K1, LN)
P7=A11*A11
P8=A9*A10
P13=A1*A10
P14=A2*A9
P15=A11*A3
J=J+1
T(J)=T(J)+X4*(P1*P7+P2*P8)
J=J+1
T(J)=T(J)+X4*P15*(P13+P14)
IF(LN.LT.MNM)GO TO 620
IF(EA(LN).GT.1.999999)GO TO 620
A13=C(I1, LP)

```

```

DAN16010
DAN16020
DAN16030
DAN16040
DAN16050
DAN16060
DAN16070
DAN16080
DAN16090
DAN16100
DAN16110
DAN16120
DAN16130
DAN16140
DAN16150
DAN16160
DAN16170
DAN16180
DAN16190
DAN16200
DAN16210
DAN16220
DAN16230
DAN16240
DAN16250
DAN16260
DAN16270
DAN16280
DAN16290
DAN16300
DAN16310
DAN16320

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A14=C(J1,LP)	DAN16330
A15=C(K1,LP)	DAN16340
P5=A15*A15	DAN16350
P6=A13*A14	DAN16360
P9=A1*A14	DAN16370
P10=A13*A2	DAN16380
P11=A15*A3	DAN16390
P17=A7*A15	DAN16400
P19=A13*A6	DAN16410
P20=A5*A14	DAN16420
J=J+1	DAN16430
T(J)=T(J)+X4*(P1*P5+P2*P6)	DAN16440
J=J+1	DAN16450
T(J)=T(J)+X4*P11*(P9+P10)	DAN16460
IF(K.LT.MNM)GO TO 620	DAN16470
IF(EA(K).GT.1.999999)GO TO 620	DAN16480
P35=A9*A6	DAN16490
P36=A5*A10	DAN16500
P37=A7*A11	DAN16510
J=J+1	DAN16520
T(J)=T(J)+X4*(P8*P4+P7*P3)	DAN16530
J=J+1	DAN16540
T(J)=T(J)+X4*P37*(P35+P36)	DAN16550
J=J+1	DAN16560
T(J)=T(J)+X4*(P3*P5+P4*P6)	DAN16570
J=J+1	DAN16580
T(J)=T(J)+X4*P17*(P19+P20)	DAN16590
J=J+1	DAN16600
T(J)=T(J)+X4*(P37*(P9+P10)+P11*(P35+P36))	DAN16610
J=J+1	DAN16620
T(J)=T(J)+X4*(P17*(P13+P14)+P15*(P19+P20))	DAN16630
620 CONTINUE	DAN16640

630	IF(MO.LE.0)GO TO 640	DAN16650
	DO 635 LQ=1,MO	DAN16660
	LN=LQ+NB	DAN16670
	A9=C(I1,LN)	DAN16680
	A10=C(J1,LN)	DAN16690
	A11=C(K1,LN)	DAN16700
	P21=A11*A11	DAN16710
	P22=A9*A10	DAN16720
	P23=A1*A10	DAN16730
	P24=A9*A2	DAN16740
	P27=A11*A3	DAN16750
	J=J+1	DAN16760
	T(J)=T(J)+X4*(P1*P21+P2*P22)	DAN16770
	J=J+1	DAN16780
	T(J)=T(J)+X4*P27*(P23+P24)	DAN16790
	IF(K.LT.MNM)GO TO 635	DAN16800
	IF(EA(K).GT.1.999999)GO TO 635	DAN16810
	P25=A11*A7	DAN16820
	P29=A5*A10	DAN16830
	P30=A6*A9	DAN16840
	J=J+1	DAN16850
	T(J)=T(J)+X4*(P3*P21+P4*P22)	DAN16860
	J=J+1	DAN16870
	T(J)=T(J)+X4*P25*(P29+P30)	DAN16880
	J=J+1	DAN16890
	T(J)=T(J)+X4*(P25*(P23+P24)+P27*(P29+P30))	DAN16900
635	CONTINUE	DAN16910
640	CONTINUE	DAN16920
	IF(MO.LE.1)GO TO 660	DAN16930
	DO 650 KQ=1,MO	DAN16940
	K=KQ+NB	DAN16950
	IF(KQ.EQ.MO)GO TO 650	DAN16960

KQ1=KQ+1	DAN16970
DO 645 LQ=KQ1,MD	DAN16980
LN=LQ+NB	DAN16990
A1=C(I1,K)	DAN17000
A2=C(J1,K)	DAN17010
A3=C(K1,K)	DAN17020
A9=C(I1,LN)	DAN17030
A10=C(J1,LN)	DAN17040
A11=C(K1,LN)	DAN17050
J=J+1	DAN17060
T(J)=T(J)+X4*(A1*A2*A11*A11+A3*A3*A9*A10)	DAN17070
J=J+1	DAN17080
645 T(J)=T(J)+X4*A3*A11*(A1*A10+A2*A9)	DAN17090
650 CONTINUE	DAN17100
660 GO TO 6000	DAN17110
6000 CONTINUE	DAN17120
10 IF(NINTS-MN1)30,20,54	DAN17130
54 MN1=MN1+1	DAN17140
GO TO 55	DAN17150
C	DAN17160
C	DAN17170
C	DAN17180
C	DAN17190
C	DAN17200
C	DAN17210
C	DAN17220
C	DAN17230
C	DAN17240
C	DAN17250
C	DAN17260
C	DAN17270
C	DAN17280
76 IF(IPTI.EQ.0.AND.IRC.EQ.1)GO TO 78	
WRITE(6,39)NMINNW	
78 CONTINUE	
19 FORMAT(1H1////37X,	

161H	INTERNAL CHECK SUMS, ETC. FROM READING TWO ELECTRON INTEGRALS//	DAN17290
16H	REC ,7(1X,17H FIRST NOS LAST)//	DAN17300
16H	NOS ,7(1X,17H LABEL OF LABEL)//	DAN17310
16X,	7(1X,17H J L INTS J L)	DAN17320
29	FORMAT (1X,I4,1X,7(I3,I3,1X,I4,I3,I3,1X))	DAN17330
39	FORMAT(12X,	DAN17340
	118H THIS NOS. OF INTS,I12)	DAN17350
	RETURN	DAN17360
C		DAN17370
C	ERROR EXIT FOR INCORRECT VALUE OF NINTS (POSSIBLE TAPE READ	DAN17380
C	ERROR)	DAN17390
C		DAN17400
30	WRITE(6,9)	DAN17410
9	FORMAT('0','ERROR IN NOINTS')	DAN17420
	CALL ABT	DAN17430
	STOP	DAN17440
	END	DAN17450
CWATE	SUBROUTINE WATE	DAN17460
	SUBROUTINE WATE(FA,H,CA,CB,BETA,TENO,EB,SOMEGA,B,AX,A,EA,BX, DEL	DAN17470
	1W,BE,SPIN,ED,A2IJ,PKD,VAL,CUT,EN,INAME,MTAPE,NRX,NTOP,NIN,NBFNS,	DAN17480
	INA,NB,NR)	DAN17490
		DAN17500
C	REFERENCES: (1) PHILLIPS AND SCHUG, J.CHEM.PHYS. 61, 1031	DAN17510
C	(1974); (2) HARRIMAN, IBID. 40, 2827(1964); (3) HARDISSON AND	DAN17520
C	HARRIMAN, IBID. 46, 3639(1967); (4) SANDO AND HARRIMAN, IBID.	DAN17530
C	47,180(1967); (5) SASAKI AND OHNO, J. MATH. PHYS. 7, 1140	DAN17540
C	(1963).	DAN17550
C	ERRATUM FOR REFERENCE (1): EQN. (24) SHOULD READ	DAN17560
C	$E(I)=(1-D(I)**2)**0.5 = 2*T(I)*U(I)$	DAN17570
C	THIS IS A TYPOGRAPHICAL ERROR. THE CORRECT FORM WAS USED IN	DAN17580
C	THE CALCULATIONS.	DAN17590
C		DAN17600

IMPLICIT REAL*8(A-H,O-Z)	DAN17610
REAL*8 ILBL,ILAB,ILABL,INTNAM,INAME	DAN17620
COMMON/ZEIT/LAPSE,LAPST	DAN17630
COMMON/LABELS/ILBL(12),ILAB(12)	DAN17640
COMMON/IDIND/ICON(24)	DAN17650
DIMENSION FA(NRX,NRX),H(NRX,NRX),CA(NRX,NRX),CB(NRX,NRX),BETA(NRX,	DAN17660
1NRX)	DAN17670
DIMENSION INAME(6)	DAN17680
DIMENSION TENO(NTOP)	DAN17690
DIMENSION EB(NRX),SOMEGA(NRX),B(NRX),AX(NRX),A(NRX),EA(NRX),BX(NRX)	DAN17700
1),DELW(NRX),BE(NRX),SPIN(NRX),ED(NRX),AZIJ(NRX)	DAN17710
DIMENSION PKD(NIN),VAL(NIN)	DAN17720
REAL*8 ILBL,ILAB	DAN17730
EXTERNAL F,CK	DAN17740
	DAN17750
SET CONSTANTS	DAN17760
	DAN17770
NTI=5	DAN17780
NTO=6	DAN17790
READ(NTI,169)KIKMAX	DAN17800
XNA=DFLOAT(NA)	DAN17810
XNB=DFLOAT(NB)	DAN17820
XM=0.500*(XNA-XNB)	DAN17830
XN=0.500*(XNA+XNB)	DAN17840
S2=XM	DAN17850
NBP=NB+1	DAN17860
M=NA+NB	DAN17870
NC=NBFNS	DAN17880
N=NR	DAN17890
NTT=(N*(N+1))/2	DAN17900
NP=N+1	DAN17910
NM=N-1	DAN17920

C
C
C

NAP=NA+1	DAN17930
NAM=NA-1	DAN17940
NBM=NB-1	DAN17950
N2=N/2	DAN17960
N2P=N2+1	DAN17970
MP=M+1	DAN17980
MU=NA-NB+1	DAN17990
MO=NA-NB	DAN18000
WRITE(NT0,209)	DAN18010
WRITE(NT0,299)NA,NB	DAN18020
C	DAN18030
C	DAN18040
C	DAN18050
DO 10 I=1,N	DAN18060
SOMEGA(I)=EB(N-I+1)	DAN18070
10 A(I)=0.00	DAN18080
DO 20 I=1,N	DAN18090
IF(SOMEGA(I).LT.0.)SOMEGA(I)=0.00	DAN18100
IF(SOMEGA(I).GT.1.)SOMEGA(I)=1.00	DAN18110
20 EB(I)=SOMEGA(I)	DAN18120
C	DAN18130
C	DAN18140
C	DAN18150
C	DAN18160
DO 30 I=1,NB	DAN18170
B(I)=0.00	DAN18180
30 AX(I)=1.00-EB(I)	DAN18190
I=1	DAN18200
B(I)=1.00	DAN18210
A(I)=1.00	DAN18220
B(NBP)=1.00	DAN18230
A(NBP)=1.00	DAN18240

	WRITE(NT0,9)	DAN18250
	WRITE(NT0,19)(EB(I),I=1,N)	DAN18260
C		DAN18270
C	CALCULATE SUMS OF CONTINUING PRODUCTS	DAN18280
C		DAN18290
	FA(1,1)=EB(1)	DAN18300
	FA(2,1)=0.DO	DAN18310
	IF(NB.LE.1)GO TO 221	DAN18320
	DO 50 J=2,NB	DAN18330
	JM=J-1	DAN18340
	FA(1,J)=FA(1,JM)+EB(J)	DAN18350
	DO 40 K=2,J	DAN18360
	40 FA(K,J)=FA(K,JM)+EB(J)*FA(K-1,JM)	DAN18370
	FA(J+1,J)=0.DO	DAN18380
	50 CONTINUE	DAN18390
	221 DO 60 I=1,NB	DAN18400
	60 A(I+1)=FA(I,NB)	DAN18410
C		DAN18420
C	THESE ARE HARRIMAN'S ASUBK. SEE EQN. (21) OF REF. (2)	DAN18430
C		DAN18440
	WRITE(NT0,29)	DAN18450
	WRITE(NT0,19)(A(I),I=1,NBP)	DAN18460
	FA(1,1)=AX(1)	DAN18470
	FA(2,1)=0.DO	DAN18480
	IF(NB.LE.1)GO TO 222	DAN18490
	DO 80 J=2,NB	DAN18500
	JM=J-1	DAN18510
	FA(1,J)=FA(1,JM)+AX(J)	DAN18520
	DO 70 K=2,J	DAN18530
	70 FA(K,J)=FA(K,JM)+AX(J)*FA(K-1,JM)	DAN18540
	FA(J+1,J)=0.DO	DAN18550
	80 CONTINUE	DAN18560

222	DO 90 I=1,NB	DAN18570
90	B(I+1)=FA(I,NB)	DAN18580
C		DAN18590
C	THESE ARE BSUBK OF REFS. (1), (2), AND (3).	DAN18600
C		DAN18610
	WRITE(NTD,119)	DAN18620
	WRITE(NTD,19)(B(I),I=1,NBP)	DAN18630
C		DAN18640
C	CALCULATION OF WEIGHTS FROM EQN. (26) OF REF. (1).	DAN18650
C		DAN18660
	DO 110 I=1,NBP	DAN18670
	SI=XM+I-1.DO	DAN18680
	XZ=XN-SI	DAN18690
	MM=XZ+1.01	DAN18700
	IS=2.*SI+0.01	DAN18710
	MS=SI+XM+0.01	DAN18720
	NS=SI-XM+0.01	DAN18730
	XS=DFLOAT(IS)	DAN18740
	SOMEGA(I)=0.DO	DAN18750
	DO 100 J=1,MM	DAN18760
	JM=J-1	DAN18770
100	SOMEGA(I)=SOMEGA(I)+(-1.DO)**JM*(F(NS+JM,1)**2*B(NS+J))/(F(IS+J,1)	DAN18780
	1*F(JM,1))	DAN18790
	SOMEGA(I)=(XS+1.DO)*F(MS,1)*SOMEGA(I)/F(NS,1)	DAN18800
	IM=I-1	DAN18810
110	WRITE(NTD,39)SI,SOMEGA(I)	DAN18820
C		DAN18830
C	INVERT THE ORDER OF THE NATURAL ORBITAL OF CHARGE EIGENVALUES	DAN18840
C	SO THAT THE LOWEST ORBITAL HAS THE HIGHEST OCCUPATION	DAN18850
C		DAN18860
	DO 120 I=1,N	DAN18870
	AX(I)=EA(N-I+1)	DAN18880

	DO 120 J=1,NC	DAN18890
120	H(J,I)=CA(J,N-I+1)	DAN18900
	DO 130 J=1,NR	DAN18910
	EA(J)=AX(J)	DAN18920
	DO 130 I=1,NC	DAN18930
130	CA(I,J)=H(I,J)	DAN18940
	DO 1200 I=1,N	DAN18950
	DO 1200 J=1,NC	DAN18960
1200	H(J,I)=CB(J,N-I+1)	DAN18970
	DO 1210 I=1,NC	DAN18980
	DO 1210 J=1,N	DAN18990
1210	CB(I,J)=H(I,J)	DAN19000
	IF(NA.NE.NB.OR.ICON(4).EQ.0)GO TO 5	DAN19010
	DO 140 I=1,NC	DAN19020
	CA(I,NA)=TEND(I)	DAN19030
140	CA(I,NBP)=TEND(N+I)	DAN19040
	CALL MPRY2(CA,EA,B,6HMCDIF,6HED N.0,6HRBS CG,0,NR,NC,NRX)	DAN19050
	5 CONTINUE	DAN19060
C		DAN19070
C	CALCULATION OF A(K+1)'S FROM RECURSION RELATION	DAN19080
C		DAN19090
	DO 150 I=1,N	DAN19100
	H(1,I)=1.DO	DAN19110
150	FA(1,I)=1.DO	DAN19120
	IF(NB.LE.1)GO TO 223	DAN19130
	DO 170 I=2,NB	DAN19140
	IM=I-1	DAN19150
	DO 160 J=1,NB	DAN19160
C		DAN19170
C	EQN. (31) OF REF. (2)	DAN19180
C		DAN19190
160	FA(I,J)=A(I)-EB(J)*FA(IM,J)	DAN19200

170	CONTINUE	DAN19210
C		DAN19220
C	FA(K,L) IS ASUBK(L) OF REF. (2)	DAN19230
C		DAN19240
223	WRITE(NT0,129)	DAN19250
	CALL MWRITE(FA,6HFA(K,L,6H) = AS,6HUBK(L),1,NB,NB,NRX)	DAN19260
C		DAN19270
C	CORRECT PHASES OF NATURAL ORBITALS TO INSURE THAT TSUBI AND	DAN19280
C	USUBI ARE POSITIVE. SEE EQNS. (14), AND (15) OF REF. (1).	DAN19290
C		DAN19300
	NBMM=NB-1	DAN19310
	IF(NA.NE.NB.OR.ICON(4).EQ.0)NBMM=NB	DAN19320
	DO 210 I=1,NBMM	DAN19330
	JI=M-I+1	DAN19340
	IF(JI.GT.N)GO TO 210	DAN19350
	XV=1.D-06	DAN19360
	KK=1	DAN19370
1875	IF(DABS(CA(KK,I)).GE.XV.AND.DABS(CA(KK,JI)).GE.XV.AND.	DAN19380
	1 DABS(CB(KK,I)).GE.XV) GO TO 1900	DAN19390
	KK=KK+1	DAN19400
	GO TO 1875	DAN19410
1900	LL=KK+1	DAN19420
1905	IF(DABS(CA(LL,I)).GE.XV.AND.DABS(CA(LL,JI)).GE.XV.AND.	DAN19430
	1 DABS(CB(LL,I)).GE.XV) GO TO 1910	DAN19440
1906	LL=LL+1	DAN19450
	GO TO 1905	DAN19460
1910	XXV=CA(LL,JI)*CA(KK,I)-CA(LL,I)*CA(KK,JI)	DAN19470
	IF(DABS(XXV).LT.1.D-06)GO TO 1906	DAN19480
	XV=CA(LL,JI)/CA(KK,JI)	DAN19490
	AX(I)=(CB(LL,I)-CB(KK,I)*XV)/(CA(LL,I)-CA(KK,I)*XV)	DAN19500
	XV=CA(LL,I)/CA(KK,I)	DAN19510
	BX(I)=(CB(LL,I)-CB(KK,I)*XV)/(CA(KK,JI)*XV-CA(LL,JI))	DAN19520

	IF(AX(I).GT.0.)GO TO 15	DAN19530
	DO 190 J=1,NC	DAN19540
	190 CA(J,I)=-1.DO*CA(J,I)	DAN19550
	15 IF(BX(I).LE.0.)GO TO 210	DAN19560
	DO 200 J=1,NC	DAN19570
	200 CA(J,JI)=-1.DO*CA(J,JI)	DAN19580
	210 CONTINUE	DAN19590
	CALL MPRY2(CA,EA,B,6HNATL D,6HRBS OF,6H CHG ,O,NR,NC,NRX)	DAN19600
C		DAN19610
C	NATURAL ORBITALS OF SPIN CALCULATION	DAN19620
C		DAN19630
	DO 213 I=1,M	DAN19640
	BX(I)=0.DO	DAN19650
	213 AX(I)=0.DO	DAN19660
	DO 240 I=1,N	DAN19670
	DELW(I)=DSQRT(1.DO-EB(I))	DAN19680
	240 BE(I)=DSQRT(EB(I))	DAN19690
	E1UP=0.DO	DAN19700
	E2UP=0.DO	DAN19710
	XAL=0.DO	DAN19720
	MNM=M-N+1	DAN19730
C		DAN19740
C	ATOMIC SPIN DENSITIES CALCULATION	DAN19750
C	SEE TABLE II IN REF. (2)	DAN19760
C		DAN19770
C		DAN19780
C	CALCULATE INTEGRALS OVER NATURAL ORBITALS	DAN19790
C		DAN19800
	CALL NOINTS(EA,PKD,VAL,CA,TENO,CUT,INAME,NB,MNM,MO,M,NINTS,NIN,NRXDAN19810	DAN19810
	1,NTOP,NTAPE)	DAN19820
	DO 470 KIK=1,KIKMAX	DAN19830
	IF(SOMEGA(KIK).LE.1.D-16)GO TO 470	DAN19840

XKIK=KIK-1.DO	DAN19850
S2=XM+XKIK	DAN19860
WRITE(NT0,59)S2	DAN19870
IF(MU.EQ.1)GO TO 65	DAN19880
CALL MCLEAR(H,NRX,NRX,NRX)	DAN19890
AD=1.DO/DSQRT(2.DO)	DAN19900
DO 220 I=1,NB	DAN19910
N1=M-I+1	DAN19920
DO 220 J=1,NC	DAN19930
IF(N1.GT.N)GO TO 25	DAN19940
H(J,N1)=AD*(CA(J,I)-CA(J,N1))	DAN19950
H(J,I)=AD*(CA(J,I)+CA(J,N1))	DAN19960
GO TO 220	DAN19970
25 H(J,I)=CA(J,I)	DAN19980
220 CONTINUE	DAN19990
IF(NA.EQ.NB)GO TO 35	DAN20000
DO 230 I=NBP,NA	DAN20010
DO 230 J=1,NC	DAN20020
230 H(J,I)=CA(J,I)	DAN20030
35 CONTINUE	DAN20040
P=0.DO	DAN20050
DO 250 K=1,NB	DAN20060
KM=K-1	DAN20070
250 P=P+(-1.DO)**K*CK(KM,1,NA,NB,KIK)*A(K+1)*K	DAN20080
B(1)=0.DO	DAN20090
IF(NB.LE.1)GO TO 45	DAN20100
DO 260 I=1,NB	DAN20110
B(I)=0.DO	DAN20120
DO 260 K=1,NBM	DAN20130
KM=K-1	DAN20140
KP=K+1	DAN20150
260 B(I)=B(I)+(-1.DO)**K*CK(KM,2,NA,NB,KIK)*FA(KP,I)*K	DAN20160

45	CONTINUE	DAN20170
	DO 270 I=1,NB	DAN20180
	BX(I)=0.DO	DAN20190
	DO 270 K=1,NB	DAN20200
	KM=K-1	DAN20210
270	BX(I)=BX(I)+(-1.DO)**KM*CK(KM,1,NA,NB,KIK)*FA(K,I)	DAN20220
	DO 290 I=1,NA	DAN20230
	JI=M-I+1	DAN20240
	IF(JI.GT.N)GO TO 61	DAN20250
	SS=XM/(S2*(S2+1.DO))	DAN20260
	IF(I.GT.NB)GO TO 55	DAN20270
	AA=SS+SS*(XN*SOMEGA(KIK)+P-XN*BX(I)-B(I))/SOMEGA(KIK)	DAN20280
	BB=SS*XM*BX(I)*DELW(I)/SOMEGA(KIK)	DAN20290
	EA(I)=AA+BB	DAN20300
	EA(JI)=AA-BB	DAN20310
	GO TO 290	DAN20320
55	EA(I)=SS*(XM+1.)	DAN20330
	DO 280 J=1,NB	DAN20340
280	EA(I)=EA(I)+SS*(1.DO-BX(J)/SOMEGA(KIK))	DAN20350
	GO TO 290	DAN20360
61	EA(I)=0.DO	DAN20370
290	CONTINUE	DAN20380
	DO 300 I=1,NC	DAN20390
	SPIN(I)=0.DO	DAN20400
	DO 300 K=1,M	DAN20410
	IF(K.GT.N.OR.K.LT.MNM)GO TO 300	DAN20420
	SPIN(I)=SPIN(I)+EA(K)*H(I,K)**2	DAN20430
300	CONTINUE	DAN20440
	WRITE(NT0,69)S2	DAN20450
	WRITE(NT0,19)(SPIN(I),I=1,NC)	DAN20460
65	CONTINUE	DAN20470
	CALL MCLEAR(H,NRX,NRX,NRX)	DAN20480

C		DAN20490
C	CALCULATION OF D PARAMETERS	DAN20500
C	UPPER HALF OF H MATRIX=D2(I,J)	DAN20510
C	LOWER HALF OF H MATRIX=D0(I,J)	DAN20520
C	UPPER HALF OF BETA = CORE HAMILTONIAN	DAN20530
C	LOWER HALF OF BETA MATRIX=D1(I,J)	DAN20540
C	ED(I)=D1(I); AX(I)=D0(I)	DAN20550
C	SEE REF. (3), TABLE V AND EQN. (9) OF REF. (4)	DAN20560
C		DAN20570
	DO 360 I=1,NB	DAN20580
	AX(I)=0.00	DAN20590
	ED(I)=0.00	DAN20600
	DO 310 J=1,NB	DAN20610
	JM=J-1	DAN20620
	AX(I)=AX(I)+(-1.00)**JM*CK(JM,0,NA,NB,KIK)*FA(J,I)	DAN20630
310	CONTINUE	DAN20640
	AX(I)=AX(I)/SOMEGA(KIK)	DAN20650
	IM=I-1	DAN20660
	DO 320 K=1,NB	DAN20670
320	ED(I)=ED(I)+(-1.00)**K*CK(K,0,NA,NB,KIK)*FA(K,I)	DAN20680
	ED(I)=ED(I)/SOMEGA(KIK)	DAN20690
	IF(I.EQ.1) GO TO 360	DAN20700
	DO 350 J=1,IM	DAN20710
	A2IJ(1)=1.00	DAN20720
	IF(NB.LE.1)GO TO 224	DAN20730
	DO 324 K=2,NB	DAN20740
324	A2IJ(K)=FA(K,I)-EB(J)*A2IJ(K-1)	DAN20750
C		DAN20760
C	A2IJ(K) IS ASUBK(I,J) OF REF. (2)	DAN20770
C		DAN20780
224	H(I,J)=0.00	DAN20790
	H(J,I)=0.00	DAN20800

IF(NB.LE.1)GO TO 225	DAN20810
DO 330 K=1,NBM	DAN20820
KM=K-1	DAN20830
330 H(I,J)=H(I,J)+(-1.DO)**KM*CK(KM,0,NA,NB,KIK)*A2IJ(K)	DAN20840
340 H(I,J)=H(I,J)/SOMEGA(KIK)	DAN20850
225 BETA(I,J)=(AX(I)-H(I,J))/EB(J)	DAN20860
H(J,I)=(ED(I)-BETA(I,J))/EB(J)	DAN20870
350 CONTINUE	DAN20880
360 CONTINUE	DAN20890
C	DAN20900
C	DAN20910
C	DAN20920
C	DAN20930
DO 380 I=1,NC	DAN20940
DO 380 J=1,I	DAN20950
CB(I,J)=0.DO	DAN20960
DO 370 K=1,M	DAN20970
IF(K.LE.NB)GO TO 75	DAN20980
IF(K.LE.NA)GO TO 85	DAN20990
IF(K.GT.N)GO TO 370	DAN21000
IF(K.GT.NA)GO TO 95	DAN21010
75 CB(I,J)= CB(I,J)+(1.DO+DSQRT(EB(K))*(AX(K)+ED(K)))*CA(I,K)*CA(J	DAN21020
I,K)	DAN21030
GO TO 370	DAN21040
85 CB(I,J)= CB(I,J)+CA(I,K)*CA(J,K)	DAN21050
GO TO 370	DAN21060
95 II=M-K+1	DAN21070
CB(I,J)= CB(I,J)+(1.DO-DSQRT(EB(II))*(AX(II)+ED(II)))*CA(I,K)*C	DAN21080
IA(J,K)	DAN21090
370 CONTINUE	DAN21100
380 CB(J,I)=CB(I,J)	DAN21110
WRITE(NT0,79)S2	DAN21120

CALL MWRITE(CB,6HPROJ. ,6HCHARGE,6HDENS. ,0,NC,NC,NRX)	DAN21130
E1P=CB(1,1)*BETA(1,1)	DAN21140
DO 390 I=2,NC	DAN21150
E1P=E1P+CB(I,I)*BETA(I,I)	DAN21160
IM=I-1	DAN21170
DO 390 J=1,IM	DAN21180
390 E1P=E1P+(CB(I,J)+CB(J,I))*BETA(J,I)	DAN21190
WRITE(6,89)E1P	DAN21200
E1UP=E1UP+SOMEGA(KIK)*E1P	DAN21210
E2P=0.DO	DAN21220
QM=0	DAN21230
J=0	DAN21240
DO 430 K=1,NB	DAN21250
KP=M-K+1	DAN21260
C CALCULATE IIII	DAN21270
J=J+1	DAN21280
GX=0.2500*((1.DO+BE(K))**2)*(AX(K)+ED(K))	DAN21290
QM=QM+GX*TENO(J)	DAN21300
IF(K.LT.MNM)GO TO 115	DAN21310
IF(BE(K).GT.0.999999)GO TO 115	DAN21320
C CALCULATE I'I'I'I'	DAN21330
J=J+1	DAN21340
GX=0.2500*((1.DO-BE(K))**2)*(AX(K)+ED(K))	DAN21350
QM=QM+GX*TENO(J)	DAN21360
C CALCULATE III'I'	DAN21370
J=J+1	DAN21380
GX=-0.2500*(DELW(K)**2)*(AX(K)+ED(K))	DAN21390
QM=QM+GX*TENO(J)	DAN21400
C CALCULATE II'II'	DAN21410
J=J+1	DAN21420
GX=0.2500*(DELW(K)**2)*(AX(K)-ED(K))	DAN21430
QM=QM+GX*TENO(J)	DAN21440

C	CALCULATE I I' I' I	DAN21450
	GX=-0.25D0*(DELW(K)**2)*(AX(K)-ED(K))	DAN21460
	QM=QM+GX*TENO(J-1)	DAN21470
	IF(K.EQ.NB)GO TO 125	DAN21480
115	KAND=K+1	DAN21490
	DO 410 LN=KAND,NB	DAN21500
	LP=M-LN+1	DAN21510
C	CALCULATE I J I J	DAN21520
	J=J+1	DAN21530
	GX=0.5D0*(1.D0+BE(K))*(1.D0+BE(LN))*(H(LN,K)+(BE(K)+BE(LN))*BETA(LN,K)+BE(K)*BE(LN)*H(K,LN))	DAN21540
	QM=QM+GX*TENO(J)	DAN21560
C	CALCULATE I J J I	DAN21570
	J=J+1	DAN21580
	GX=-0.25D0*(1.D0+BE(K))*(1.D0+BE(LN))*(H(LN,K)-BETA(LN,K)+2.D0*(BE(LN,K)+BE(LN))*BETA(LN,K)-BE(K)*BE(LN)*(BETA(LN,K)-H(K,LN)))	DAN21590
	QM=QM+GX*TENO(J)	DAN21610
	IF(LN.LT.MNM)GO TO 116	DAN21620
	IF(BE(LN).GT.0.999999)GO TO 116	DAN21630
C	CALCULATE I J' I J'	DAN21640
	J=J+1	DAN21650
	GX=0.5D0*(1.D0+BE(K))*(1.D0-BE(LN))*(H(LN,K)+(BE(K)-BE(LN))*BETA(LN,K)-BE(K)*BE(LN)*H(K,LN))	DAN21660
	QM=QM+GX*TENO(J)	DAN21680
C	CALCULATE I J' J' I	DAN21690
	J=J+1	DAN21700
	GX=-0.25D0*(1.D0+BE(K))*(1.D0-BE(LN))*(H(LN,K)-BETA(LN,K)+2.D0*(BE(LN,K)-BE(LN))*BETA(LN,K)+BE(K)*BE(LN)*(BETA(LN,K)-H(K,LN)))	DAN21710
	QM=QM+GX*TENO(J)	DAN21730
116	IF(K.LT.MNM)GO TO 410	DAN21740
	IF(BE(K).GT.0.999999)GO TO 410	DAN21750
C	CALCULATE J I' J I'	DAN21760

	J=J+1	DAN21770
	GX=0.5D0*(1.D0+BE(LN))*(1.D0-BE(K))*(H(LN,K)+(BE(LN)-BE(K))*BETA(LN,K)-BE(LN)*BE(K)*H(K,LN))	DAN21780
	QM=QM+GX*TENO(J)	DAN21790
C	CALCULATE JI'I'J	DAN21800
	J=J+1	DAN21810
	GX=-0.25D0*(1.D0+BE(LN))*(1.D0-BE(K))*(H(LN,K)-BETA(LN,K)+2.D0*(BETA(LN,K)+BE(LN)*BE(K)*(BETA(LN,K)-H(K,LN))))	DAN21820
	QM=QM+GX*TENO(J)	DAN21830
C	CALCULATE I'J'I'J'	DAN21840
	J=J+1	DAN21850
	GX=0.5D0*(1.D0-BE(K))*(1.D0-BE(LN))*(H(LN,K)-(BE(K)+BE(LN))*BETA(LN,K)+BE(K)*BE(LN)*H(K,LN))	DAN21860
	QM=QM+GX*TENO(J)	DAN21870
C	CALCULATE I'J'J'I'	DAN21880
	J=J+1	DAN21890
	GX=-0.25D0*(1.D0-BE(K))*(1.D0-BE(LN))*(H(LN,K)-BETA(LN,K)-2.D0*(BETA(LN,K)+BE(LN))*(BETA(LN,K)-BE(K)*BE(LN)*(BETA(LN,K)-H(K,LN))))	DAN21900
	QM=QM+GX*TENO(J)	DAN21910
C	CALCULATE IJJ'I'	DAN21920
	J=J+1	DAN21930
	GX=-0.25D0*DELW(K)*DELW(LN)*(H(LN,K)+BETA(LN,K)+BE(K)*BE(LN)*(BETA(LN,K)+H(K,LN)))	DAN21940
	QM=QM+GX*TENO(J)	DAN21950
C	CALCULATE IJ'JI'	DAN21960
	J=J+1	DAN21970
	GX=-0.25D0*DELW(K)*DELW(LN)*(H(LN,K)+BETA(LN,K)-BE(K)*BE(LN)*(BETA(LN,K)+H(K,LN)))	DAN21980
	QM=QM+GX*TENO(J)	DAN21990
C	CALCULATE IJ'JI'	DAN22000
	J=J+1	DAN22010
	GX=-0.25D0*DELW(K)*DELW(LN)*(H(LN,K)+BETA(LN,K)-BE(K)*BE(LN)*(BETA(LN,K)+H(K,LN)))	DAN22020
	QM=QM+GX*TENO(J)	DAN22030
410	CONTINUE	DAN22040
125	IF(MO.LE.0)GO TO 430	DAN22050
	DO 425 LQ=1,MO	DAN22060
		DAN22070
		DAN22080

	LN=LQ+NB	DAN22090
C	CALCULATE ITIT	DAN22100
	J=J+1	DAN22110
	GX=0.500*(1.00+BE(K))*(AX(K)+BE(K)*ED(K))	DAN22120
	QM=QM+GX*TEND(J)	DAN22130
C	CALCULATE ITTI	DAN22140
	J=J+1	DAN22150
	GX=-0.500*(1.00+BE(K))*(0.500*(AX(K)-ED(K))+BE(K)*ED(K))	DAN22160
	QM=QM+GX*TEND(J)	DAN22170
	IF(K.LT.MNM)GO TO 425	DAN22180
	IF(BE(K).GT.0.999999)GO TO 425	DAN22190
C	CALCULATE I'TI'T	DAN22200
	J=J+1	DAN22210
	GX=0.500*(1.00-BE(K))*(AX(K)-BE(K)*ED(K))	DAN22220
	QM=QM+GX*TEND(J)	DAN22230
C	CALCULATE I'TTI'	DAN22240
	J=J+1	DAN22250
	GX=-0.500*(1.00-BE(K))*(0.500*(AX(K)-ED(K))-BE(K)*ED(K))	DAN22260
	QM=QM+GX*TEND(J)	DAN22270
C	CALCULATE ITTI'	DAN22280
	J=J+1	DAN22290
	GX=-.2500*(DELW(K)*(AX(K)+ED(K)))	DAN22300
420	QM=QM+GX*TEND(J)	DAN22310
425	CONTINUE	DAN22320
430	CONTINUE	DAN22330
421	IF(MO.LE.1)GO TO 441	DAN22340
	DO 440 KQ=1,MO	DAN22350
	K=KQ+NB	DAN22360
	IF(KQ.EQ.MO)GO TO 440	DAN22370
	KQ1=KQ+1	DAN22380
	DO 435 LQ=KQ1,MO	DAN22390
	LN=LQ+NB	DAN22400

C	CALCULATE TUTU	DAN22410
	J=J+1	DAN22420
	GX=.500	DAN22430
	QM=QM+GX*TEND(J)	DAN22440
C	CALCULATE TUUT	DAN22450
	J=J+1	DAN22460
	GX=-.500	DAN22470
435	QM=QM+GX*TEND(J)	DAN22480
440	CONTINUE	DAN22490
441	CONTINUE	DAN22500
	E2P=E2P+QM	DAN22510
5030	CONTINUE	DAN22520
6000	CONTINUE	DAN22530
	ETP=E1P+E2P	DAN22540
	E2UP=E2UP+SOMEGA(KIK)*E2P	DAN22550
	WRITE(6,259)E2P	DAN22560
259	FORMAT('0',3X,'TWO-ELECTRON PART OF ENERGY = ',1PD14.6)	DAN22570
	WRITE(6,99)S2,ETP	DAN22580
	XA12=ETP*SOMEGA(KIK)	DAN22590
	WRITE(6,139)XA12	DAN22600
	ETP1=ETP1+XA12	DAN22610
	WRITE(6,149)ETP1	DAN22620
	WRITE(NT0,279)E1UP	DAN22630
	WRITE(NT0,269)E2UP	DAN22640
470	CONTINUE	DAN22650
9	FORMAT('0','EB')	DAN22660
19	FORMAT(' ',5(1PD15.6,2X))	DAN22670
29	FORMAT('0','A')	DAN22680
39	FORMAT('-', 'THE WEIGHTING FACTOR FOR THE S=',F6.4, ' STATE =',1PD15	DAN22690
	1.7)	DAN22700
49	FORMAT('0','NATURAL ORBITALS OF CHARGE')	DAN22710
59	FORMAT('1',25X,'RESULTS OF PROJECTION FOR S=',F6.4)	DAN22720

69	FORMAT('0','ATOMIC SPIN DENSITIES FOR S=',F6.4)	DAN22730
79	FORMAT('0','PROJECTED CHARGE DENSITY FOR S=',F6.4)	DAN22740
89	FORMAT('0','ONE-ELECTRON PART OF ENERGY =',1PD14.6)	DAN22750
99	FORMAT('0','FOR S=',F8.4,5X,'ENERGY =',1PD14.6)	DAN22760
119	FORMAT('0','B')	DAN22770
129	FORMAT('0','A(K+1)')	DAN22780
139	FORMAT('0','THE WEIGHTED ENERGY FOR THIS PROJECTION =',1PD14.6)	DAN22790
149	FORMAT('0','THE SUM OF THE WEIGHTED ENERGIES FOR THE ABOVE PROJECT	DAN22800
	IONS INCLUDING THIS'/5X,'PROJECTION=',1PD14.6)	DAN22810
169	FORMAT(3I5)	DAN22820
179	FORMAT(' ','MODIFIED NATURAL ORBITALS OF CHARGE')	DAN22830
209	FORMAT('1','BEGINNING OF HARRIMAN PROJECTION TREATMENT')	DAN22840
269	FORMAT('0','UNPROJECTED TWO-ELECTRON ENERGY =',1PD15.8)	DAN22850
279	FORMAT('0','UNPROJECTED ONE-ELECTRON ENERGY =',1PD15.8)	DAN22860
299	FORMAT('0','CALCULATION FOR ',I5,' ALPHA ELECTRONS AND ',I5,' BETA	DAN22870
	1ELECTRONS')	DAN22880
	RETURN	DAN22890
	END	DAN22900
CF	FUNCTION F	DAN22910
	FUNCTION F(INM,MNR)	DAN22920
C		DAN22930
C	CALCULATES FACTORIAL(INM)/FACTORIAL(MNR-1)	DAN22940
C		DAN22950
	IMPLICIT REAL*8 (A-H,O-Z)	DAN22960
	XF=1.00	DAN22970
	IF(INM.LE.1) GO TO 5	DAN22980
	DO 10 J=MNR,INM	DAN22990
	XJ=J	DAN23000
10	XF=XF*XJ	DAN23010
5	F=XF	DAN23020
	RETURN	DAN23030
	END	DAN23040

CCK	FUNCTION CK	DAN23050
	FUNCTION CK(I,NLM,NA,NB,KIK)	DAN23060
C		DAN23070
C	SUMS FACTORIALS USING EQUATION (20) OF REFERENCE (2)	DAN23080
C	CSUBK(S,M,NP) WHERE K=I, 2S=NA-NB+2*(KIK-1), 2M=NA-NB,	DAN23090
C	2*NP=NA+NB-NLM*2	DAN23100
C		DAN23110
	IMPLICIT REAL*8 (A-H,O-Z)	DAN23120
	IB=NB-KIK+2-NLM	DAN23130
	IS=KIK-1	DAN23140
	JS=NA-NB+KIK-1	DAN23150
	NS=NB-NLM	DAN23160
	IS2=NA-NB+2*KIK-2	DAN23170
	XSX=DFLOAT(IS2)	DAN23180
	WY=0.00	DAN23190
	IF(IB.LE.0)GO TO 45	DAN23200
	IF((NS-1).LT.0)GO TO 45	DAN23210
	DO 10 J=1,IB	DAN23220
	JM=J-1	DAN23230
	IF((IB-JM-1).LT.0)GO TO 10	DAN23240
	I1=J	DAN23250
	I2=IS+JM	DAN23260
	IF(IS.GT.0)GO TO 5	DAN23270
	ZZ=1.00	DAN23280
	GO TO 15	DAN23290
5	ZZ=F(I2,I1)	DAN23300
15	I1=IS+J-1	DAN23310
	I2=IS+JM	DAN23320
	IF((I1-1).LT.0)GO TO 10	DAN23330
	IF(I.EQ.0)GO TO 25	DAN23340
	YY=F(I2,I1)	DAN23350
	GO TO 35	DAN23360

25	YY=1.DO	DAN23370
35	WY=(-1.DO)**JM*ZZ*YY*F(NS-I,2)/(F(IB-JM-1,2)*F(IS2+J,2))+WY	DAN23380
10	CONTINUE	DAN23390
	CK=(XSX+1.DO)*F(JS,1)/F(IS,1)*WY	DAN23400
	RETURN	DAN23410
45	CK=0.DO	DAN23420
	RETURN	DAN23430
	END	DAN23440
CMTBSYM	SUBROUTINE MTBSYM	DAN23450
	SUBROUTINE MTBSYM(A,N,NMAX)	DAN23460
	IMPLICIT REAL*8(A-H,O-Z)	DAN23470
	DIMENSION A(NMAX,NMAX)	DAN23480
C	THIS SUBROUTINE SYMMETRIZES THE MATRIX A.	DAN23490
C	A IS ORIGINALLY STORED IN THE TOP HALF OF A.	DAN23500
C	A(J,I)=A(I,J)	DAN23510
C		DAN23520
	DO 1 J=2,N	DAN23530
	JM=J-1	DAN23540
	DO 1 I=1,JM	DAN23550
	A(J,I)=A(I,J)	DAN23560
1	CONTINUE	DAN23570
	RETURN	DAN23580
	END	DAN23590
CMBTSYM	SUBROUTINE MBTSYM	DAN23600
	SUBROUTINE MBTSYM(A,N,NMAX)	DAN23610
	IMPLICIT REAL*8(A-H,O-Z)	DAN23620
	DIMENSION A(NMAX,NMAX)	DAN23630
C	THIS SUBROUTINE SYMMETRIZES THE MATRIX A.	DAN23640
C	A IS ORIGINALLY STORED IN THE LOWER HALF OF A.	DAN23650
C	A(I,J)=A(J,I)	DAN23660
	DO 1 J=2,N	DAN23670
	JM=J-1	DAN23680

DO 1 I=1, JM	DAN23690
A(I, J)=A(J, I)	DAN23700
1 CONTINUE	DAN23710
RETURN	DAN23720
END	DAN23730
C SWITCH SUBROUTINE SWITCH	DAN23740
SUBROUTINE SWITCH(A, B, NR, NC, NRX)	DAN23750
IMPLICIT REAL*8(A-H, O-Z)	DAN23760
DIMENSION A(NRX, NRX), B(NRX, NRX)	DAN23770
C SUBROUTINE SWITCHES ROWS FOR COLUMNS IN MATRIX A.	DAN23780
C B IS A DUMMY MATRIX USED TO SWITCH ROWS FOR COLUMNS	DAN23790
DO 10 I=1, NC	DAN23800
DO 10 J=1, NR	DAN23810
10 B(I, J)=A(J, I)	DAN23820
DO 20 I=1, NC	DAN23830
DO 20 J=1, NR	DAN23840
20 A(I, J)=B(I, J)	DAN23850
RETURN	DAN23860
END	DAN23870
C MMBAT2 SUBROUTINE MMBAT2	DAN23880
SUBROUTINE MMBAT2(A, B, NCA, NR, NCB, X, NBMX)	DAN23890
IMPLICIT REAL*8(A-H, O-Z)	DAN23900
DIMENSION A(NBMX, NBMX), B(NBMX, NBMX), X(NBMX)	DAN23910
C	DAN23920
C THIS SUBROUTINE COMPUTES THE MATRIX PRODUCT	DAN23930
C C = B * AT	DAN23940
C WHERE AT IS THE TRANSPOSE OF A, A IS NR BY NCA, B IS NCB BY NR	DAN23950
C AND THE RESULT C IS NCB BY NCA (ROWS BY COLUMNS)	DAN23960
C ON RETURN FROM THIS SUBROUTINE B CONTAINS C, A CONTAINS AT.	DAN23970
C TAKE THE TRANSPOSE OF A. STORE RESULTS IN A.	DAN23980
DOUBLE PRECISION SUM	DAN23990
NMAX=NR	DAN24000

IF(NCA.GT.NR)NMAX=NCA	DAN24010
DO 3 J=2,NMAX	DAN24020
IHI=J-1	DAN24030
DO 3 I=1,IHI	DAN24040
FT=A(I,J)	DAN24050
A(I,J)=A(J,I)	DAN24060
A(J,I)=FT	DAN24070
3 CONTINUE	DAN24080
C	DAN24090
C	DAN24100
C	DAN24110
C	DAN24120
DO 7 I=1,NCB	DAN24130
C	DAN24140
C	DAN24150
C	DAN24160
DO 5 K=1,NCA	DAN24170
SUM=0.DO	DAN24180
DO 4 J=1,NR	DAN24190
SUM=SUM+B(I,J)*A(J,K)	DAN24200
4 CONTINUE	DAN24210
X(K)=SUM	DAN24220
5 CONTINUE	DAN24230
C	DAN24240
C	DAN24250
DO 6 K=1,NCA	DAN24260
B(I,K)=X(K)	DAN24270
6 CONTINUE	DAN24280
7 CONTINUE	DAN24290
RETURN	DAN24300
END	DAN24310
CMULT2 SUBROUTINE MULT2	DAN24320

	SUBROUTINE MULT2(A,B,C,N,NRX)	DAN24330
C	MATRIX MULTIPLICATION ROUTINE FOR SQUARE MATRICES.	DAN24340
C	C = A * B	DAN24350
	IMPLICIT REAL*8(A-H,O-Z)	DAN24360
	DIMENSION A(NRX,NRX),B(NRX,NRX),C(NRX,NRX)	DAN24370
	DO 10 I=1,N	DAN24380
	DO 10 J=1,N	DAN24390
	C(I,J)=0.DO	DAN24400
	DO 10 M=1,N	DAN24410
10	C(I,J)=C(I,J)+A(I,M)*B(M,J)	DAN24420
	RETURN	DAN24430
	END	DAN24440
CLAB	SUBROUTINE LAB	DAN24450
	SUBROUTINE LAB	DAN24460
	COMMON/LABELS/ILBL(12),ILAB(12)	DAN24470
	COMMON/ZEIT/LAPSE,LAPST	DAN24480
	REAL*8 ILBL,ILAB	DAN24490
	REAL*4 LAPSE,LAPST	DAN24500
	COMMON/IOIND/ICON(24)	DAN24510
	WRITE(6,101)ILAB	DAN24520
	READ(5,100)ILBL	DAN24530
	WRITE(6,102)ILBL	DAN24540
	READ(5,200) (ICON(I),I=1,24)	DAN24550
	WRITE(6,201) (I,I=1,24),(ICON(I),I=1,24)	DAN24560
	LAPSN=0.0	DAN24570
	CALL STIME(ITIME)	DAN24580
	LAPSE=(FLOAT(ITIME))*0.36	DAN24590
	LAPST=LAPSE	DAN24600
	RETURN	DAN24610
100	FORMAT(12A6)	DAN24620
101	FORMAT(1H1////29X,12A6//)	DAN24630
102	FORMAT(29X,12A6//)	DAN24640

200	FORMAT(24I3)	DAN24650
201	FORMAT(51X,28H** INPUT - OUTPUT OPTIONS **/29X,24I3/29X,24I3)	DAN24660
	END	DAN24670
CFILE	SUBROUTINE FILE (NAMFIL,NTAPE,LABLE)	DAN24680
	SUBROUTINE FILE(NAMFIL,NTAPE,LABLE)	DAN24690
C	THE SUBROUTINE FILE SEARCHES THE FILE UNIT NTAPE FOR THE DATA	DAN24700
C	FILE NAMED NAMFIL. IF IT FINDS IT THE FILE UNIT IS POSITIONED TO	DAN24710
C	READ THE FILE.	DAN24720
	REAL*8 NAMFIL,LABLE,NAMTAP	DAN24730
	EQUIVALENCE (NOFILE,XNOFIL)	DAN24740
	COMMON /IOIND/ ICON(24)	DAN24750
	DIMENSION LABLE(1)	DAN24760
	NT=NTAPE	DAN24770
	IF(ICON(10).GT.0) WRITE(6,100) NT,NAMFIL	DAN24780
	M=3	DAN24790
1	CALL EFSKIP (NT,1)	DAN24800
	READ(NT) NAMTAP,NOFILE,(LABLE(I),I=3,NOFILE)	DAN24810
C	SEARCH FOR FILE NAME	DAN24820
	DO3I=M,NOFILE	DAN24830
	II=I	DAN24840
	IF(LABLE(I).EQ.NAMFIL) GOTO6	DAN24850
3	CONTINUE	DAN24860
	IF(LABLE(NOFILE).EQ.0) GOTO10	DAN24870
	M=NOFILE+1	DAN24880
	GOTO1	DAN24890
C	FOUND FILE NAME	DAN24900
6	IF(ICON(10).GT.0) WRITE(6,105)	DAN24910
	IF(NOFILE.EQ.I) GOTO9	DAN24920
C	CALL EFSKIP(NT,(I-NOFILE-1))	DAN24930
C	CALL EFSKIP(NT,1)	DAN24940
	REWIND NT	DAN24950
	CALL EFSKIP (NT,I-2)	DAN24960

READ(NT) NAMTAP,NOFILE,(LABEL(I),I=3,NOFILE)	DAN24970
IF(LABEL(NOFILE).EQ.NAMFIL) GOTO9	DAN24980
10 WRITE(6,107)NT,NAMFIL	DAN24990
107 FORMAT(33HOFILE LABELLED WRONG ON FILE NO. I3/	DAN25000
112HOFILE LABEL A6,17H CAN NOT BE FOUND)	DAN25010
CALL ABT	DAN25020
9 LABEL(1)=NAMTAP	DAN25030
LABEL(2)=XNOFIL	DAN25040
RETURN	DAN25050
100 FORMAT(70X,4HTAPE,I3, 19H SEARCHED FOR FILE A6)	DAN25060
105 FORMAT(70X,15HFILE NAME FOUND)	DAN25070
END	DAN25080
CSEC SUBROUTINE SEC	DAN25090
SUBROUTINE SEC(A,B,C)	DAN25100
COMMON/ZEIT/LAPSE,LAPST	DAN25110
REAL*4 LAPSE,LAPST,LAPSN	DAN25120
REAL*8 A,B,C	DAN25130
CALL STIME(ITIME)	DAN25140
LAPSN=(FLOAT(ITIME))*0.36	DAN25150
TIM=LAPSN-LAPSE	DAN25160
LAPSE=LAPSN	DAN25170
WRITE(6,100) A,B,C, TIM	DAN25180
RETURN	DAN25190
100 FORMAT(/50X,3A6,15H ELAPSED TIME =,F9.3,8H SECONDS)	DAN25200
END	DAN25210
CMMOVE SUBROUTINE MMOVE	DAN25220
SUBROUTINE MMOVE(A,B,NR,NC,NMAX)	DAN25230
IMPLICIT REAL*8 (A-H,O-Z)	DAN25240
DIMENSION A(NMAX,NMAX),B(NMAX,NMAX)	DAN25250
C...THIS SUBROUTINE SETS THE NR BY NC ELEMENTS OF A EQUAL TO THE	DAN25260
C...CORRESPONDING ELEMENTS OF B.	DAN25270
DO 1 I=1,NR	DAN25280

DO 1 J=1,NC	DAN25290
B(I,J)=A(I,J)	DAN25300
1 CONTINUE	DAN25310
RETURN	DAN25320
END	DAN25330
CMWRITT SUBROUTINE MWRITT	DAN25340
SUBROUTINE MWRITT(A,WA,WB,WC,ITR,NC,NRX)	DAN25350
IMPLICIT REAL*8 (A-H,O-Z)	DAN25360
C...THIS SUBROUTINE PRINTS OUT THE UPPER TRIANGULAR HALF (INCLUDING THE	DAN25370
C...DIAGONAL) OF THE MATRIX A.	DAN25380
DIMENSION A(NRX,NRX)	DAN25390
REAL*8 WA,WB,WC,ILBL,ILAB	DAN25400
COMMON/LABELS/ILBL(12),ILAB(12)	DAN25410
WRITE(6,100) (ILBL(I),I=1,12),WA,WB,WC	DAN25420
IF(ITR.GT.0) WRITE(6,101) ITR	DAN25430
WRITE(6,102) (M,M=1,10)	DAN25440
DO 1 I=1,NC	DAN25450
WRITE(6,104) I,(A(J,I),J=1,I)	DAN25460
1 CONTINUE	DAN25470
RETURN	DAN25480
100 FORMAT(1H1////31X,12A6/58X,3A6)	DAN25490
101 FORMAT(61X,10HITERATION ,I3)	DAN25500
102 FORMAT(4HOROW,5X,I2,9(10X,I2))	DAN25510
104 FORMAT(I4,10F12.7/(4X,10F12.7))	DAN25520
END	DAN25530
CMMATB1 SUBROUTINE MMATB1	DAN25540
SUBROUTINE MMATB1(A,B,NCA,NR,NCB,X,NBMX)	DAN25550
IMPLICIT REAL*8 (A-H,O-Z)	DAN25560
DIMENSION A(NBMX,NBMX),B(NBMX,NBMX),X(1)	DAN25570
C...THIS SUBROUTINE COMPUTES THE MATRIX PRODUCT -	DAN25580
C... C = AT * B	DAN25590
C...WHERE AT IS THE TRANSPOSE OF A, A IS NR BY NCA, B IS NR BY NCB,	DAN25600

C...AND THE RESULT, C, IS NCA BY NCB. (ROWS BY COLUMNS)	DAN25610
C...ON RETURN FROM THIS SUBROUTINE A CONTAINS C, B IS UNAFFECTED.	DAN25620
C...THE VECTOR X IS USED FOR TEMPORARY STORAGE.	DAN25630
C...TAKE TRANSPOSE OF A. STORE RESULT IN A.	DAN25640
DOUBLE PRECISION SUM	DAN25650
NMAX=NR	DAN25660
IF(NCA.GT.NR) NMAX=NCA	DAN25670
DO 3 J=2,NMAX	DAN25680
IHI=J-1	DAN25690
DO 3 I=1,IHI	DAN25700
FT=A(I,J)	DAN25710
A(I,J)=A(J,I)	DAN25720
A(J,I)=FT	DAN25730
3 CONTINUE	DAN25740
C...COMPUTE C ONE ROW AT A TIME. STORE THE ROW IN X. THEN STORE X BACK	DAN25750
C...IN A.	DAN25760
DO 7 I=1,NCA	DAN25770
C...COMPUTE A ROW OF C. STORE IT IN X.	DAN25780
DO 5 K=1,NCB	DAN25790
SUM=0.000	DAN25800
DO 4 J=1,NR	DAN25810
SUM=SUM+A(I,J)*B(J,K)	DAN25820
4 CONTINUE	DAN25830
X(K)=SUM	DAN25840
5 CONTINUE	DAN25850
C...STORE THE ROW BACK IN A.	DAN25860
DO 6 K=1,NCB	DAN25870
A(I,K)=X(K)	DAN25880
6 CONTINUE	DAN25890
7 CONTINUE	DAN25900
RETURN	DAN25910
END	DAN25920

CMCLRT	SUBROUTINE MCLRT	DAN25930
	SUBROUTINE MCLRT(A,N,NMAX)	DAN25940
	IMPLICIT REAL*8 (A-H,O-Z)	DAN25950
	DIMENSION A(NMAX,NMAX)	DAN25960
C...	THIS SUBROUTINE SETS ALL THE ELEMENTS IN THE UPPER TRIANGULAR HALF	DAN25970
C...	(INCLUDING THE DIAGONAL) OF A EQUAL TO 0.0 THE POSITION OF THE	DAN25980
C...	1,1 ELEMENT OF A IS DEFINED BY THE CALLING PROGRAM.	DAN25990
	DO 1 J=1,N	DAN26000
	DO 1 I=1,J	DAN26010
	A(I,J)=0.0	DAN26020
1	CONTINUE	DAN26030
	RETURN	DAN26040
	END	DAN26050
CMCLEAR	SUBROUTINE MCLEAR	DAN26060
	SUBROUTINE MCLEAR(A,NR,NC,NMAX)	DAN26070
	IMPLICIT REAL*8 (A-H,O-Z)	DAN26080
	DIMENSION A(NMAX,NMAX)	DAN26090
C...	THIS SUBROUTINE SETS THE NR BY NC ELEMENTS OF A EQUAL TO 0.0	DAN26100
C...	THE 1,1 ELEMENT OF A IS DEFINED BY THE CALLING PROGRAM.	DAN26110
	DO 1 J=1,NC	DAN26120
	DO 1 I=1,NR	DAN26130
	A(I,J)=0.0	DAN26140
1	CONTINUE	DAN26150
	RETURN	DAN26160
	END	DAN26170
CHDIAG	SUBROUTINE HDIAG	DAN26180
	SUBROUTINE HDIAG(H,U,X,IQ,N,NBMX,IEGEN,NR)	DAN26190
	IMPLICIT REAL*8 (A-H,O-Z)	DAN26200
C	FORTRAN IV DIAGONALIZATION OF A REAL SYMMETRIC MATRIX BY THE	DAN26210
C	JACOBI METHOD.	DAN26220
C	MAY 19,1959,REVISED TO FORTRAN IV AUG 17,1966	DAN26230
C	CALLING SEQUENCE FOR DIAGONALIZATION	DAN26240

C	CALL HDIAG(H,U,X,IQ,N,NBMX,IEGEN,NR)	DAN26250
C	WHERE H IS THE ARRAY TO BE DIAGONALIZED.	DAN26260
C	N IS THE ORDER OF THE MATRIX, H.	DAN26270
C	IEGEN MUST BE SET UNEQUAL TO ZERO IF ONLY EIGENVALUES ARE	DAN26280
C	TO BE COMPUTED.	DAN26290
C	IEGEN MUST BE SET EQUAL TO ZERO IF EIGENVALUES AND EIGENVECTORS	DAN26300
C	ARE TO BE COMPUTED.	DAN26310
C	U IS THE UNITARY MATRIX USED FOR FORMATION OF THE EIGENVECTORS.	DAN26320
C	NR IS THE NUMBER OF ROTATIONS.	DAN26330
C	NBMX IS THE MAXIMUM ORDER OF THE MATRIX H TO BE DIAGONALISED	DAN26340
C	X,IQ ARE ADDITIONAL ARRAYS BOTH ARE OF LENGTH AT LEAST NBMX	DAN26350
C	THE SUBROUTINE OPERATES ONLY ON THE ELEMENTS OF H THAT ARE TO THE	DAN26360
C	RIGHT OF THE MAIN DIAGONAL. THUS, ONLY A TRIANGULAR	DAN26370
C	SECTION NEED BE STORED IN THE ARRAY H.	DAN26380
C	DIMENSION H(NBMX,NBMX),U(NBMX,NBMX),X(1),IQ(1)	DAN26390
C	SET INDICATOR FOR SHUT OFF RAP IS APPROX 2**-46.	DAN26400
C	SPECIFICALLY FOR THE CDC6600 48 BIT MANTISSA	DAN26410
	DATA RAPS/2.0E-13/,HDTES/1.0E38/	DAN26420
	IF(IEGEN.NE.0) GO TO 15	DAN26430
	DO 10 I=1,N	DAN26440
	DO 10 J=1,N	DAN26450
	U(I,J)=0.	DAN26460
	IF(I.EQ.J) U(I,J)=1.	DAN26470
10	CONTINUE	DAN26480
15	NR=0	DAN26490
	IF(N.LE.1) RETURN	DAN26500
C	SCAN FOR LARGEST OFF DIAGONAL ELEMENT IN EACH ROW	DAN26510
C	X(I) CONTAINS LARGEST ELEMENT IN ITH ROW	DAN26520
C	IQ(I) HOLDS SECOND SUBSCRIPT DEFINING POSITION OF ELEMENT	DAN26530
	NM1=N-1	DAN26540
	DO 30 I=1,NM1	DAN26550
	X(I)=0.	DAN26560

	IPL1=I+1	DAN26570
	DO 30 J=IPL1,N	DAN26580
	IF(X(I).GT.DABS(H(I,J))) GO TO 30	DAN26590
	X(I)=DABS(H(I,J))	DAN26600
	IQ(I)=J	DAN26610
30	CONTINUE	DAN26620
C	SET UP ZERO CUT OFF (RAP) , INITIALIZE HDTEST.	DAN26630
	RAP=7.45058060E-9	DAN26640
	HDTEST=1.0E38	DAN26650
C	FIND MAXIMUM OF X(I) S FOR PIVOT ELEMENT AND TEST FOR END OF PROB	DAN26660
40	DO 70 I=1,NM11	DAN26670
	IF(I.LE.1) GO TO 60	DAN26680
	IF(XMAX.GE.X(I)) GO TO 70	DAN26690
60	XMAX=X(I)	DAN26700
	IPIV=I	DAN26710
	JPIV=IQ(I)	DAN26720
70	CONTINUE	DAN26730
C	IS MAX. X(I) EQUAL TO ZERO, IF LESS THAN HDTEST, REVISE HDTEST	DAN26740
	IF(XMAX.LE.0.0) RETURN	DAN26750
	IF(HDTEST.LE.0.0) GO TO 90	DAN26760
	IF(XMAX.GT.HDTEST) GO TO 148	DAN26770
90	HDIMIN=DABS(H(1,1))	DAN26780
	DO 110 I= 2,N	DAN26790
	IF(HDIMIN.GT.DABS(H(I,I))) HDIMIN=DABS(H(I,I))	DAN26800
110	CONTINUE	DAN26810
	HDTEST=HDIMIN*RAP	DAN26820
C	RETURN IF MAX.H(I,J)LESS THAN RAP*ABS(MIN(H(K,K)))	DAN26830
	IF(HDTEST.GE.XMAX) RETURN	DAN26840
148	NR = NR+1	DAN26850
C	COMPUTE TANGENT, SINE AND COSINE,H(I,I),H(J,J)	DAN26860
150	TANG=DSIGN(2.DO,(H(IPIV,IPIV)-H(JPIV,JPIV)))*H(IPIV,JPIV)/(DABS	DAN26870
	1(H(IPIV,IPIV)-H(JPIV,JPIV))+DSQRT((H(IPIV,IPIV)-H(JPIV,JPIV))**2	DAN26880

	2 +4.0*H(IPIV,JPIV)**2))	DAN26890
	COSINE=1./DSQRT(1.+TANG**2)	DAN26900
	SINE=TANG*COSINE	DAN26910
	HII=H(IPIV,IPIV)	DAN26920
	H(IPIV,IPIV)=COSINE**2*(HII+TANG*(2.*H(IPIV,JPIV)+TANG*H(JPIV,JPIV	DAN26930
	1)))	DAN26940
	H(JPIV,JPIV)=COSINE**2*(H(JPIV,JPIV)-TANG*(2.*H(IPIV,JPIV)-TANG*H	DAN26950
	1I))	DAN26960
	H(IPIV,JPIV)=0.	DAN26970
C	PSEUDO RANK THE EIGENVALUES	DAN26980
C	ADJUST SINE AND COS FOR COMPUTATION OF H(IK) AND U(IK)	DAN26990
	IF(H(IPIV,IPIV).GE.H(JPIV,JPIV)) GO TO 153	DAN27000
	HTEMP=H(IPIV,IPIV)	DAN27010
	H(IPIV,IPIV)=H(JPIV,JPIV)	DAN27020
	H(JPIV,JPIV)=HTEMP	DAN27030
C	RECOMPUTE SINE AND COS	DAN27040
	HTEMP=DSIGN(1.DO,-SINE)*COSINE	DAN27050
	COSINE=DABS(SINE)	DAN27060
	SINE=HTEMP	DAN27070
153	CONTINUE	DAN27080
C	THE I OR J ROW.	DAN27090
	DO 350 I=1,NMII	DAN27100
	IF(I.EQ.IPIV.OR.I.EQ.JPIV) GO TO 350	DAN27110
	IF(IQ(I).NE.IPIV.AND.IQ(I).NE.JPIV) GO TO 350	DAN27120
	K=IQ(I)	DAN27130
	HTEMP=H(I,K)	DAN27140
	H(I,K)=0.	DAN27150
	IPL1=I+1	DAN27160
	X(I)=0.	DAN27170
C	SEARCH IN DEPLETED ROW FOR NEW MAXIMUM	DAN27180
	DO 320 J=IPL1,N	DAN27190
	IF(X(I).GT.DABS(H(I,J))) GO TO 320	DAN27200

	X(I)=DABS(H(I,J))	DAN27210
	IQ(I)=J	DAN27220
320	CONTINUE	DAN27230
	H(I,K)=HTEMP	DAN27240
350	CONTINUE	DAN27250
	X(IPIV)=0.	DAN27260
	X(JPIV)=0.	DAN27270
	DO 530 I=1,N	DAN27280
	IF(I-IPIV)370,530,420	DAN27290
370	HTEMP = H(I,IPIV)	DAN27300
	H(I,IPIV) = COSINE*HTEMP + SINE*H(I,JPIV)	DAN27310
	IF(X(I).GE.DABS(H(I,IPIV))) GO TO 390	DAN27320
	X(I)=DABS(H(I,IPIV))	DAN27330
	IQ(I)=IPIV	DAN27340
390	H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)	DAN27350
	IF(X(I).GE.DABS(H(I,JPIV))) GO TO 530	DAN27360
	X(I)=DABS(H(I,JPIV))	DAN27370
	IQ(I)=JPIV	DAN27380
	GO TO 530	DAN27390
420	IF(I-JPIV)430,530,480	DAN27400
430	HTEMP = H(IPIV,I)	DAN27410
	H(IPIV,I) = COSINE*HTEMP + SINE*H(I,JPIV)	DAN27420
	IF(X(IPIV).GE.DABS(H(IPIV,I))) GO TO 450	DAN27430
	X(IPIV)=DABS(H(IPIV,I))	DAN27440
	IQ(IPIV)=I	DAN27450
450	H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)	DAN27460
	IF(X(I).GE.DABS(H(I,JPIV))) GO TO 530	DAN27470
	X(I)=DABS(H(I,JPIV))	DAN27480
	IQ(I)=JPIV	DAN27490
	GO TO 530	DAN27500
480	HTEMP = H(IPIV,I)	DAN27510
	H(IPIV,I) = COSINE*HTEMP + SINE*H(JPIV,I)	DAN27520

	IF(X(IPIV).GE.DABS(H(IPIV,I))) GO TO 500	DAN27530
	X(IPIV)=DABS(H(IPIV,I))	DAN27540
	IQ(IPIV)=I	DAN27550
500	H(JPIV,I) = -SINE*HTEMP + COSINE*H(JPIV,I)	DAN27560
	IF(X(JPIV).GT.DABS(H(JPIV,I))) GO TO 530	DAN27570
	X(JPIV)=DABS(H(JPIV,I))	DAN27580
	IQ(JPIV)=I	DAN27590
530	CONTINUE	DAN27600
C	TEST FOR COMPUTATION OF EIGENVECTORS	DAN27610
	IF(IEGEN.NE.0) GO TO 40	DAN27620
	DO 550 I=1,N	DAN27630
	HTEMP=U(I,IPIV)	DAN27640
	U(I,IPIV)=COSINE*HTEMP+SINE*U(I,JPIV)	DAN27650
550	U(I,JPIV)=-SINE*HTEMP+COSINE*U(I,IPIV)	DAN27660
	GO TO 40	DAN27670
	END	DAN27680
CFOLLOW	SUBROUTINE FOLLOW	DAN27690
	SUBROUTINE FOLLOW	DAN27700
	COMMON /ZEIT/ LAPSE,LAPST	DAN27710
	COMMON /LABELS/ ILBL(12),ILAB(12)	DAN27720
	REAL*8 ILBL,ILAB	DAN27730
	REAL*4 LAPSE,LAPST	DAN27740
	LAPSE = LAPST	DAN27750
	WRITE (6,100) ILAB	DAN27760
	WRITE (6,101) ILBL	DAN27770
	CALL SEC (6HFINISH,6HED PRO,6HBLEM)	DAN27780
	STOP	DAN27790
100	FORMAT(1H1 //// 15X 12A6)	DAN27800
101	FORMAT (15X 12A6)	DAN27810
	END	DAN27820
CFMFUHF	SUBROUTINE FMFUHF	DAN27830
	SUBROUTINE FMFUHF(A,B,C,NC,NRX)	DAN27840

IMPLICIT REAL*8 (A-H,O-Z)	DAN27850
DIMENSION A(NRX,NRX),B(NRX,NRX),C(NRX,NRX)	DAN27860
C...THIS SUBROUTINED FORMS THE UNRESTRICTED HARTREE FOCK HAMILTONIAN	DAN27870
C...MATICES, FA AND FB.	DAN27880
C... FA = H + JT - KA	DAN27890
C... FB = H + JT - KB	DAN27900
C...ON ENTRY C CONTAINS THE MATRIX FT, FT = H + JT, A CONTAINS KA, AND	DAN27910
C...B CONTAINS KB. ON EXIT A CONTAINS FA, AND B CONTAINS FB. ONLY THE	DAN27920
C...UPPER TRIANGULAR HALF (INCLUDING THE DIAGONAL) OF A, B, AND C IS	DAN27930
C...USED IN THIS ROUTINE AS ALL THE MATRICES ARE SYMMETRIC.	DAN27940
DO 2 J=1,NC	DAN27950
DO 1 I=1,J	DAN27960
A(I,J)= C(I,J)-A(I,J)	DAN27970
B(I,J)= C(I,J)-B(I,J)	DAN27980
1 CONTINUE	DAN27990
2 CONTINUE	DAN28000
RETURN	DAN28010
END	DAN28020
CFMJUHF SUBROUTINE FMJUH	DAN28030
SUBROUTINE FMJUH(T,R,S,TT,RR,SS,NBFNS,NBMX,NAM,NITAPE,ILABL,	DAN28040
1 PKLABL,VALUEM,NINMAX,IPTI,CUTLO,IX)	DAN28050
IMPLICIT REAL*8 (A-H,O-Z)	DAN28060
REAL*8 INTNAM,ILABL,ILAB,ILBL,NAM	DAN28070
DIMENSION T(NBMX,NBMX),TT(NBMX,NBMX),R(NBMX,NBMX),	DAN28080
1 RR(NBMX,NBMX),S(NBMX,NBMX),SS(NBMX,NBMX),	DAN28090
1 PKLABL(NINMAX),VALUEM(NINMAX),	DAN28100
1 IPRT(36),ILABL(1)	DAN28110
C...INITIALIZE COUNTERS.	DAN28120
NRECENT=0	DAN28130
LSUMNW=0	DAN28140
NMINNW=0	DAN28150
IRC=1	DAN28160

C...PRINT HEADER IF CHECK SUM FLAG IS ON.	DAN28170
IF(IPTI.EQ.0) GO TO 70	DAN28180
WRITE(6,100)	DAN28190
70 CONTINUE	DAN28200
C...POSITION TAPE TO READ TWO ELECTRON INTEGRALS.	DAN28210
CALL FILE(NAM,NITAPE,ILABL)	DAN28220
C...LOOP UNTIL LAST RECORD OF TWO ELECTRON INTEGRALS IS REACHED	DAN28230
C...READ A RECORD OF INTEGRALS.	DAN28240
72 READ(NITAPE) NINTS,LSTRCD,PKLABL,VALUEM	DAN28250
C...UP RECORD COUNTER.	DAN28260
NRECNT=NRECNT+1	DAN28270
C...SET UP AND PRINT CHECKSUMS IF CHECKSUM PRINT FLAG IS ON.	DAN28280
IF(IPTI.EQ.0) GO TO 75	DAN28290
IF(IRC.EQ.1) IPRT(1)=NRECNT	DAN28300
CALL UNPACK(PKLABL(1),IA,JA,KA,LA,IZ,ITA)	DAN28310
CALL UNPACK(PKLABL(NINTS),IB,JB,KB,LB,IZ,ITB)	DAN28320
IPRT(IRC+1)=JA	DAN28330
IPRT(IRC+2)=LA	DAN28340
IPRT(IRC+3)=NINTS	DAN28350
IPRT(IRC+4)=JB	DAN28360
IPRT(IRC+5)=LB	DAN28370
IRC=IRC+5	DAN28380
IF(IRC.NE.36) GO TO 75	DAN28390
WRITE(6,103) IPRT	DAN28400
IRC=1	DAN28410
C...CHECK FOR ERRONEOUS VALUES OF NINTS.	DAN28420
75 IF(NINTS.GT.NINMAX.OR.NINTS.LE.0) GO TO 500	DAN28430
C...LOOP ON EACH INTEGRAL.	DAN28440
C...PLACE EACH INTEGRAL WITH ITS PROPER MULTIPLIER IN THE MATRICES.	DAN28450
DO 29 M=1,NINTS	DAN28460
V=VALUEM(M)	DAN28470
CALL UNPACK(PKLABL(M),I,J,K,L,MU,IZ)	DAN28480

C...SKIP THE INTEGRAL IF ITS VALUE IS SMALL.	DAN28490
IF(DABS(V).LT.CUTLO) GO TO 29	DAN28500
LSUMNW=LSUMNW+L	DAN28510
NMINNW=NMINNW+1	DAN28520
C...DEPENDING ON THE TYPE OF LABEL OF THE INTEGRAL AS GIVEN BY THE	DAN28530
C...INDEX MU, MULTIPLY THE VALUE OF THE INTEGRAL BY ITS PROPER	DAN28540
C...DENSITY MATRIX PREFACTORS AND ADD THE PRODUCTS TO THE PROPER ELEMENT	DAN28550
C...OF THE MATRICES TO BE FORMED.	DAN28560
GOTO(12,13,14,15,16,17,18,19,20,21,22,23,24,25),MU	DAN28570
C...I/I/I/I..	DAN28580
12 T(I,I)=T(I,I)+TT(I,I)*V	DAN28590
R(I,I)=R(I,I)+RR(I,I)*V	DAN28600
S(I,I)=S(I,I)+SS(I,I)*V	DAN28610
GO TO 29	DAN28620
C...I/J/I/J...I.GT.J	DAN28630
13 T(J,I)=T(J,I)+2.*TT(I,J)*V	DAN28640
R(J,I)=R(J,I)+RR(I,J)*V	DAN28650
S(J,I)=S(J,I)+SS(I,J)*V	DAN28660
R(I,I)=R(I,I)+RR(J,J)*V	DAN28670
S(I,I)=S(I,I)+SS(J,J)*V	DAN28680
R(J,J)=R(J,J)+RR(I,I)*V	DAN28690
S(J,J)=S(J,J)+SS(I,I)*V	DAN28700
GO TO 29	DAN28710
C...I/I/K/K...I.GT.K	DAN28720
14 T(I,I)=T(I,I)+TT(K,K)*V	DAN28730
T(K,K)=T(K,K)+TT(I,I)*V	DAN28740
R(K,I)=R(K,I)+RR(I,K)*V	DAN28750
S(K,I)=S(K,I)+SS(I,K)*V	DAN28760
GO TO 29	DAN28770
C...I/I/I/L...I.GT.L	DAN28780
15 T(L,I)=T(L,I)+TT(I,I)*V	DAN28790
T(I,I)=T(I,I)+2.*TT(I,L)*V	DAN28800

	R(L,I)=R(L,I)+RR(I,I)*V	DAN28810
	S(L,I)=S(L,I)+SS(I,I)*V	DAN28820
	R(I,I)=R(I,I)+2.*RR(I,L)*V	DAN28830
	S(I,I)=S(I,I)+2.*SS(I,L)*V	DAN28840
	GO TO 29	DAN28850
C...I/I/K/L...I.GT.K.GT.L		DAN28860
16	T(L,K)=T(L,K)+TT(I,I)*V	DAN28870
	T(I,I)=T(I,I)+2.*TT(K,L)*V	DAN28880
	R(L,I)=R(L,I)+RR(I,K)*V	DAN28890
	S(L,I)=S(L,I)+SS(I,K)*V	DAN28900
	R(K,I)=R(K,I)+RR(I,L)*V	DAN28910
	S(K,I)=S(K,I)+SS(I,L)*V	DAN28920
	GO TO 29	DAN28930
C...I/J/J/J...I.GT.J		DAN28940
17	T(J,J)=T(J,J)+2.*TT(I,J)*V	DAN28950
	T(J,I)=T(J,I)+TT(J,J)*V	DAN28960
	R(J,J)=R(J,J)+2.*RR(I,J)*V	DAN28970
	S(J,J)=S(J,J)+2.*SS(I,J)*V	DAN28980
	R(J,I)=R(J,I)+RR(J,J)*V	DAN28990
	S(J,I)=S(J,I)+SS(J,J)*V	DAN29000
	GO TO 29	DAN29010
C...I/J/K/K...I.GT.J.GT.K		DAN29020
18	T(K,K)=T(K,K)+2.*TT(I,J)*V	DAN29030
	T(J,I)=T(J,I)+TT(K,K)*V	DAN29040
	R(K,J)=R(K,J)+RR(I,K)*V	DAN29050
	S(K,J)=S(K,J)+SS(I,K)*V	DAN29060
	R(K,I)=R(K,I)+RR(J,K)*V	DAN29070
	S(K,I)=S(K,I)+SS(J,K)*V	DAN29080
	GO TO 29	DAN29090
C...I/J/K/K...I.GT.K.GT.J		DAN29100
19	T(K,K)=T(K,K)+2.*TT(I,J)*V	DAN29110
	T(J,I)=T(J,I)+TT(K,K)*V	DAN29120

R(J,K)=R(J,K)+RR(I,K)*V	DAN29130
S(J,K)=S(J,K)+SS(I,K)*V	DAN29140
R(K,I)=R(K,I)+RR(K,J)*V	DAN29150
S(K,I)=S(K,I)+SS(K,J)*V	DAN29160
GO TO 29	DAN29170
C...I/J/J/L...I.GT.J.GT.L	DAN29180
20 T(J,I)=T(J,I)+2.*TT(J,L)*V	DAN29190
T(L,J)=T(L,J)+2.*TT(I,J)*V	DAN29200
R(J,J)=R(J,J)+2.*RR(I,L)*V	DAN29210
S(J,J)=S(J,J)+2.*SS(I,L)*V	DAN29220
R(J,I)=R(J,I)+RR(J,L)*V	DAN29230
S(J,I)=S(J,I)+SS(J,L)*V	DAN29240
R(L,J)=R(L,J)+RR(I,J)*V	DAN29250
S(L,J)=S(L,J)+SS(I,J)*V	DAN29260
R(L,I)=R(L,I)+RR(J,J)*V	DAN29270
S(L,I)=S(L,I)+SS(J,J)*V	DAN29280
GO TO 29	DAN29290
C...I/J/I/L...I.GT.J.GT.L	DAN29300
21 T(J,I)=T(J,I)+2.*TT(I,L)*V	DAN29310
T(L,I)=T(L,I)+2.*TT(I,J)*V	DAN29320
R(I,I)=R(I,I)+2.*RR(J,L)*V	DAN29330
S(I,I)=S(I,I)+2.*SS(J,L)*V	DAN29340
R(J,I)=R(J,I)+RR(I,L)*V	DAN29350
S(J,I)=S(J,I)+SS(I,L)*V	DAN29360
R(L,J)=R(L,J)+RR(I,I)*V	DAN29370
S(L,J)=S(L,J)+SS(I,I)*V	DAN29380
R(L,I)=R(L,I)+RR(I,J)*V	DAN29390
S(L,I)=S(L,I)+SS(I,J)*V	DAN29400
GO TO 29	DAN29410
C...I/J/K/J...I.GT.K.GT.J	DAN29420
22 T(J,I)=T(J,I)+2.*TT(K,J)*V	DAN29430
T(J,K)=T(J,K)+2.*TT(I,J)*V	DAN29440

R(J,J)=R(J,J)+2.*RR(I,K)*V	DAN29450
S(J,J)=S(J,J)+2.*SS(I,K)*V	DAN29460
R(J,K)=R(J,K)+RR(I,J)*V	DAN29470
S(J,K)=S(J,K)+SS(I,J)*V	DAN29480
R(J,I)=R(J,I)+RR(K,J)*V	DAN29490
S(J,I)=S(J,I)+SS(K,J)*V	DAN29500
R(K,I)=R(K,I)+RR(J,J)*V	DAN29510
S(K,I)=S(K,I)+SS(J,J)*V	DAN29520
GO TO 29	DAN29530
C...I/J/K/L...I.GT.J.GT.K.GT.L	DAN29540
23 T(J,I)=T(J,I)+2.*TT(K,L)*V	DAN29550
T(L,K)=T(L,K)+2.*TT(I,J)*V	DAN29560
R(K,I)=R(K,I)+RR(J,L)*V	DAN29570
S(K,I)=S(K,I)+SS(J,L)*V	DAN29580
R(K,J)=R(K,J)+RR(I,L)*V	DAN29590
S(K,J)=S(K,J)+SS(I,L)*V	DAN29600
R(L,J)=R(L,J)+RR(I,K)*V	DAN29610
S(L,J)=S(L,J)+SS(I,K)*V	DAN29620
R(L,I)=R(L,I)+RR(J,K)*V	DAN29630
S(L,I)=S(L,I)+SS(J,K)*V	DAN29640
GO TO 29	DAN29650
C...I/J/K/L...I.GT.K.GT.J.GT.L	DAN29660
24 T(J,I)=T(J,I)+2.*TT(K,L)*V	DAN29670
T(L,K)=T(L,K)+2.*TT(I,J)*V	DAN29680
R(K,I)=R(K,I)+RR(J,L)*V	DAN29690
S(K,I)=S(K,I)+SS(J,L)*V	DAN29700
R(J,K)=R(J,K)+RR(I,L)*V	DAN29710
S(J,K)=S(J,K)+SS(I,L)*V	DAN29720
R(L,J)=R(L,J)+RR(I,K)*V	DAN29730
S(L,J)=S(L,J)+SS(I,K)*V	DAN29740
R(L,I)=R(L,I)+RR(K,J)*V	DAN29750
S(L,I)=S(L,I)+SS(K,J)*V	DAN29760

GO TO 29	DAN29770
C...I/J/K/L...I.GT.K.GT.L.GT.J	DAN29780
25 T(J,I)=T(J,I)+2.*TT(K,L)*V	DAN29790
T(L,K)=T(L,K)+2.*TT(I,J)*V	DAN29800
R(K,I)=R(K,I)+RR(L,J)*V	DAN29810
S(K,I)=S(K,I)+SS(L,J)*V	DAN29820
R(J,K)=R(J,K)+RR(I,L)*V	DAN29830
S(J,K)=S(J,K)+SS(I,L)*V	DAN29840
R(J,L)=R(J,L)+RR(I,K)*V	DAN29850
S(J,L)=S(J,L)+SS(I,K)*V	DAN29860
R(L,I)=R(L,I)+RR(K,J)*V	DAN29870
S(L,I)=S(L,I)+SS(K,J)*V	DAN29880
29 CONTINUE	DAN29890
C...IF THIS WAS NOT THE LAST RECORD GO BACK INTO THE LOOP AND READ	DAN29900
C...ANOTHER RECORD OF INTEGRALS IN.	DAN29910
IF(LSTRCD.EQ.0) GO TO 72	DAN29920
C...IF CHECK SUM PRINT FLAG IS ON AND THERE ARE MORE CHECKSUMS THEN	DAN29930
C...PRINT THEM.	DAN29940
IF(IPTI.EQ.0.AND.IRC.EQ.1) GO TO 76	DAN29950
WRITE(6,103) (IPRT(MN),MN=1,IRC)	DAN29960
C...COMPARE THE CHECKSUMS OBTAINED ON THIS RUN THROUGH THIS ROUTINE	DAN29970
C...WITH THOSE OBTAINED ON THE PREVIOUS RUN THROUGH. IN CASE OF ERROR	DAN29980
C...ABORT. ALSO PRINT CHECK SUMS IF PRINT FLAG IS SET.	DAN29990
76 IF(IX.EQ.0) GO TO 79	DAN30000
IF(LSUM.NE.LSUMNW.OR.NOSINT.NE.NMINNW) GO TO 500	DAN30010
IF(IPTI.EQ.0) GO TO 79	DAN30020
WRITE(6,102) LSUM,LSUMNW,NOSINT,NMINNW	DAN30030
C...STORE THE CHECK SUMS OF THIS RUN THROUGH FOR CHECKING LATER ON NEXT	DAN30040
C...PASS	DAN30050
79 LSUM=LSUMNW	DAN30060
NOSINT=NMINNW	DAN30070
C...SET FLAG TO INDICATE THAT A PASS THROUGH THIS ROUTINE HAS BEEN MADE.	DAN30080

IX=1	DAN30090
C...RETURN TO SCFUHF PROGRAM.	DAN30100
RETURN	DAN30110
C...ERROR EXIT.	DAN30120
500 WRITE(6,501)	DAN30130
CALL ABT	DAN30140
STOP	DAN30150
100 FORMAT(1H1////37X,	DAN30160
161HINTERNAL CHECK SUMS, ETC. FROM READING TWO ELECTRON INTEGRALS//	DAN30170
1 6H REC ,7(1X,17H FIRST NOS LAST)//	DAN30180
1 6H NOS ,7(1X,17H LABEL OF LABEL)//	DAN30190
1 6X,7(1X,17H J L INTS J L))	DAN30200
102 FORMAT(1X,10HLAST L SUM,I12,11H THIS L SUM,I12/1X,17HLAST NOS. OF	DAN30210
1INTS,I12,18H THIS NOS. OF INTS,I12)	DAN30220
103 FORMAT(1X,I4,1X,7(I3,I3,1X,I4,I3,I3,1X))	DAN30230
501 FORMAT(22HOREAD ERROR IN FMJUHF)	DAN30240
END	DAN30250
CFMEXTB SUBROUTINE FMEXTB	DAN30260
SUBROUTINE FMEXTB(A,P,NBFNS,NBMX,PRE,EX)	DAN30270
IMPLICIT REAL*8 (A-H,G-Z)	DAN30280
DIMENSION A(NBMX,NBMX),P(NBMX,NBMX)	DAN30290
DOUBLE PRECISION EY	DAN30300
C...SUBROUTINE FMEXTB COMPUTES THE TRACE OF THE PRODUCT OF THE	DAN30310
C...SYMMETRIC MATRICES A AND P. FURTHER IT MULTIPLIES THE VALUE	DAN30320
C...OF THE TRACE BY THE FACTOR PRE. THE UPPER TRIANGULAR HALF (INCLUDING	DAN30330
C...THE DIAGONAL) OF A IS USED AND THE LOWER TRIANGULAR HALF (INCLUDING	DAN30340
C...THE DIAGONAL) OF P IS USED. THUS	DAN30350
C... EX = PRE*TRACE(A * P)	DAN30360
EY=0.0D0	DAN30370
DO 2 I=1,NBFNS	DAN30380
DO 1 J=1,I	DAN30390
COD=2.0	DAN30400

	IF(I.EQ.J) COD=1.0	DAN30410
	EY=EY+COD*A(J,I)*P(I,J)	DAN30420
1	CONTINUE	DAN30430
2	CONTINUE	DAN30440
	EX=PRE*EY	DAN30450
	RETURN	DAN30460
	END	DAN30470
CEFSKIP	SUBROUTINE EFSKIP(NTAPE,NFILS)	DAN30480
	SUBROUTINE EFSKIP(NTAPE,NFILS)	DAN30490
C	THIS SUBROUTINE MOVES TAPE NO. NTAPE JUST OVER NFILS NUMBER OF	DAN30500
C	END-OF-FILE MARKS, EITHER FORWARD OR BACKWARDS DEPENDING ON THE	DAN30510
C	SIGN OF NFILS. IFNFILS=0, THE SUBROUTINE DOES NOTHING.	DAN30520
	REAL*8 EOF,WORD1	DAN30530
	DATA EOF/6H***EOF/	DAN30540
	NT=NTAPE	DAN30550
	IF(NFILS) 20,18,10	DAN30560
C	FORWARD SPACE OVER NFILS END-OF-FILES ON TAPE NTAPE	DAN30570
10	DO16K=1,NFILS	DAN30580
12	READ(NT) WORD1	DAN30590
	IF(WORD1.NE.EOF) GOTO12	DAN30600
16	CONTINUE	DAN30610
18	RETURN	DAN30620
20	N=-NFILS	DAN30630
C	BACKSPACE FILE UNIT NTAPE OVER NFILS FILE MARKS	DAN30640
	DO30K=1,N	DAN30650
	KOUNT=0	DAN30660
32	BACKSPACE NT	DAN30670
	KOUNT=KOUNT+1	DAN30680
	READ(NT) WORD1	DAN30690
	BACKSPACE NT	DAN30700
	IF(KOUNT.GT.50) GO TO 40	DAN30710
	IF(WORD1.NE.EOF) GOTO32	DAN30720

30	CONTINUE	DAN30730
	RETURN	DAN30740
40	WRITE (6,99) K	DAN30750
	CALL ABT	DAN30760
99	FORMAT(7H0 FILE 13,30H CONTAINS MORE THAT 50 RECORDS)	DAN30770
	END	DAN30780
CADDT	SUBROUTINE ADDT	DAN30790
	SUBROUTINE ADDT(NAM,NITAPE,ILABL,ARRAY,NBMX,PKDLBL,VALINT,NINMAX)	DAN30800
	IMPLICIT REAL*8 (A-H,O-Z)	DAN30810
	DIMENSION PKDLBL(NINMAX),VALINT(NINMAX)	DAN30820
	DIMENSION ARRAY(NBMX,NBMX),ILABL(1)	DAN30830
	REAL*8 NAM,ILABLE	DAN30840
	C...POSITION TAPE, NITAPE, TO READ THE FILE WHOSE NAME IS NAM.	DAN30850
	C...FILE NAM CONTAINS BINARY RECORDS OF INTEGRAL LABELS AND VALUES.	DAN30860
	CALL FILE(NAM,NITAPE,ILABL)	DAN30870
	C...READ A RECORD OF INTEGRAL LABELS AND VALUES.	DAN30880
	1 READ (NITAPE) NINTS,LSTRCD,PKDLBL,VALINT	DAN30890
	IF(NINTS.GT.NINMAX.OR.NINTS.LE.0) GO TO 500	DAN30900
	C...LOOP OVER THE NINTS LABELS AND VALUES IN THE RECORD JUST READ IN.	DAN30910
	DO 2 M=1,NINTS	DAN30920
	C...UNPACK A LABEL.	DAN30930
	CALL UNPACK(PKDLBL(M),I,J,IZ,IZ,IZ,IZ)	DAN30940
	C...PUT VALUE INTO CORRECT POSITION IN ARRAY (UPPER TRIANGULAR HALF)	DAN30950
	ARRAY(J,I)=ARRAY(J,I)+VALINT(M)	DAN30960
	2 CONTINUE	DAN30970
	C...IF THE RECORD JUST READ IN WAS NOT THE LAST GO TO 1 AND READ ANOTHER	DAN30980
	C...FROM TAPE. IF LSTRCD IS NONZERO THEN THE RECORD JUST READ WAS THE	DAN30990
	C...LAST.	DAN31000
	IF(LSTRCD.EQ.0) GO TO 1	DAN31010
	RETURN	DAN31020
	C...ERROR EXIT FOR INCORRECT VALUE OF NINTS (POSSIBLE TAPE READ ERROR).	DAN31030
	500 WRITE(6,510)	DAN31040

CALL ABT	DAN31050
STOP	DAN31060
510 FORMAT(22HOREAD ERROR IN ADDT)	DAN31070
END	DAN31080
CABT SUBROUTINE ABT	DAN31090
SUBROUTINE ABT	DAN31100
A=2./0.	DAN31110
A=A+2.	DAN31120
STOP	DAN31130
END	DAN31140
CMWRITE SUBROUTINE MWRITE	DAN31150
SUBROUTINE MWRITE(A,WA,WB,WC,ITR,NR,NC,NRX)	DAN31160
IMPLICIT REAL*8 (A-H,O-Z)	DAN31170
C...THIS SUBROUTINE PRINTS OUT THE MATRIX A.	DAN31180
DIMENSION A(NRX,NRX)	DAN31190
REAL*8 WA,WB,WC,ILBL,ILAB	DAN31200
COMMON/LABELS/ILBL(12),ILAB(12)	DAN31210
WRITE(6,100) (ILBL(I),I=1,12),WA,WB,WC	DAN31220
IF(ITR.GT.0) WRITE(6,101) ITR	DAN31230
WRITE(6,102) (M,M=1,10)	DAN31240
DO 1 I=1,NR	DAN31250
WRITE(6,104) I,(A(I,J),J=1,NC)	DAN31260
1 CONTINUE	DAN31270
RETURN	DAN31280
100 FORMAT(1H1///31X,12A6/58X,3A6)	DAN31290
101 FORMAT(61X,10HITERATION ,I3)	DAN31300
102 FORMAT(4HOROW,5X,I2,9(10X,I2))	DAN31310
104 FORMAT(I4,10F12.7/(4X,10F12.7))	DAN31320
END	DAN31330
CREORD SUBROUTINE REORD	DAN31340
SUBROUTINE REORD(A,B,X,X1,NR,NC,NRX)	DAN31350
C	DAN31360

C	ORDERS EIGENVECTORS FROM LOWEST TO HIGHEST EIGENVALUES.	DAN31370
C	EIGENVECTORS ARE IN B. REORDERED EIGENVECTORS ARE IN A.	DAN31380
C	REORDERED EIGENVALUES ARE IN X.	DAN31390
C		DAN31400
	IMPLICIT REAL*8(A-H,O-Z)	DAN31410
	DIMENSION A(NRX,NRX),B(NRX,NRX),X(NRX),X1(NRX)	DAN31420
	AB=X1(1)	DAN31430
	DO 20 I=2,NR	DAN31440
	IF(X1(I).LE.AB)GO TO 20	DAN31450
	AB=X1(I)	DAN31460
20	CONTINUE	DAN31470
	BA=2.D0*DABS(AB)	DAN31480
	DO 30 K=1,NR	DAN31490
	J=1	DAN31500
	AB=X1(1)	DAN31510
	DO 40 I=2,NR	DAN31520
	IF(X1(I).GE.AB)GO TO 40	DAN31530
	AB=X1(I)	DAN31540
	J=I	DAN31550
40	CONTINUE	DAN31560
	X(K)=X1(J)	DAN31570
	X1(J)=BA	DAN31580
	DO 50 I=1,NC	DAN31590
50	A(K,I)=B(J,I)	DAN31600
30	CONTINUE	DAN31610
	RETURN	DAN31620
	END	DAN31630
CFMDB	SUBROUTINE FMDB	DAN31640
	SUBROUTINE FMDB(Y,D,FR,GA,NSDS,NBFNS,NBMX)	DAN31650
	IMPLICIT REAL*8 (A-H,O-Z)	DAN31660
	DIMENSION Y(NBMX,NBMX),D(NBMX,NBMX),FR(1)	DAN31670
	DOUBLE PRECISION DD	DAN31680

C...THIS SUBROUTINE COMPUTES THE DENSITY MATRIX, D, FROM THE MOLECULAR	DAN31690
C...ORBITAL COEFFICIENTS STORED IN THE ROWS OF Y. THUS -	DAN31700
C... $D(I,J) = GA * \text{SUM}(\text{OVER } K) FR(K) * Y(K,I) * Y(K,J)$	DAN31710
C...WHERE FR(K) IS THE FRACTIONAL OCCUPANCY OF THE KTH ORBITAL AND	DAN31720
C...GA IS A CONSTANT GIVEN BY THE CALLING ROUTINE.	DAN31730
C...SINCE D IS SYMMETRIC ONLY ITS LOWER TRIANGULAR HALF (INCLUDING	DAN31740
C...THE DIAGONAL) IS COMPUTED AND RETURNED TO THE CALLING PROGRAM.	DAN31750
DO 2 I=1,NBFNS	DAN31760
DO 2 J=1,I	DAN31770
DD=0.000	DAN31780
DO 1 K=1,NSOS	DAN31790
FRO=FR(K)	DAN31800
IF(FRO.EQ.0.) GO TO 1	DAN31810
DD=DD+Y(K,I)*Y(K,J)*FRO	DAN31820
1 CONTINUE	DAN31830
D(I,J)=GA*DD	DAN31840
2 CONTINUE	DAN31850
RETURN	DAN31860
END	DAN31870
CFMDTB SUBROUTINE FMDTB	DAN31880
SUBROUTINE FMDTB(A,B,C,T,NC,NRX)	DAN31890
IMPLICIT REAL*8 (A-H,O-Z)	DAN31900
DIMENSION A(NRX,1),B(NRX,1),C(NRX,1)	DAN31910
C...THIS SUBROUTINE FORMS THE MATRIX C WHERE	DAN31920
C... $C(I,J) = A(I,J) + T*B(I,J)$	DAN31930
C...THE MATRICES A, B, AND C ARE PRESUMABLY SYMMETRIC, AND THEREFORE	DAN31940
C...ONLY THE LOWER TRIANGULAR HALF (INCLUDING THE DIAGONAL) OF C IS	DAN31950
C...FORMED FROM THE CORRESPONDING SECTIONS OF A AND B.	DAN31960
DO 2 J=1,NC	DAN31970
DO 1 I=J,NC	DAN31980
C(I,J)=A(I,J)+T*B(I,J)	DAN31990
1 CONTINUE	DAN32000

2	CONTINUE	DAN32010
	RETURN	DAN32020
	END	DAN32030
C	TEST2	DAN32040
	SUBROUTINE TEST2(NT,JNAM)	DAN32050
	SUBROUTINE TEST2(NT,JNAM)	DAN32060
C	TEST2 REWINDS TAPE NO. NT AND CHECKS TO SEE IF THE CORRECT TAPE	DAN32070
C	HAS BEEN MOUNTED. IN CASE OF ERROR PROGRAM IS TERMINATED.	DAN32080
	REAL*8 IEOF,JNAM,NAMTAP,IWRD	DAN32090
	COMMON /IOIND/ ICON(24)	DAN32100
	DATA IEOF /6H***EOF/	DAN32110
	NTAPE=NT	DAN32120
	REWIND NTAPE	DAN32130
1	READ(NTAPE) IWRD	DAN32140
	IF(IWRD.NE.IEOF) GOT01	DAN32150
	READ(NTAPE) NAMTAP	DAN32160
	CALL EFSKIP (NTAPE,-1)	DAN32170
	IF(JNAM.EQ.NAMTAP) GOT06	DAN32180
4	WRITE(6,5) NTAPE	DAN32190
	CALL ABT	DAN32200
6	IF(ICON(10).GT.0) WRITE(6,3) NTAPE,JNAM	DAN32210
	RETURN	DAN32220
5	FORMAT(30H0 WRONG TAPE NAME ON TAPE NO. I3)	DAN32230
3	FORMAT(70X,4HTAPE I3,2X,24HIS LOADED WITH THE NAME A6)	DAN32240
	END	DAN32250
C	MWRITB	DAN32260
	SUBROUTINE MWRITB	DAN32270
	SUBROUTINE MWRITB(A,WA,WB,WC,ITR,NC,NRX)	DAN32280
	IMPLICIT REAL*8 (A-H,O-Z)	DAN32290
C	...THIS SUBROUTINE PRINTS OUT THE LOWER TRIANGULAR HALF (INCLUDING THE	DAN32300
C	...DIAGONAL) OF THE MATRIX A.	DAN32310
	DIMENSION A(NRX,1)	DAN32320
	REAL*8 WA,WB,WC,ILBL,ILAB	
	COMMON/LABELS/ILBL(12),ILAB(12)	

WRITE(6,100) (ILBL(I),I=1,12),WA,WB,WC	DAN32330
IF(ITR.GT.0) WRITE(6,101) ITR	DAN32340
WRITE(6,102) (M,M=1,10)	DAN32350
DO 1 I=1,NC	DAN32360
WRITE(6,104) I,(A(I,J),J=1,I)	DAN32370
1 CONTINUE	DAN32380
RETURN	DAN32390
100 FORMAT(1H1////31X,12A6/58X,3A6)	DAN32400
101 FORMAT(61X,10HITERATION ,I3)	DAN32410
102 FORMAT(4HORDW,5X,I2,9(10X,I2))	DAN32420
104 FORMAT(I4,10F12.7/(4X,10F12.7))	DAN32430
END	DAN32440
CMODBLK SUBROUTINE MODBLK	DAN32450
SUBROUTINE MODBLK(V,F,Y,NS,OE,GQ,CA,NSOS,NBFNS,NBMX,WA,ITR,IX)	DAN32460
IMPLICIT REAL*8 (A-H,O-Z)	DAN32470
DIMENSION CA(NBMX,NBMX)	DAN32480
DIMENSION V(NBMX,NBMX),F(NBMX,NBMX),Y(NBMX,NBMX),	DAN32490
1 NS(1),OE(1),GQ(1)	DAN32500
REAL*8 WA	DAN32510
C	DAN32520
C THE MATRIX TO BE BLOCK DIAGONALIZED IS STORED IN F. THE	DAN32530
C SYMMETRY BLOCKING TRANSFORMATION MATRIX IS STORED IN V.	DAN32540
C THE SYMMETRY BLOCKED MATRIX, F, IS DIAGONALIZED A BLOCK AT A	DAN32550
C TIME. THE EIGENVALUES ARE ORDERED BY BLOCKS - MOST NEGATIVE	DAN32560
C FIRST - AND THEN THE EIGENVECTORS ARE TRANSFORMED BACK INTO	DAN32570
C THE BASIS FUNCTION REPRESENTATION.	DAN32580
C	DAN32590
C...TAKE TRACE OF F MATRIX	DAN32600
5 TRFM=0.	DAN32610
DO 1 I=1,NSOS	DAN32620
1 TRFM=TRFM+F(I,I)	DAN32630
C...INITIALIZE EIGENVECTOR MATRIX	DAN32640

CALL MCLEAR(Y,NSOS,NSOS,NBMX)	DAN32650
C...PERFORM DIAGONALIZATION BY BLOCKS	DAN32660
NR=0	DAN32670
ISYM=1	DAN32680
ILO=1	DAN32690
2 NSYM=NS(ISYM)	DAN32700
C...DIAGONALIZE THE BLOCK OF FSYM WHOSE 1,1 ELEMENT IS AT F(ILO,ILO)	DAN32710
C...THE EIGENVECTORS OF THAT BLOCK ARE STORED IN THE NSYM BY NSYM	DAN32720
C...BLOCK OF Y STARTING WITH Y(ILO,ILO)	DAN32730
IF(NSYM.EQ.0) GOTO4	DAN32740
CALL HDIAG(F(ILO,ILO),Y(ILO,ILO),DE,GQ,NSYM,NBMX,0,NROT)	DAN32750
NR=NR+NROT	DAN32760
ILO=ILO+NSYM	DAN32770
4 CONTINUE	DAN32780
ISYM=ISYM+1	DAN32790
IF(ILO.LE.NSOS) GO TO 2	DAN32800
C...ORDER THE EIGENVALUES AND EIGENVECTORS SUCH THAT THE I+1 TH EIGEN-	DAN32810
C...VALUE IS GREATER THAN THE ITH AND SUCH THAT THE EIGENVECTOR	DAN32820
C...CORRESPONDING TO THE ITH EIGENVALUE IS IN THE ITH COLUMN OF Y.	DAN32830
CALL DRDREI(F,Y,DE,NS,GQ,NSOS,NBMX)	DAN32840
C...TRANSFORM EIGENVECTORS BACK TO ORIGINAL NON BLOCKED BASIS	DAN32850
C...AT THIS POINT THE EIGENVECTORS OF FSYM, W, ARE CONTAINED IN THE	DAN32860
C...COLUMNS OF Y. TO EFFECT THE TRANSFORMATION OF W BACK TO THE ORIGINAL	DAN32870
C...BASIS PERFORM THE FOLLOWING -	DAN32880
C... X = WT * V	DAN32890
C...WHERE X IS THE MATRIX OF EIGENVECTORS IN THE ORIGINAL BASIS	DAN32900
C...AND CONTAINS THOSE EIGENVECTORS AS ROWS.	DAN32910
C...ON ENTRY TO MMATB1 THE MATRIX W IS CONTAINED IN Y AND THE MATRIX V	DAN32920
C...IS CONTAINED IN V.	DAN32930
C...ON RETURN FROM MMATB1 THE MATRIX X IS CONTAINED IN Y.	DAN32940
CALL MMATB1(Y,CA,NSOS,NSOS,NBFNS,GQ,NBMX)	DAN32950
C...TAKE TRACE OF EIGENVALUES	DAN32960

TROE=0.	DAN32970
DO 3 I=1,NSOS	DAN32980
3 TROE=TROE+DE(I)	DAN32990
C...DOE IS THE DIFFERENCE BETWEEN THE TRACE BEFORE AND AFTER	DAN33000
C...DIAGONALIZATION.	DAN33010
DOE=TROE-TRFM	DAN33020
WRITE(6,130) WA,DOE,NR	DAN33030
RETURN	DAN33040
130 FORMAT(1H0,60X,A6,35H FSYM MATRIX DIAGONALIZATION ERROR ,	DAN33050
1 E15.8/80X, 20HNUMBER OF ROTATIONS ,I6)	DAN33060
END	DAN33070
CORDREI SUBROUTINE ORDREI	DAN33080
SUBROUTINE ORDREI(F,U,DE,NS,NEXT,N,NBMX)	DAN33090
IMPLICIT REAL*8 (A-H,O-Z)	DAN33100
DIMENSION F(NBMX,NBMX),U(NBMX,NBMX),DE(1),NS(1),NEXT(1)	DAN33110
C...THIS SUBROUTINE ORDERS THE EIGENVALUES, WITHIN SYMMETRY BLOCKS,	DAN33120
C...PLACING THE MOST NEGATIVE FIRST.	DAN33130
C...ON ENTRY TO THIS SUBROUTINE THE DIAGONAL ELEMENTS OF F CONTAIN	DAN33140
C...THE EIGENVALUES, DIAGONAL ELEMENTS 1 THRU NS(1) BELONG TO THE FIRST	DAN33150
C...BLOCK, ELEMENTS NS(1)+1 THRU NS(2) +NS(1) TO THE SECOND BLOCK, ETC.	DAN33160
C...THE CORRESPONDING COLUMNS OF U CONTAIN THE EIGENVECTORS.	DAN33170
C...ON EXIT FROM THIS SUBROUTINE THE ORDERED EIGENVALUES ARE IN DE AND	DAN33180
C...THE EIGENVECTORS IN THE CORRESPONDING ORDER ARE IN U (AS COLUMNS).	DAN33190
ILO=1	DAN33200
ISYM=1	DAN33210
1 IF(NS(ISYM).EQ.0) GOTO19	DAN33220
IHI=ILO+NS(ISYM)-1	DAN33230
IF(ILO.EQ.IHI) GOTO9	DAN33240
DO 2 I=ILO,IHI	DAN33250
2 NEXT(I)=I	DAN33260
KLO=ILO	DAN33270
3 K=NEXT(KLO)	DAN33280

	FMAX=F(K,K)	DAN33290
	KLP1=KLO+1	DAN33300
	DO 4 I=KLP1,IHI	DAN33310
	J=NEXT(I)	DAN33320
	IF(F(J,J).GE.FMAX) GO TO 4	DAN33330
	M=NEXT(KLO)	DAN33340
	NEXT(KLO)=J	DAN33350
	NEXT(I)=M	DAN33360
	FMAX=F(J,J)	DAN33370
4	CONTINUE	DAN33380
	KLO=KLP1	DAN33390
	IF(KLP1.LT.IHI) GO TO 3	DAN33400
	I=ILO	DAN33410
5	J=NEXT(I)	DAN33420
	FMAX=F(I,I)	DAN33430
	DO 6 K=1,N	DAN33440
6	OE(K)=U(K,I)	DAN33450
	F(I,I)=F(J,J)	DAN33460
	F(J,J)=FMAX	DAN33470
	DO 7 K=1,N	DAN33480
	U(K,I)=U(K,J)	DAN33490
7	U(K,J)=OE(K)	DAN33500
	DO 8 M=ILO,IHI	DAN33510
	IF(NEXT(M).EQ.I) NEXT(M)=J	DAN33520
8	CONTINUE	DAN33530
	I=I+1	DAN33540
	IF(I.LT.IHI) GO TO 5	DAN33550
9	ILO=IHI+1	DAN33560
19	ISYM=ISYM+1	DAN33570
	IF(ILO.LE.N) GO TO 1	DAN33580
	DO 10 KK=1,N	DAN33590
10	OE(KK)=F(KK,KK)	DAN33600

RETURN	DAN33610
END	DAN33620
CMABAT	DAN33630
SUBROUTINE MABAT	DAN33640
SUBROUTINE MABAT(A,B,NR,NC,Y,NBMX)	DAN33650
IMPLICIT REAL*8 (A-H,O-Z)	DAN33660
DIMENSION A(NBMX,1),B(NBMX,1),Y(NBMX,1)	DAN33670
C...THIS SUBROUTINE TAKES THE MATRIX PRODUCT -	DAN33680
C... C = A * B * AT	DAN33690
C...WHERE THE MATRIX AT IS THE TRANSPOSE OF A, A IS NR BY NC, B IS	DAN33700
C...NC BY NC, AND C IS NR BY NR.	DAN33710
C...THE MATRIX B IS ASSUMED SYMMETRIC THUS ONLY ITS UPPER TRIANGULAR	DAN33720
C...HALF (INCLUDING THE DIAGONAL) IS USED. THE MATRIX C IS ALSO ASSUMED	DAN33730
C...TO BE SYMMETRIC, AND THEREFORE ONLY ITS UPPER TRIANGULAR HALF IS	DAN33740
C...CALCULATED. THIS UPPER TRIANGULAR HALF OF C IS RETURNED IN THE UPPER	DAN33750
C...TRIANGULAR HALF OF B.	DAN33760
C...COMPUTE A * B . STORE THAT IN Y TEMPORARILY.	DAN33770
DOUBLE PRECISION SUM	DAN33780
DO 10 I=1,NR	DAN33790
DO 10 K=1,NC	DAN33800
SUM=0.000	DAN33810
DO 8 J=1,K	DAN33820
SUM=SUM+A(I,J)*B(J,K)	DAN33830
8 CONTINUE	DAN33840
K1 = K + 1	DAN33850
IF(K1.GT.NC) GOTO13	DAN33860
DO 9 J=K1,NC	DAN33870
SUM=SUM+A(I,J)*B(K,J)	DAN33880
9 CONTINUE	DAN33890
13 Y(I,K)=SUM	DAN33900
10 CONTINUE	DAN33910
C...MULTIPLY Y * A TO GET UPPER HALF OF C, STORING THAT IN B.	DAN33920
DO 12 K=1,NR	

DO 12 I=1,K	DAN33930
SUM=0.000	DAN33940
DO 11 J=1,NC	DAN33950
SUM=SUM+Y(I,J)*A(K,J)	DAN33960
11 CONTINUE	DAN33970
B(I,K)=SUM	DAN33980
12 CONTINUE	DAN33990
RETURN	DAN34000
END	DAN34010
CMPRY2 SUBROUTINE MPRY2	DAN34020
SUBROUTINE MPRY2(A,E,FR,WA,WB,WC,ITR,NR,NC,NRX)	DAN34030
C...THIS SUBROUTINE PRINTS OUT THE MOLECULAR ORBITALS (IN COLS), THEIR	DAN34040
C...EIGENVALUES, AND FRACTIONAL OCCUPANCIES(IF ITR .NE.0)	DAN34050
IMPLICIT REAL*8 (A-H,O-Z)	DAN34060
DIMENSION A(NRX,1),E(1),FR(1),NS(1),NSN(1)	DAN34070
COMMON/LABELS/ILBL(12),ILAB(12)	DAN34080
REAL*8 WA,WB,WC,ILBL,ILAB	DAN34090
C...THIS SUBROUTINE PRINTS OUT THE MOLECULAR ORBITALS WITH THEIR	DAN34100
C...SYMMETRY DESIGNATIONS, THEIR EIGENVALUES, AND THEIR FRACTIONAL	DAN34110
C...OCCUPANCIES.	DAN34120
WRITE(6,100) (ILBL(I),I=1,12),WA,WB,WC	DAN34130
WRITE(6,102) (M,M=1,10)	DAN34140
DO 4 I=1,NR	DAN34150
IF(ITR)1,2,1	DAN34160
1 WRITE(6,103)M,E(I),FR(I)	DAN34170
GO TO 3	DAN34180
2 WRITE(6,103)M,E(I)	DAN34190
3 WRITE(6,104)I,(A(J,I),J=1,NC)	DAN34200
4 CONTINUE	DAN34210
5 CONTINUE	DAN34220
6 RETURN	DAN34230
100 FORMAT(1H1////31X,12A6/58X,3A6)	DAN34240

102	FORMAT(4HORDW,5X,I2,9(10X,I2))	DAN34250
103	FORMAT('0',I3,F15.7,F10.5)	DAN34260
104	FORMAT(I4,10F12.7/(4X,10F12.7))	DAN34270
	END	DAN34280
CMCRY1	SUBROUTINE MCRY1	DAN34290
	SUBROUTINE MCRY1(A,E,FR,WA,WB,WC,ITR,NR,NC,NRX)	DAN34300
	IMPLICIT REAL*8 (A-H,O-Z)	DAN34310
	DIMENSION A(NRX,1),E(1),FR(1),NS(1),NSN(1)	DAN34320
	COMMON/LABELS/ILBL(12),ILAB(12)	DAN34330
	REAL*8 WA,WB,WC,ILBL,ILAB	DAN34340
C...	THIS SUBROUTINE PRINTS OUT THE MOLECULAR ORBITALS (ALREADY IN ROWS)	DAN34350
C...	TOGETHER WITH THEIR EIGENVALUES AND FRACTIONAL OCCUPANCIES(IF .TR .NDAN34360	
	WRITE(6,100) (ILBL(I),I=1,12),WA,WB,WC	DAN34370
	WRITE(6,102) (M,M=1,10)	DAN34380
	DO 4 I=1,NR	DAN34390
	IF(ITR)1,2,1	DAN34400
	1 WRITE(6,103)M,E(I),FR(I)	DAN34410
	GO TO 3	DAN34420
	2 WRITE(6,103)M,E(I)	DAN34430
	3 WRITE(6,104)I,(A(I,J),J=1,NC)	DAN34440
	4 CONTINUE	DAN34450
	5 CONTINUE	DAN34460
	6 RETURN	DAN34470
100	FORMAT(1H1////31X,12A6/58X,3A6)	DAN34480
102	FORMAT(4HORDW,5X,I2,9(10X,I2))	DAN34490
103	FORMAT('0',I3,F15.7,F10.5)	DAN34500
104	FORMAT(I4,10F12.7/(4X,10F12.7))	DAN34510
	END	DAN34520

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SPIN PROJECTION OF SEMI-EMPIRICAL AND AB INITIO
UNRESTRICTED HARTREE-FOCK WAVEFUNCTIONS

by

Dana Alice Brewer

(ABSTRACT)

The method of spin projection was examined by developing and applying computer programs to calculate projected semi-empirical and ab initio unrestricted Hartree-Fock (UHF) wavefunctions.

The electronic spectra of naphthalene, anthracene, naphthalene and pentacene were calculated using the Pariser-Pople-Parr (PPP) π -electron approximations and both UHF and configurational interaction (CI) techniques. The results of both techniques were compared with experimentally determined spectra with reasonable agreement between the CI and projected UHF results. While the CI calculations generally produced lower energies for the triplet states than the UHF calculations, the spectra from UHF calculations were in somewhat better agreement with experiment. Anomalies encountered with degeneracies and the presence of open shell ground states are also discussed.

The geometry of monohomocyclooctatetraene anion radical (MHCOT) was studied using spin projection of the UHF INDO wavefunction. The theoretical molecular geometry was varied until the

experimental hyperfine coupling constants matched hyperfine constants obtained from using both projected and unprojected UHF wavefunctions. The two types of calculations resulted in slightly different energies and geometries with the projected calculations giving a higher energy for the doublet state; essentially no differences were noted in the bond orders obtained from the two types of calculations. The geometry from the projected calculations was a somewhat more strained conformation than the geometry from the unprojected calculation.

Ab initio UHF calculations with spin projection were performed on $\text{H}_2\text{O}(+)$ to compare the energies of pure spin states from ab initio multi-configurational self-consistent field with CI (MCSCF/CI) with those from spin projection. The MCSCF/CI calculations are superior to the UHF plus spin projection calculations. This result will always be observed when the UHF wavefunction is very close to a pure spin state before spin projection.

The dissociation of CF_2O was studied using ab initio wavefunctions. The energies of the unprojected UHF wavefunctions were examined along with those for the dissociated $\text{CF}_2 + \text{O}$ fragments. Good agreement exists between the calculated and experimental vertical ionization potentials for CF_2O at the equilibrium geometry.