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The separated-pair independent particle model and the generalized Brillouin theorem: ab initio calculations on the dissocation of polyatomic molecules

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The separated-pair independent particle model and the generalized Brillouin theorem: *ab initio* calculations on the dissociation of polyatomic molecules

by

Kenneth Randall Sundberg

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PREFACE

Over the last decade theoretical chemists have perfected several mathematical structures within which we can conceptualize and articulate our notions about the nature and behavior of the chemical bond; and concomitant with this effort, the very rapid rise in the availability and speed of the modern digital computer has permitted these theories to become valuable tools to accompany the experimentalist in his research. As evidence of this progress one need only count the number of _ab_ _initio_ calculations reported in the community's major research organs; notably the "Journal of the American Chemical Society."

Most of these later efforts have been Hartree-Fock (HF) self-consistent field (SCF) studies of isolated molecules or chemical systems which can be addressed in this manner. Notable contributions are due, in particular, to the minimal gaussian basis set studies initiated by Pople and his coworkers (Lathan, Hehre and Pople, 1971).

The HF-SCF approach, however, is with some exceptions limited to structural problems. Most reactions are accompanied by changes in electronic structure that cannot be described by this single configurational theory. The theoretician's task was thus defined: Develop a multiconfiguration self-consistent field (MCSCF) approximation that embodies three essential features: (1) it must involve enough configurations to properly account for the changes experienced by a molecule in chemical reaction; (2) the number of configurations must be small enough that the theory remains intelligible, and (3), it should be nearly as economical as the HF-SCF approach.

Several theories have been directed at this problem. The first such highly optimized functions were the separated-pair (Hurley, Lennard-Jones and Pople, 1953) calculations by Miller and Ruedenberg (1968a,b,c) and Mehler, Ruedenberg and Silver, (1970). Other developments are the bonding studies by Goddard and his colleagues (Hay et al., 1972a,b,c), the MCSCF theories by Bertoncini, Das, and Wahl (1970) and by Hinze and Roothaan (1967). Lastly, an MCSCF theory developed by Grein and Chang (1971) has been modified by Cheung and Ruedenberg (to be published) and holds great potential for future applications.

The present investigation develops some new techniques and concepts relevant to applying the MCSCF method to the study of chemical reactions. The applicability of the general theory is extended by developing an efficient limited procedure that accomplishes much of the orbital optimization obtained from a full MCSCF calculation; thus a limited theory allows one to reserve the general method for the recovery of subtle effects (such as elaborate correlations, spin recoupling, or small orbital adjustments) by providing it with a very refined initial wavefunction. We have developed such a method, the separated-pair independent particle (SPIP) model. It is related to the work by Goddard and the work by Ruedenberg and by their coworkers mentioned above. A detailed development of the theory is presented in Parts I, II, and a discussion of the theory's economy and implementation is presented in Part III. For some problems, the SPIP model can be used alone to produce results not obtainable with the HF-SCF approximation by itself, for example the reaction energies associated with the dissociation of the dimers discussed in Part IV. In other applications, the SPIP model can be combined with the general MCSCF method to study a complex reaction which, at the present state of the art, cannot be handled otherwise. Such an application is our study of the thermolysis of 1,2-dioxetane in Part V; there we also introduce several new concepts concerning the configurational and orbital spaces in which the chemical reaction can be meaningfully discussed.

PART I: THE SEPARATED-PAIR INDEPENDENT PARTICLE MODEL AND THE GENERALIZED BRILLOUIN THEOREM

INTRODUCTION

Chemistry is a study of atoms and the chemical bonds that hold them together in molecules. A chemical reaction is the formation or cleavage of one or more of these bonds, so to understand a chemical reaction we need to know about its reactants and products: the systems joined or parted by forming or cleaving bonds. More than this, we need to understand any metastable combinations produced during the course of a reaction. The most common quantum mechanical description of a molecule is the linear combination of atomic orbital (LCAO) molecular orbital (MO) theory of Hund (1928) and Mulliken (1928, 1935). The basic feature of this method is its emphasis on independent particles; in MO theory, the electrons independently move over the whole molecule. And it is just this essential feature of the theory that keeps it from giving us what we want: a description of the cleavage or formation of a chemical bond. The independent electron motions assure us that two electrons in a bond will spend time together on a single nuclear center. Such an arrangement of the electrons is an appropriate element in a picture of a bond near the molecular equilibrium. But it is unsuitable for a description of the atoms or radicals produced by dissociation. If we are to understand how molecules dissociate to atoms, then our theory must let the electrons correlate one another.

FORMULATION OF THE WAVEFUNCTION

SCF-MO Wavefunction

The most powerful force acting between electrons is the coulombic repulsion. In the MO approach, it enters the potential for each orbital in an average way. Hartree (1928a,b) first formulated this in his atomic self-consistent field (SCF) method, and Fock (1930) derived the rigorous equations for atomic and molecular orbitals from the variation principle. Roothaan (1951) adapted the Fock equations for use with the LCAO-MO expansion. While the SCF-MO theory restricts the orbitals to be doubly occupied, it yields the best possible MO's; and it is therefore the point of departure for further discussions. The defects remaining in the model are collectively called the correlation effect (Lowdin, 1959).

An M-electron MO wavefunction has the form

$$\Phi^N(1,\cdots,M) = A_N\{[\prod_{i=1}^{N} \phi_i(2i-1)\phi_i(2i)\Theta_-(2i-1,2i)] \times$$

$$\prod_{k=2N+1}^{M} \phi_k(k)\alpha(k)\} , \tag{1-1}$$

$$\Theta_-(1,2) = \{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}/\sqrt{2} . \tag{1-2}$$

Here ϕ_i is an MO; α and β are the usual spin up and spin down spinors (Pauli, 1925), and

$$A_N = (2^N M!)^{\frac{1}{2}} \sum_{P_\mu \in S(1,M)} (-1)^N P_\mu \tag{2}$$

is an antisymmetrizer for the indices 1,2,$\cdots$,M. The summation in equation 2 extends over all the permutations in the symmetric group of order M, and N is the number of symmetric space functions or closed shells (Mulliken, 1928) in equation 1-1. The MO's are real and orthogonal,

$$\langle i|j\rangle = \int dV_1 \phi_i(1)\phi_j(1) = \delta_{i,j} = \begin{cases} 0 & i\neq j \\ 1 & i=j \end{cases}, \tag{3}$$

so the antisymmetrizer in equation 2 normalizes the wavefunction.

The orbitals ϕ_i with $1\leq i\leq N$ are called closed shells; we'll reserve the indices (i) and (j) for closed shells. Similarly, the orbitals ϕ_k with $2N + 1 \leq k \leq M$ are called singles; we'll reserve the indices (k), (ℓ), and (m) for singles. Looking ahead, we'll reserve the indices (a) and (b) for unoccupied or virtual orbitals. Departures from these conventions will be explicitly defined or clear from context.

Each closed shell can be associated with some chemical notion like an inner shell, lone pair, or bond (Coulson, 1961; Edminston and Ruedenberg, 1963). Let's suppose that ϕ_N represents a bond; we can rewrite the MO wavefunction as

$$\Phi^{N} = A_{N} \{ F_{c}^{N-1} \phi_{N}\phi_{N}\Theta_{-}F_{o} \} , \qquad (4)$$

where

$$F_{c}^{N-1} = \prod_{i=1}^{N-1} \phi_{i}\phi_{i}\Theta_{-} , \qquad (5\text{-}1)$$

$$F_{o} = \prod_{\ell=2N+1}^{M} \phi_{\ell}\alpha . \qquad (5\text{-}2)$$

We use the order of the factors in the product $F_{c}^{N-1}\phi_{N}\phi_{N}\Theta_{-}F_{o}$ to determine their arguments; we just compare factors term by term to equations 1-1,2.

Right-Left Correlation in the Independent Particle Model

The configuration interaction (CI) method (Hylleraas, 1928) can be used to introduce correlation to a bond. For example, in the bond represented by ϕ_{N} in equation 4, an effective way to introduce correlation is by a two-term CI (Mulliken, 1932; Longuett-Higgins, 1948; Mehler _et_ _al_., 1970). Such a function can be written as

$$\Phi^{N-1} = A_{N} \{ F_{c}^{N-1} \Omega_{N}F_{o} \} , \qquad (6\text{-}1)$$

$$\Omega_{N} = \Lambda_{N}\Theta_{-} = \{ f_{N_0}\phi_{N_0}\phi_{N_0} + f_{N_1}\phi_{N_1}\phi_{N_1} \} \Theta_{-} , \qquad (6\text{-}2)$$

$$< N\mu | N\nu > = \delta_{\mu,\nu} , \tag{6-3}$$

$$< N\mu | i > = < N\mu | \ell > = 0, \tag{6-4}$$

$$f^2_{N_0} + f^2_{N_1} = 1. \tag{6-5}$$

By an appropriate choice of the orbitals ϕ_{N_0} and ϕ_{N_1} we can introduce correlation into the electron motion along the bond represented by ϕ_N in equation 4; these effects are called right-left correlation. The functions Ω_N and Λ_N are called spin and space geminals (Shull, 1959).

Additionally, equations 6-1,5 give more freedom to our description of the dissociation. By continuously varying the orbitals ϕ_{N_0} and ϕ_{N_1} and the coefficients f_{N_0} and f_{N_1} along the reaction path, we can slowly change from an MO description, near the molecular equilibrium, to a superposition of separated atoms, at the dissociation limit (Coulson, 1961).

Separated-Geminals and the SPIP model

An extension of equations 6-1,5 is given by

$$\Phi^\Gamma = A_N \{ F^\Gamma_C \, \Omega_{\Gamma+1} \cdots \Omega_N \, F_O \} , \tag{7-1}$$

$$\Omega_K = \Lambda_K \, \Theta_- , \tag{7-2}$$

$$\Lambda_\kappa = \sum_{\mu=0}^{1} f_{\kappa\mu}\phi_{\kappa\mu}\phi_{\kappa\mu} , \tag{7-3}$$

$$< \kappa\mu | \lambda\nu > = \delta_{\kappa,\lambda}\delta_{\mu,\nu} , \tag{7-4}$$

$$< \kappa\mu | i > = < \kappa\mu | \ell > = 0, \tag{7-5}$$

$$\sum_{\mu=0}^{1} f^2{}_{\kappa\mu} = 1 . \tag{7-6}$$

This function replaces several closed shells by two term geminals.

Equation 7-1 illustrates some conventions. When we write an antisymmetrized product of closed shells, geminals, and singles, we will always put the closed shells first, the geminals second, and the singles last. Moreover, we'll reserve the double index notation $\phi_{\kappa\mu}$ and $\phi_{\lambda\nu}$ for orbitals in the geminals. $\phi_{\kappa\mu}$ is the μ(th) orbital in the natural expansion (Lowdin, 1955) of the κ(th) geminal.

The orthogonality relations in equations 7-4,5 imply that

$$\int dv_2 \, \Lambda_\kappa(1,2)\Lambda_\lambda(1,2) \equiv 0 \tag{8}$$

identically for all $\kappa \neq \lambda$ and all values of the coordinates of particle 1. This is the strong orthogonality condition of Hurley, Lennard-Jones, and Pople (1953). Aria (1960) and

and Lowdin (1961) have shown that strong orthogonality implies the separation evident in equations 7-3,5: no orbital can appear in the natural expansion of more than one geminal. Thus wavefunctions like equations 7-1,6 are called separated-pair (SP) approximations.

An alternative form of the geminal is obtained from the transformation (Coulson and Fischer, 1949)

$$\begin{pmatrix} \phi_{\kappa 0} \\ \phi_{\kappa 1} \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2(1+\Delta\kappa)} & 1/\sqrt{2(1+\Delta\kappa)} \\ 1/\sqrt{2(1-\Delta\kappa)} & -1/\sqrt{2(1-\Delta\kappa)} \end{pmatrix} \begin{pmatrix} u_\kappa \\ v_\kappa \end{pmatrix}, \qquad (9\text{-}1)$$

$$\Delta_\kappa = \int dv_1 u_\kappa(1) v_\kappa(1), \qquad (9\text{-}2)$$

$$(1-\Delta_\kappa)/(1+\Delta_\kappa) = -f_{\kappa 1}/f_{\kappa 0} \; . \qquad (9\text{-}3)$$

Substitution of equations 9-1,3 into equation 7-3 gives

$$\Lambda_\kappa = 1/\sqrt{2(1+\Delta_\kappa)}\{u_\kappa v_\kappa + v_\kappa u_\kappa\} \, . \qquad (10)$$

Hay, Hunt, and Goddard (1972a,b,c) explored equation 7-1 using the pair function form of the geminal in equation 10. This formula closely resembles the Heitler-London (1927) valence bond wavefunction for a two electron bond. So Hay, Hunt, and Goddard called their method the generalized valence bond (GVB) theory.

We made a study of equation 7-1 using the two-term natural expansion of the geminal in equation 7-3. We emphasized the similarity of the geminal and MO pictures, and we deferred to the major premise of the MO theory; we called equations 7-1,6 the separated-pair independent particle (SPIP) model.

DETERMINATION OF THE WAVEFUNCTION

Variational Equations of the SPIP Model

The SPIP wavefunction Φ^{Γ} is an approximation to the true solution of the time-independent Schrodinger equation

$$\hat{H}(1,\cdots,M)\Psi(1,\cdots,M) = E\Psi(1,\cdots,M). \tag{11}$$

E is the total energy of the molecule in a state corresponding to the wavefunction $\Psi(1,\cdots,M)$. $\hat{H}$ is the Hamiltonian operator (Born and Oppenheimer, 1927); in atomic units (Eyring *et al.*, 1944) it is given by

$$\hat{H}(1,\cdots,M) = \sum_{s=1}^{M} \{-\tfrac{1}{2}\nabla_s^2 - \sum_{a=1}^{A} Z_a/R_{sa}\}$$

$$+ \sum_{s=2}^{M} \sum_{t=1}^{s-1} 1/r_{st} + \sum_{a=2}^{A} \sum_{b=1}^{a-1} Z_a Z_b/R_{ab}\,. \tag{12}$$

A is the total number of atoms in the molecule; Z_a is the atomic number of nucleus (a); and R_{ab}, R_{sa}, and r_{st} are the distances between nuclei (a) and (b), between nucleus (a) and electron (s), and between electrons (s) and (t) respectively. ∇_s^2 is the Laplacian operator for the coordinates of electron (s).

A common technique to approximate solutions to eigenvalue problems is to appeal to the variation theorem (Courant and Hilbert, 1953):

$$< \delta \Psi|\hat{H}|\Psi > = 0, \qquad (13)$$

where $\delta\Psi$ is the first-order variation of Ψ. Equation 13, unlike equation 11, can be satisfied by an approximation like the SPIP function Φ^{Γ}. We systematically examine all the parameters in Φ^{Γ}, and we select their values to satisfy the variation theorem and produce as low an energy as possible. That particular function is the best separated-pair independent particle model of the true wavefunction Ψ.

The first-order variation of Φ^{Γ} with respect to the geminal expansion coefficients and MO's is

$$\delta\Phi^{\Gamma} = \sum_{\kappa=\Gamma+1}^{N} \sum_{\mu=0}^{1} \Phi^{\Gamma}(\delta f_{\kappa\mu}) + \sum_{r}{}^{*}\Phi^{\Gamma}(\delta\phi_{r}). \qquad (14)$$

The double sum over κ and μ covers all the coefficients in the two term geminals, and the starred sum over r covers all the occupied orbitals: closed shell, geminal, and single. The variation theorem holds for arbitrary variations, so it must hold for the geminal and orbital variations separately. Thus

$$\sum_{\kappa=\Gamma+1}^{N} \sum_{\mu=0}^{1} < \Phi^{\Gamma}(\delta f_{\kappa\mu})|\hat{H}|\Phi^{\Gamma} > = 0, \qquad (15\text{-}1)$$

and

$$\sum_{r}{}^{*} < \Phi^{\Gamma}(\delta\phi_r)\,|\hat{H}|\,\Phi^{\Gamma} > . \qquad (15\text{-}2)$$

Equations 15-1,2 are the variational equations to be satisfied by the SPIP function Φ^{Γ}.

Optimization of the Geminal Expansion Coefficients

Minimizing the total energy with respect to the geminal expansion coefficients under the constraint of equation 7-6 leads to a set of coupled eigenvalue problems (Kutzelnigg, 1964);

$$\sum_{\nu=0}^{1} \{\hat{H}^{\kappa}_{\mu\nu} - \hat{\varepsilon}_{\kappa}\,\delta_{\mu\nu}\} f_{\kappa\nu} = 0, \qquad (16\text{-}1)$$

$$\hat{H}^{\kappa}_{\mu\nu} = < \Phi_{\kappa\mu}|\hat{H}|\Phi_{\kappa\nu} > , \qquad (16\text{-}2)$$

$$\Phi_{\kappa\mu} = A\{F_c^{\Gamma}\,\Omega_{\Gamma+1}\cdots\Omega_{\kappa-1}\phi_{\kappa\mu}\phi_{\kappa\mu}\Theta_{-}\Omega_{\kappa+1}\cdots\Omega_N F_o\} . \qquad (16\text{-}3)$$

Given a set of MO's and an initial guess of the expansion coefficients $f_{\kappa\mu}$, equations 16-1,3 can be solved by serially executing the 2 x 2 CI problem in equation 16-1 for every geminal in Φ^{Γ}. The solution is found when the expansions are self-consistent (Miller and Ruedenberg, 1968a).

The Generalized Brillouin Theorem

It has been shown that the variational conditions in equation 15-2 and the orthogonality constraints in equations 7-4,5 lead to a set of coupled integrodifferential equations. Their form (Kutzelnigg, 1964; Miller and Ruedenberg, 1968a; Silver et al., 1970) is essentially given by

$$\hat{F}_\mu \phi_\mu = \sum_\nu \phi_\nu \lambda_{\nu\mu} . \tag{17}$$

$\hat{F}_\mu$ is an integrodifferential operator, and $\lambda_{\nu\mu}$ is a Lagrange multiplier.

These equations were inspected by Kutzelnigg (1964), and they were treated with coupling operators (Roothaan, 1960) by Huzinaga (1964) and Krauss and Weiss (1964). Silver, Mehler, and Ruedenberg (1970) unified equation 17 to a single operator equation determining all the orbitals; but in application to some diatomic hydrides (Mehler et al., 1970) they used a generalization (Raffenetti and Ruedenberg, 1970) of Miller and Ruedenberg's (1968a) direct optimization method, and they calculated their orbitals by direct minimization on the energy surface. Hay, Hunt, and Goddard (1972a,b,c) expanded their MO's in terms of a basis set contained to eliminate the off-diagonal Lagrange multipliers from equation 17 (Hunt et al., 1969).

We borrowed the orbital variation method of Lefebvre and Moser (Lefebvre and Moser, 1956; Lefebvre, 1957); the first-order variations of the MO's are expanded in the "complete space" of the MO's themselves:

$$\delta\phi_r = \sum_{s\neq(r)} C_{r\to s}\phi_s . \tag{18}$$

Here $C_{r\to s}$ is a numerical coefficient, and the sum extends over all the virtual orbitals and all the occupied orbitals except ϕ_r. The orthogonality constraints in equations 7-4,5 are maintained to first order in $C_{r\to s}$ by the relation

$$C_{r\to s} = -C_{s\to r} . \tag{19}$$

Substitution of equations 18 and 19 into equation 14 defines the first-order variation of the SPIP function Φ^{Γ} with respect to the occupied orbitals. We have

$$\sum_r^{*}\Phi^{\Gamma}(\delta\phi_r) = \sum_r^{*}\sum_{s>(r)} C_{r\to s}\,\Phi^{\Gamma}_{rs} , \tag{20-1}$$

$$\Phi^{\Gamma}_{r,s} = \begin{cases} \Phi^{\Gamma}(r\to s) - \Phi^{\Gamma}(s\to r) & \text{for r in geminal, s occupied} \\ \Phi^{\Gamma}(r\to s) & \begin{cases} \text{for r occupied, s virtual} \\ \text{or r double, s not double,} \end{cases} \end{cases} \tag{20-2}$$

and $\Phi^{\Gamma}(r \rightarrow s)$ is the wavefunction obtained by singly exciting orbital ϕ_r in Φ^{Γ} to orbital ϕ_s. The differences appearing in equation 20-2 are created by the orthogonality constraint in equation 19.

The variational conditions in equation 15-2 thus take the form

$$\sum_{r}^{*} \sum_{s>(r)} C_{r \rightarrow s} < \Phi^{\Gamma}_{rs} | \hat{H} | \Phi^{\Gamma} > = 0. \tag{21}$$

It can readily be seen that all the Φ^{Γ}_{rs} appearing in equations 20-1,2 are linearly independent, so equation 21 clearly implies that

$$< \Phi^{\Gamma}_{rs} | \hat{H} | \Phi^{\Gamma} > = 0. \tag{22}$$

The self-consistent orbitals satisfy equation 22 and the variational conditions in equation 15-2.

Levy and Berthier (1968) established equation 22 for the single excitations connecting orthogonal orbitals for any superposition of orthogonal configurations. They called their result the generalized Brillouin theorem. If the wavefunction is the simple closed shell specialization of the SPIP function Φ^{Γ}, then equation 20-2 specializes the generalized Brillouin theorem to the classical Brillouin theorem (Brillouin, 1934). It has been shown (Hirao and Nakatsuji, 1973) that equation 22 must be considered in formulating any general SCF operator to correctly unify the operators in equation 17.

Single Excitations of the SPIP Wavefunction

To produce an actual variation of a SPIP function Φ^{Γ}, we need to know the explicit forms of its single excitations Φ^{Γ}_{rs} in equation 20-2. Our first task is to enumerate the excitations we need.

Since a closed shell can be thought of as a geminal with coefficients unity and zero, the types of excitations arising from geminals include those arising from closed shells. Therefore, we consider Φ^0 instead of Φ^{Γ}. Φ^0 defines three kinds of MO's: the MO's $\phi_{\kappa\mu}$ in the natural expansions of the geminals $\Lambda_1,\cdots,\Lambda_N$; the MO's ϕ_k that are singly occupied in the product F_o; and the unoccupied or virtual orbitals ϕ_a. Simple counting reveals six kinds of excitations: intrageminal, $\phi_{\kappa_0} \to \phi_{\kappa_1}$; intergeminal, $\phi_{\kappa\mu} \to \phi_{\lambda\nu}$; geminal to single, $\phi_{\kappa\mu} \to \phi_{\ell}$; geminal to virtual, $\phi_{\kappa\mu} \to \phi_a$; single to geminal, $\phi_k \to \phi_{\lambda_0}$, and single to virtual $\phi_k \to \phi_a$.

We can discover what these excited functions look like by studying a sufficiently complicated function. All six kinds of excitations appear for the function

$$\hat{\Phi}(1,\cdots,5) = A\,\{\Omega(\kappa_0,\kappa_1)\,\Omega'(\lambda_0,\lambda_1)\,\phi_{\ell}\alpha\} \tag{23}$$

and a sixth virtual orbital ϕ_a. Generalization of the remarks by Levy and Berthier (1968) leads to the following:

$$\hat{\Phi}(\kappa_0 \to \kappa_1) = f_{\kappa_0} A \{(\phi_{\kappa_1}\phi_{\kappa_0} + \phi_{\kappa_0}\phi_{\kappa_1})\Theta_- \Omega'(\lambda_0, \lambda_1)\phi_\ell \alpha\}, \qquad (24\text{-}1)$$

$$\hat{\Phi}(\kappa_0 \to \lambda_0) = f_{\kappa_0} f_{\lambda_1} A \{(\phi_{\lambda_0}\phi_{\kappa_0} + \phi_{\kappa_0}\phi_{\lambda_0})\Theta_- \phi_{\lambda_1}\phi_{\lambda_1}\Theta_- \phi_\ell \alpha\}, \qquad (24\text{-}2)$$

$$\hat{\Phi}(\kappa_0 \to \ell) = f_{\kappa_0} A \{(\phi_\ell \phi_{\kappa_0} + \phi_{\kappa_0}\phi_\ell)\Theta_- \Omega'(\lambda_0, \lambda_1)\phi_\ell \alpha\}, \qquad (24\text{-}3)$$

$$\hat{\Phi}(\kappa_0 \to a) = f_{\kappa_0} A \{(\phi_a \phi_{\kappa_0} + \phi_{\kappa_0}\phi_a)\Theta_- \Omega'(\lambda_0, \lambda_1)\phi_\ell \alpha\}, \qquad (24\text{-}4)$$

$$\hat{\Phi}(\ell \to \kappa_0) = f_{\kappa_1} A \{\phi_{\kappa_1}\phi_{\kappa_1}\Theta_- \Omega'(\lambda_0, \lambda_1)\phi_{\kappa_0} \alpha\}, \qquad (24\text{-}5)$$

$$\hat{\Phi}(\ell \to a) = A\{\Omega(\kappa_0, \kappa_1)\Omega'(\lambda_0, \lambda_1)\phi_a \alpha\}. \qquad (24\text{-}6)$$

Equation 24-3 for $\hat{\Phi}(\kappa_0 \to \ell)$ is not in the form we want; the orbital ϕ_ℓ is doubly occupied, so we'll move it forward with the other doubles. Rewriting the orbital product slightly we find

$$\begin{aligned}\hat{\Phi}(\kappa_0 \to \ell) &= f_{\kappa_0} A\{(\phi_\ell \phi_{\kappa_0} + \phi_{\kappa_0}\phi_\ell)\Lambda'(\lambda_0, \lambda_1)\phi_\ell \Theta_- \Theta_- \alpha\} \\ &= 2 f_{\kappa_0} A\{\phi_\ell \phi_{\kappa_0}\Lambda'(\lambda_0, \lambda_1)\phi_\ell \Theta_- \Theta_- \alpha\} \\ &= -2 f_{\kappa_0} A\{\phi_\ell \phi_\ell \Lambda'(\lambda_0, \lambda_1)\phi_{\kappa_0}(2,5)\Theta_- \Theta_- \alpha\}. \qquad (25)\end{aligned}$$

Here (i,j) denotes the permutation interchanging (i) and (j). An expansion of the spin function shows

$$<\Theta_-\Theta_-\alpha|(2,5)|\Theta_-\Theta_-\alpha> = \tfrac{1}{2}\,, \tag{26}$$

so

$$(2,5)\Theta_-\Theta_-\alpha = \tfrac{1}{2}\,\Theta_-\Theta_-\alpha + \text{"other spin functions orthogonal to } \Theta_-\Theta_-\alpha\text{"}. \tag{27}$$

The "other spin functions" must be symmetric with respect to the permutation of the electrons in at least one geminal (Salmon et al., 1972). Since the geminals are symmetric in their electrons, the wavefunctions the "other spin functions" generate must be symmetric with respect to the permutation of at least two electrons. The antisymmetrizer annihilates these functions, and equation 24 becomes

$$\hat{\Phi}(\kappa_0 \rightarrow \ell) = -f_{\kappa_0}A\{\phi_\ell\phi_\ell\Theta_-\Omega'(\lambda_0,\lambda_1)\phi_{\kappa_0}\alpha\}. \tag{28}$$

This result holds for the corresponding excitations of any SPIP wavefunction.

Equations 24 and 28 give us enough information to write equations for the differences, Φ^0_{rs}, in equation 20-2. Only we combine the differences to a single normalized function Ψ^0_{rs}. For the M-electron SPIP function Φ^0 we have

$$\Psi^{0}_{\kappa_0,\kappa_1} = A_N\{\Omega_1\cdots\Omega_{\kappa-1}(\phi_{\kappa_1}\phi_{\kappa_0} + \phi_{\kappa_0}\phi_{\kappa_1})/\sqrt{2}\ \Theta_-\Omega_{\kappa+1}\cdots$$

$$\cdots\Omega_N\phi_{2N+1}\alpha\cdots\phi_M\alpha\}, \tag{28-1}$$

$$\Psi^{0}_{\kappa_0,\lambda_0} = A_N\{\Omega_1\cdots\Omega_{\kappa-1}(\phi_{\lambda_0}\phi_{\kappa_0} + \phi_{\kappa_0}\phi_{\lambda_0})/\sqrt{2}\ \Theta_-\Omega_{\kappa+1}\cdots$$

$$\cdots\Omega_{\lambda-1}(f_{\kappa_0}f_{\lambda_1}\phi_{\lambda_1}\phi_{\lambda_1} - f_{\kappa_1}f_{\lambda_0}\phi_{\kappa_1}\phi_{\kappa_1})/\sqrt{f^2_{\kappa_0}f^2_{\lambda_1} + f^2_{\kappa_1}f^2_{\lambda_0}}\,\Theta_-\Omega_{\lambda+1}$$

$$\cdots\Omega_N\phi_{2N+1}\alpha\cdots\phi_M\alpha\}, \tag{28-2}$$

$$\Psi^{0}_{\kappa_0,\ell} = -A_N\{\Omega_1\cdots\Omega_{\kappa-1}(f_{\kappa_0}\phi_\ell\phi_\ell + f_{\kappa_1}\phi_{\kappa_1}\phi_{\kappa_1})\Theta_-\Omega_{\kappa+1}\cdots$$

$$\cdots\Omega_N\phi_{2N+1}\alpha\cdots\phi_{\ell-1}\alpha\phi_{\kappa_0}\alpha\phi_{\ell+1}\alpha\cdots\phi_M\alpha\}, \tag{28-3}$$

$$\Psi^{0}_{\kappa_0,a} = A_N\{\Omega_1\cdots\Omega_{\kappa-1}(\phi_a\phi_{\kappa_0} + \phi_{\kappa_0}\phi_a)/\sqrt{2}\,\Theta_-\Omega_{\kappa+1}\cdots$$

$$\cdots\Omega_N\phi_{2N+1}\alpha\cdots\phi_M\alpha\}, \tag{28-4}$$

$$\Psi^{0}_{k,\lambda_0} = -\Psi^{0}_{\lambda_0,k}, \tag{28-5}$$

$$\Psi^{0}_{k,a} = A_N\{\Omega_1\cdots\Omega_N\phi_{2N+1}\alpha\cdots$$

$$\phi_{k-1}\alpha\phi_a\alpha\phi_{k+1}\alpha\cdots\phi_M\alpha\}. \tag{28-6}$$

Here we used the conventions discussed earlier: namely,

$\phi_{\kappa\mu}, \phi_{\lambda\nu}$ are in the geminals $\Omega_\kappa, \Omega_\lambda$.

ϕ_k, ϕ_ℓ are singles in F_o .

ϕ_a is a virtual orbital.

Each function in equations 28-1,6 is itself an antisymmetrized product of separated geminals. This means that the usual separated-pair energy formula (Silver *et al.*, 1970) applies to each $\Psi^0{}_{r,s}$ separately. Equations 28-1,6 do hold for a partially closed SPIP function Φ^Γ.

Calculating the Orbital Variations, the "Super CI", the Density Matrix, and the Natural Orbitals

Suppose we calculate the CI wavefunction

$$\Psi = D_{00}\Phi^\Gamma + \sum_r{}^* \sum_{s>(r)} D_{rs}\Psi^\Gamma{}_{rs} , \qquad (29)$$

by solving the appropriate secular equations for the coefficients D_{00} and D_{rs}. Here Φ^Γ is the SPIP function, and $\Psi^\Gamma{}_{rs}$ are the functions from equations 28-1,6 generated with the optimized SPIP orbitals. Between these functions the generalized Brillouin theorem, equation 22, holds. This relation guarantees that there is no interaction between the SPIP function, Φ^Γ, and the functions $\Psi^\Gamma{}_{rs}$; and it follows that the lowest energy function from equation 29 is the SPIP function itself. This fact suggests that the CI function, equation 29, might be useful in deducing a set of optimized MO's for the SPIP function Φ^Γ.

The first effort of this nature was (Grein and Chang, 1971) a self consistent field theory for a general multiconfiguration (MC) function, not the SPIP function Φ^{Γ}. These authors first executed a "little" CI calculation to find the MC function Φ, then they executed a CI calculation corresponding to equation 29. The coefficients, D_{rs}, of this second CI wavefunction were renormalized to yield the variational coefficients, $C_{r \rightarrow s}$, in equation 18. From there an improved set of orbitals can be calculated, and the whole procedure be repeated again and again until self-consistency is obtained. Equation 18, however, only preserves orbital orthogonality to the first-order in $C_{r \rightarrow s}$. Thus the MO's are orthogonalized after each iteration of the Grein-Chang method. This destroys the strict application of the variation theorem to the calculation, and it could cause convergence problems.

Cheung and Ruedenberg (to be published) have derived a different procedure to deduce improved MO's from the "super CI" coefficients, D_{00} and D_{rs} of equation 29, by making use of natural orbitals (NO's)(Lowdin, 1955). At each interation the NO's, ψ_s, of the MC function, Φ, obtained by diagonalizing its first-order density matrix, are related to the occupied MO's, ϕ_t, by an orthogonal transformation

$$\psi_s = \sum_t \phi_t \hat{T}_{ts} . \tag{30-1}$$

This equation's inverse is

$$\phi_t = \sum_s \hat{T}_{ts} \psi_s . \qquad (30\text{-}2)$$

In general $\hat{T}_{ts}$ is not unity; i.e., the NO's are not identical with the MO's. As long as the "super CI" function Ψ of equation 29, obtained from the lowest root of the "super CI" problem generated from the occupied and unoccupied orbitals of that iteration, is different than the MC function Φ, then it must have a lower energy, and the NO's, ψ'_s , for the "super CI" Ψ, are improvements over the MC-NO's, ψ_s. Hence, improved MO's, ϕ'_t , are obtained by inserting ψ'_s in equation 30-2; i.e.,

$$\phi'_t = \sum_s \hat{T}_{st} \psi'_s .$$

Here $\hat{T}_{st}$ is unchanged from equation 30-1. Given the new MO's ϕ'_t, a new wavefunction Φ, is obtained by solving the "little" MC-CI, and the process is repeated to self consistency.

The restricted form of the SPIP function, Φ^Γ, allows us to make a special version of the Cheung-Ruedenberg multiconfiguration self-consistent field (MCSCF) theory. Rather than using equation 29 to optimize all orbitals at once, we solve a series of "super CI" problems of the form

$$\hat{\Psi}_r = \sum_{s \geq (r)} D_{rs} \Psi^\Gamma_{rs}, \qquad (32\text{-}1)$$

$$\Psi^\Gamma_{rr} = \Phi^\Gamma , \qquad (32\text{-}2)$$

one for each occupied orbital in Φ^{Γ}. The optimized NO's are recovered from the first-order density matrix of the "super CI" $\hat{\Psi}_r$. The first-order density matrix of the SPIP function Φ^{Γ} is diagonal in its own MO's (Shull, 1959; Lowdin, 1955; Kutzelnigg, 1964), and it is given by

$$\rho(1,1') = \sum_{i=1}^{\Gamma} 2\phi_i(1)\phi_i(1') + \sum_{\kappa=\Gamma+1}^{N} \sum_{\mu=0}^{1} 2f^2_{\kappa\mu}\phi_{\kappa\mu}(1)\phi_{\kappa\mu}(1')$$

$$+ \sum_{k+2N+1}^{M} \phi_k(1)\phi_k(1') . \qquad (33)$$

So we only need to identify the MO's among the various natural orbitals generated by the wavefunction $\hat{\Psi}_r$. This is done with a maximum overlap criteria.

The first-order density matrix of $\hat{\Psi}_r$ in equation 32-1 could be calculated from an explicit formula (Ruedenberg and Poshusta, 1972). But it can also be obtained from the coefficients of the one-electron Hamiltonian integrals in the Hamiltonian matrix used to define the "super CI" problem;

$$\sum_{t \geq (r)} < \Psi^{\Gamma}_{rs} | \hat{H} | \Psi^{\Gamma}_{rt} > D_{rt} = E \, D_{rs} . \qquad (34)$$

An exhaustive treatment of the matrix elements in equation 34, see Parts II and III, shows that of all the molecular electron repulsion integrals,

$$[r\,s\,|\,t\,u\,] = \int dv_1 \int dv_2\ \phi_r(1)\,\phi_s(1)\,\phi_t(2)\,\phi_u(2)/|\vec{r}_1-\vec{r}_2|, \quad (35)$$

only the integrals $[rs|\mu\mu]$ and $[r\mu|s\mu]$ where ϕ_μ is an occupied orbital in Φ^0 are needed. This reduction in the number of integrals leads to an algorithm that is usually faster than the fifth order methods (Tang and Edminston, 1970; Diercksen, 1974) needed to calculate all the integrals in equation 35. Detailed aspects of this economy are discussed in Part III.

Beyond this, Lowdin and Shull (1956) and Coleman (1963) have shown that the NO expansion of a two-electron function, such as the geminal Λ_K, is the most rapidly convergent of all possible expansions in orthogonal orbitals. Thus the identification of the SPIP MO's with the NO's of a related and variationally more optimal function bodes well for our theory.

PART II: MATRIX ELEMENTS FOR THE SEPARATED-PAIR INDEPENDENT PARTICLE MODEL

INTRODUCTION

The separated-pair independent particle (SPIP) model discussed in Part I posed two configuration interaction (CI) problems. The optimization of the geminal expansion coefficients generated the secular equations shown in equations 16-1,3, which we called the "little CI". The orbital optimization produced the secular equations shown in equation 34, which we call the "super CI" eigenvalue problem. The solution of these CI problems requires the evaluation of many matrix elements of the Hamiltonian operator of equation 12, which will be discussed in this chapter. To accomplish this objective we start out by writing the SPIP function Φ^{Γ}, and its excitations, $\Psi^{\Gamma}{}_{rs}$, in separated-geminal form. Using this formulation, it then becomes possible to express all the matrix elements in terms of three formulas involving geminal integrals. Introducing the pertinent orbital expansions into these general expressions, we finally obtain the matrix elements in terms of orbital integrals. It is convenient to first evaluate the "little CI" matrix because certain energy quantities (collections of integrals) occurring there also simplify the formulas for the diagonal elements of the "super CI" matrix.

"SUPER CI" MATRIX IN GEMINAL FORM

Geminal Form of the SPIP Wavefunction and Its "Super CI" Basis

For a derivation of the matrix elements, it is convenient to first consider the case of an even number of electrons ($M = 2\mathcal{M}$), and to write the SPIP function, Φ^0, as well as its "super CI" basis functions, Ψ^0_{rs}, resulting from the single excitations, in geminal form. This can be accomplished with the help of the following two-term geminals (Silver et al., 1970)

$$\left.\begin{array}{l} (f_{\kappa_0}\Phi_{\kappa_0}\phi_{\kappa_0} + f_{\kappa_1}\phi_{\kappa_1}\phi_{\kappa_1})\Theta_- \\ \\ 2^{-\frac{1}{2}}(\phi_{\kappa_0}\phi_{\kappa_1} + \phi_{\kappa_1}\phi_{\kappa_0})\Theta_- \end{array}\right\} \text{singlet,}$$

$$2^{-\frac{1}{2}}(\phi_{\kappa_0}\phi_{\kappa_1} - \phi_{\kappa_1}\phi_{\kappa_0})\Theta_+, \qquad \text{triplet,} \tag{36}$$

where the orbitals form an orthonormal set, and the spin functions are given by

$$\Theta_- = \{\alpha\beta - \beta\alpha\}/\sqrt{2}\ ,$$

$$\Theta_+ = \alpha\alpha. \tag{37}$$

In this way one obtains the SPIP function,

$$\Phi^0 = A_{\mathcal{M}}\{\Omega_1 \cdots \Omega_{\mathcal{M}}\}, \tag{38}$$

and its "super CI" basis,

$$\Psi^0_{rs} = A_M\{\Omega_1^{rs} \cdots \Omega_M^{rs}\}, \tag{39}$$

where A_M is the antisymmetrizer defined by equation 2. The Ω_K are geminals of the type appearing in equation 36, and the geminals Ω^{rs}_K are obtained by comparing equation 39 with equations 38 and 28-1,6. Thereby, one finds that most Ω^{rs}_K are equal to the corresponding Ω_K, excepting those which are "affected" by one or both of the excitations $\phi_r \rightarrow \phi_s$ and $\phi_s \rightarrow \phi_r$.

All of the geminals Ω_K and Ω^{rs}_K are of the form shown in equation 36; they are antisymmetric with respect to the interchange of their electrons,

$$(1,2)\Omega^{rs}_K(1,2) = -\Omega^{rs}_K(1,2), \tag{40}$$

so the functions Φ^0 and Ψ^0_{rs} are normalized. Moreover, a member of the set $\Omega^{rs}_1,\cdots,\Omega^{rs}_M$ and a member of the set $\Omega^{rt}_1,\cdots,\Omega^{rt}_M$ often obey the orthogonality relation

$$\int dv_2 \Omega^{rs}_I(1,2)\Omega^{rt}_J(1,2) \equiv 0 \tag{41}$$

as well. This identity may not hold, however, if (a) $I = J$, and/or (b) any of the excitations $\phi_r \rightarrow \phi_s$, $\phi_s \rightarrow \phi_r$, $\phi_r \rightarrow \phi_t$, and $\phi_t \rightarrow \phi_r$ "affect" both Ω_I and Ω_J.

Reduction of the "Super CI" Matrix by Geminal Orthogonality Diagrams

In forming the "super CI" matrix arising from the excitations of <u>one</u> orbital, twenty-seven types of matrix elements can occur. These are systematically enumerated in column 1 of Table 1. There, the previous conventions about orbital indices are used: namely, $\phi_{\kappa\mu}$ and $\phi_{\lambda\nu}$ are in geminals; ϕ_k, ϕ_ℓ, and ϕ_m are in F_o; and ϕ_a and ϕ_b are virtual orbitals. It is readily seen that our one-at-a-time orbital optimization method produces matrix elements between products that differ in at most three geminals. A critical factor in calculating such matrix elements is any orthogonality relation that exists between these two sets of three geminals. In fact, the twenty-seven matrix elements can be expressed in terms of three general forms; each of which is characterized by an "orthogonality diagram".

The simplest matrix element whose diagrams display all the features that ever occur is $<\Psi^0_{\kappa_0\ell}|H|\Phi^0>$. From equations 7-1,6; 28-1,6; and 36, this integral is given by the two-term sum

$$<\Psi_{\kappa_0\ell}|\hat{H}|\Phi^0> = -f_{\kappa_0}<A_M\{\Omega_1\cdots\Omega_{\kappa-1}\phi_\ell\phi_\ell\Theta_-\Omega_{\kappa+1}\cdots\Omega_N\phi_{2N+1}\,\alpha\cdots$$

$$\cdots\phi_{\ell-1}\alpha\; 2^{-\frac{1}{2}}\;(\phi_{\kappa_0}\phi_{\ell+1}-\phi_{\ell+1}\phi_{\kappa_0})\alpha\alpha\;\phi_{\ell+2}\cdots\phi_M\alpha\}|\hat{H}|$$

$$A_M\{\Omega_1\cdots\Omega_{\kappa-1}\Omega_\kappa\Omega_{\kappa+1}\cdots$$

$$\cdots\Omega_N\phi_{2N+1}\alpha\cdots\phi_{\ell-1}\alpha\, 2^{-\frac{1}{2}}\,(\phi_\ell\phi_{\ell+1} - \phi_{\ell+1}\phi_\ell)\alpha\alpha\phi_{\ell+2}\alpha\cdots\phi_M\alpha\}>$$

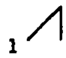
$$- f_{\kappa_1}<A_M\{\Omega_1\cdots\Omega_{\kappa-1}\phi_{\kappa_1}\phi_{\kappa_1}\Theta_-\Omega_{\kappa+1}\cdots$$

$$\Omega_N\phi_{2N+1}\alpha\cdots\phi_{\ell-1}\alpha\, 2^{-\frac{1}{2}}(\phi_{\kappa_0}\phi_{\ell+1} - \phi_{\ell+1}\phi_{\kappa_0})\alpha\alpha\phi_{\ell+2}\alpha$$

$$\cdots\phi_M\alpha\}|\hat{H}|A_M\{\Omega_1\cdots\Omega_{\kappa-1}\Omega_\kappa\Omega_{\kappa+1}\cdots\Omega_N\phi_{2N+1}\alpha\cdots\phi_{\ell-1}\alpha$$

$$2^{-\frac{1}{2}}(\phi_\ell\phi_{\ell+1} - \phi_{\ell+1}\phi_\ell)\alpha\alpha\,\phi_{\ell+2}\alpha\cdots\phi_M\alpha\} >. \tag{42}$$

We diagram this matrix element as

$<\Psi^0_{\kappa_0\ell}|\hat{H}|\Phi^0> = - f_{\kappa_0}$  $- f_{\kappa_1}$  . (43)

Here the two figures represent the first and second integrals in equation 42, and they are interpreted as follows. We concentrate our attention on, and indicate in the diagram, only those geminals that are "affected" by the two excitations in the matrix element; the upper part of the diagrams refers to the "affected" geminals in the left function of their integral and the bottom refers to the right. The points on the top and bottom of the diagram appear in the same left to right order as the "affected" geminals in the integrals of equation 42. There are two kinds of lines: (a) vertical lines, and they indicate orthogonality between geminals in the same position in the left and right products, one line indicating weak orthogonality, a double line indicating strong orthogonality; (b) slanted lines, and *they indicate* that the connected geminals (being in different positions) are *not strongly orthogonal*. Underlying this is the assumption that geminals in corresponding positions and not connected by a line are nonorthogonal, and geminals in noncorresponding positions and not connected by a line are strongly orthogonal.

The diagonal elements of the "super CI" matrix are in a class by themselves. Such an element is explicitly given by

$$\langle\Psi^0_{rs}|\hat{H}|\Psi^0_{rs}\rangle = \langle A_M\{\Omega_1^{rs}\cdots\Omega_M^{rs}\}|\hat{H}| A_M\{\Omega_1^{rs}\cdots\Omega_M^{rs}\}\rangle , \tag{44}$$

and we diagram it as

$$\langle\Psi^0_{rs}|\hat{H}|\Psi^0_{rs}\rangle = \begin{array}{cccc} - & - & & - \\ & & \cdots & \\ - & - & & - \end{array} , \tag{45}$$

where each bar represents a geminal. The upper bars correspond to the left function, and the lower bars correspond to the right.

With some rearrangement, the twenty-seven matrix elements in column 1 of Table 1 can be diagramed as shown in column 2 of Table 1. The notations near the appropriate points indicate the orbitals occupied in the geminals. At this juncture, one can examine all the orbital products in each matrix element and see that the SPIP function Φ^0 and the excitations Ψ^0_{rs} for fixed (r) form an orthogonal set.

Clearly, given the expression for the integral represented by one diagram, we can specialize it to yield the formula for any other diagram resulting from the addition of a vertical line or the erasure of a slanted line. This specialization is possible because the operations involved only strengthen and never weaken the orthogonality relations. One must approach this specialization with caution, however. Since the diagrams do not distinguish between the singlet and triplet geminals shown in equation 36, we must evaluate the integral expressions for the general diagrams using the general geminal

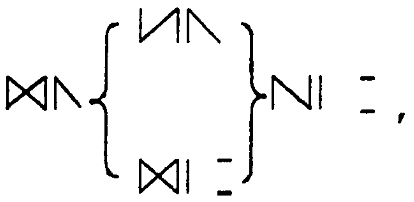
$$\Omega_K = C_s\{f_{K_0}\phi_{K_0}\phi_{K_0} + f_{K_1}\phi_{K_1}\phi_{K_1}\}\Theta_- + C_a 2^{-\frac{1}{2}}(\phi_{K_0}\phi_{K_1} - \phi_{K_1}\phi_{K_0})\Theta_+ , \tag{46}$$

before making any specializations.

An inspection of column 2 of Table 1 then shows that all diagrams can be obtained from three general forms and two sequences of specialization: namely

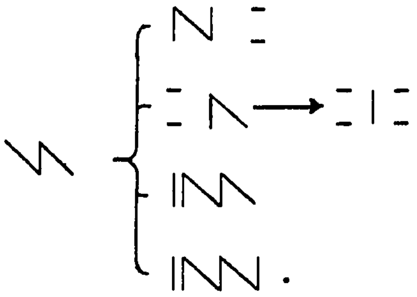
$$\text{Diagram 1} = \begin{array}{cccc} - & - & & - \\ & & \cdots & \\ - & - & & - \end{array} , \tag{47-1}$$

Diagram 2 =



(47-2)

Diagram 3 =



(47-3)

All these diagrams appear in column 2 of Table 1, and there we make use of the abbreviations

$$[a,b] = f_a a^2 + f_b b^2,$$

$$[a,o] = [o,a] = a^2,$$

$$\langle a,b \rangle = 2^{-\frac{1}{2}}(ab + ba),$$

$$(a,b) = 2^{-\frac{1}{2}}(ab - ba),$$

$$(a,) = (,a) = a. \qquad (47\text{-}4)$$

Table 1. Matrix elements and orthogonality diagrams

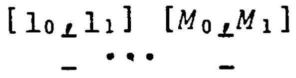
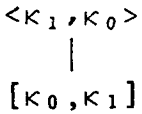
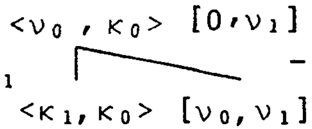
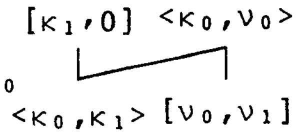
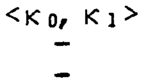
Matrix Element	Orthogonality Diagrams
(1) $\langle\Phi^0\|\hat{H}\|\Phi^0\rangle$	
(2) $\langle\Psi^0_{\kappa_0\kappa_1}\|\hat{H}\|\Phi^0\rangle$	
(3) $\langle\Psi^0_{\kappa_0\kappa_1}\|\hat{H}\|\Psi^0_{\kappa_0\nu_0}\rangle$	$1/\sqrt{f^2_{\kappa_0} f^2_{\nu_1} + f^2_{\kappa_1} f^2_{\nu_0}}\{f_{\kappa_0} f_{\nu_1}$  $-f_{\kappa_1} f_{\nu_0}$  $\}$
(4) $\langle\Psi^0_{\kappa_0\kappa_1}\|\hat{H}\|\Psi^0_{\kappa_0\kappa_1}\rangle$	

Table 1, (Continued)

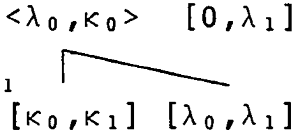
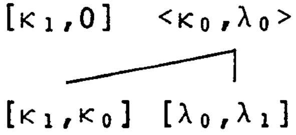
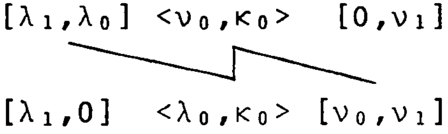
Matrix Element	Orthogonality Diagrams
(5)	
$<\Psi^0_{\kappa_0\lambda_0}\|\hat{H}\|\Phi^0>$	$1/\sqrt{f^2_{\kappa_0} f_{\lambda_1} + f^2_{\kappa_1} f^2_{\lambda_0}}\ \{f_{\kappa_0} f_{\lambda_1}$  $-$ $f_{\kappa_1} f_{\lambda_0}$  $\}$
(6)	
$<\Psi^0_{\kappa_0\lambda_0}\|\hat{H}\|\Psi^0_{\kappa_0\nu_0}>$	$1/\sqrt{(f^2_{\kappa_0} f^2_{\lambda_1} + f^2_{\kappa_1} f^2_{\lambda_0})(f^2_{\kappa_0} f^2_{\nu_1} + f^2_{\kappa_1} f^2_{\nu_0})}\ \chi$ $\{f^2_{\kappa_0} f_{\lambda_1} f_{\nu_1}$ 

Table 1, (Continued)

Matrix Element	Orthogonality Diagrams
	$[\lambda_0,\lambda_1]\ \langle\kappa_0,\nu_0\rangle\ \ [0,\nu_1]$ $- f_{\kappa_1}f_{\lambda_0}f_{\kappa_0}f_{\nu_1}$  $\langle\kappa_0,\lambda_0\rangle\ [\kappa_1,0]\ \ [\nu_0,\nu_1]$
	$[\nu_0,\nu_1]\ \langle\kappa_0,\lambda_0\rangle\ \ [0,\lambda_1]$ $- f_{\kappa_0}f_{\lambda_1}f_{\kappa_1}f_{\nu_0}$  $\langle\kappa_0,\nu_0\rangle\ [\kappa_1,0]\ \ [\lambda_0,\lambda_1]$
	$\langle\kappa_0,\lambda_0\rangle\ [\nu_0,\nu_1]\ [\kappa_1,0]$ $+ f^2_{\kappa_1}f_{\lambda_0}f_{\nu_0}$  $\}$ $[\lambda_0,\lambda_1]\ \langle\kappa_0,\nu_0\rangle\ [\kappa_1,0]$
(7)	
$\langle\Psi^0{}_{\kappa_0\lambda_0}\lvert\hat{H}\rvert\Psi^0{}_{\kappa_0\lambda_1}\rangle$	$1/\sqrt{(f^2_{\kappa_0}f^2_{\lambda_1}+f^2_{\kappa_1}f^2_{\lambda_0})(f^2_{\kappa_0}f^2_{\lambda_0}+f^2_{\kappa_1}f^2_{\lambda_1})}\ \times$

Table 1. (Continued)

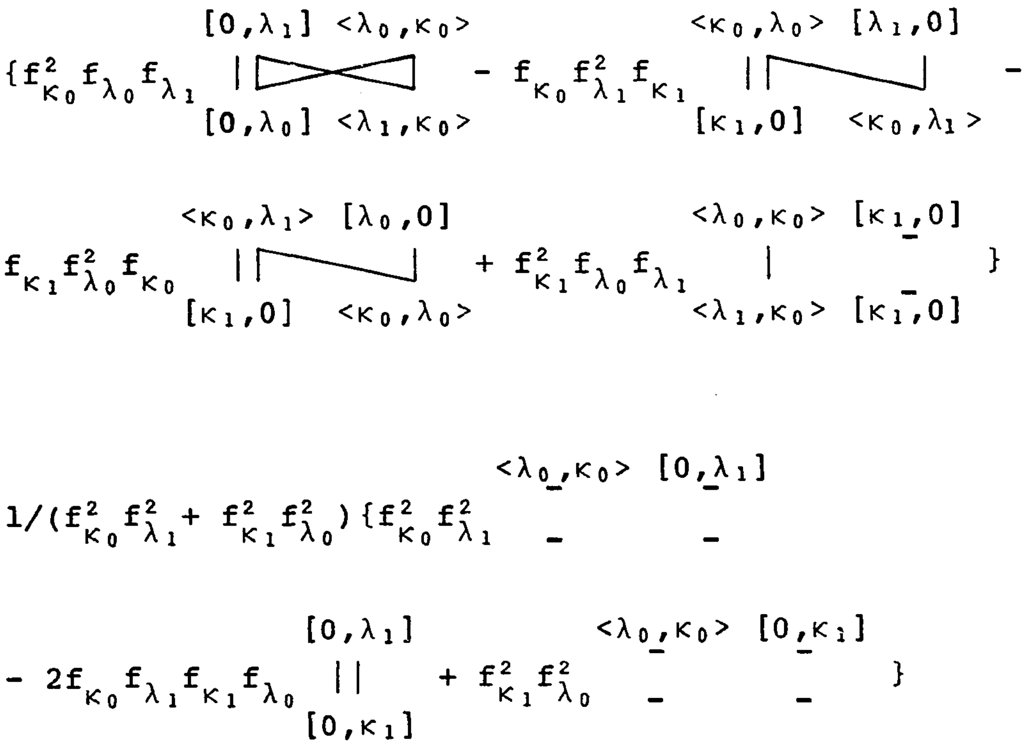
Matrix Element	Orthogonality Diagrams
(8) $\langle\Psi^0_{\kappa_0\lambda_0}\|\hat{H}\|\Psi^0_{\kappa_0\lambda_0}\rangle$	 $\{f_{\kappa_0}^2 f_{\lambda_0} f_{\lambda_1} \overset{[0,\lambda_1]\ \langle\lambda_0,\kappa_0\rangle}{\underset{[0,\lambda_0]\ \langle\lambda_1,\kappa_0\rangle}{\|}} - f_{\kappa_0} f_{\lambda_1}^2 f_{\kappa_1} \overset{\langle\kappa_0,\lambda_0\rangle\ [\lambda_1,0]}{\underset{[\kappa_1,0]\ \langle\kappa_0,\lambda_1\rangle}{\|\|}} -$ $f_{\kappa_1} f_{\lambda_0}^2 f_{\kappa_0} \overset{\langle\kappa_0,\lambda_1\rangle\ [\lambda_0,0]}{\underset{[\kappa_1,0]\ \langle\kappa_0,\lambda_0\rangle}{\|\|}} + f_{\kappa_1}^2 f_{\lambda_0} f_{\lambda_1} \overset{\langle\lambda_0,\kappa_0\rangle\ [\underline{\kappa_1},0]}{\underset{\langle\lambda_1,\kappa_0\rangle\ [\overline{\kappa_1},0]}{\|}}\}$ $1/(f_{\kappa_0}^2 f_{\lambda_1}^2 + f_{\kappa_1}^2 f_{\lambda_0}^2)\{f_{\kappa_0}^2 f_{\lambda_1}^2 \overset{\langle\underline{\lambda_0},\kappa_0\rangle\ [0,\underline{\lambda_1}]}{-\qquad -}$ $-\ 2f_{\kappa_0} f_{\lambda_1} f_{\kappa_1} f_{\lambda_0} \overset{[0,\lambda_1]}{\underset{[0,\kappa_1]}{\|\|}} + f_{\kappa_1}^2 f_{\lambda_0}^2 \overset{\langle\underline{\lambda_0},\kappa_0\rangle\ [0,\underline{\kappa_1}]}{-\qquad -}\}$

Table 1. (Continued)

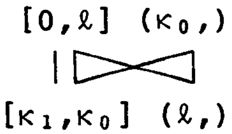
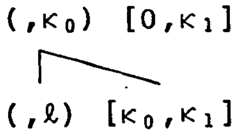
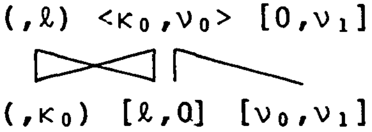
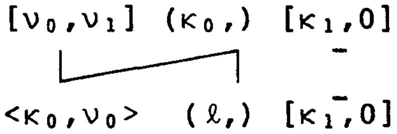
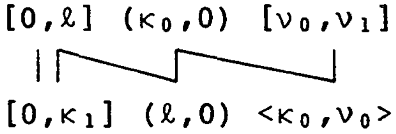
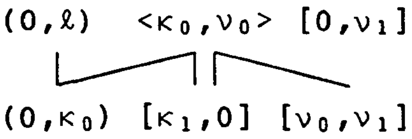
Matrix Element	Orthogonality Diagrams
(9) $<\Psi^0_{\kappa_0\ell}\|\hat{H}\|\Phi^0>$	$-f_{\kappa_0}$  $-f_{\kappa_1}$ 
(10) $<\Psi^0_{\kappa_0\ell}\|\hat{H}\|\Psi^0_{\kappa_0\nu_0}>$	$1/\sqrt{f^2_{\kappa_0} f^2_{\nu_1} + f^2_{\kappa_1} f^2_{\nu_0}}\ \{- f^2_{\kappa_0} f_{\nu_1}$  $+ f^2_{\kappa_1} f_{\nu_0}$  $+ f_{\kappa_0} f_{\kappa_1} f_{\nu_0}$  $- f_{\kappa_1} f_{\kappa_0} f_{\nu_1}$  $\}$

Table 1. (Continued)

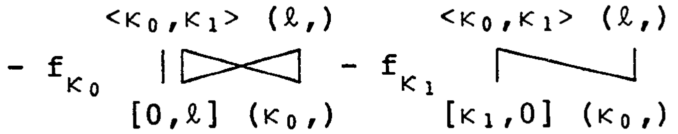
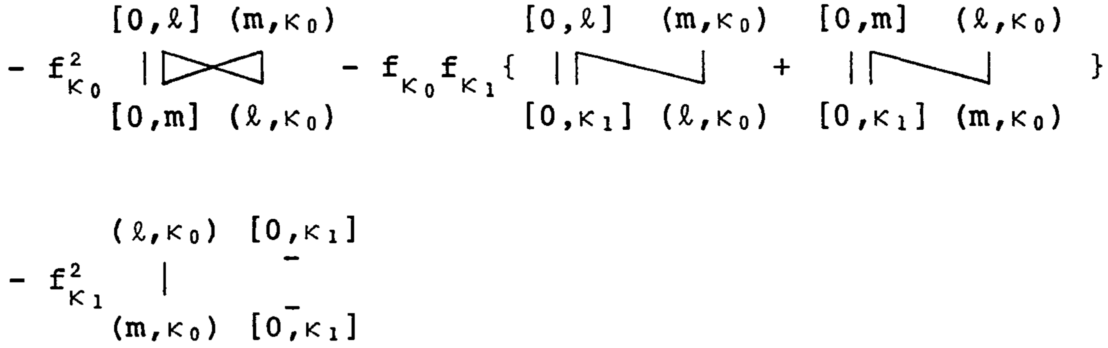
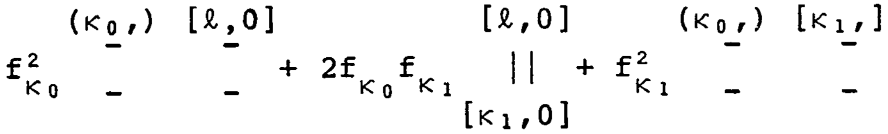
Matrix Element	Orthogonality Diagrams
(11) $\langle\Psi^{0}_{\kappa_0\ell}\|\hat{H}\|\Psi^{0}_{\kappa_0\kappa_1}\rangle$	
(12) $\langle\Psi^{0}_{\kappa_0\ell}\|\hat{H}\|\Psi^{0}_{\kappa_0 m}\rangle$	
(13) $\langle\Psi^{0}_{\kappa_0\ell}\|\hat{H}\|\Psi^{0}_{\kappa_0\ell}\rangle$	

Table 1. (Continued)

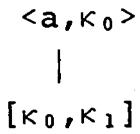
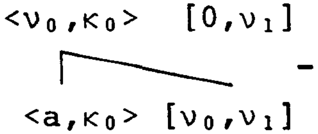
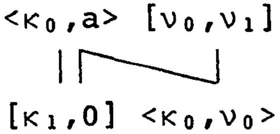
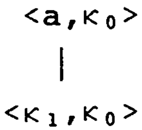
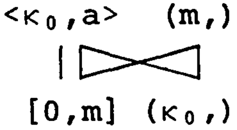
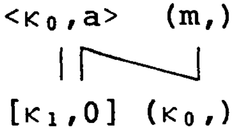
Matrix Element	Orthogonality Diagrams
(14) $<\Psi^0_{\kappa_0 a}\vert\hat{H}\vert\Phi^0>$	
(15) $<\Psi^0_{\kappa_0 a}\vert\hat{H}\vert\Psi^0_{\kappa_0 \nu_0}>$	$1/\sqrt{f^2_{\kappa_0} f^2_{\nu_1} + f^2_{\kappa_1} f^2_{\nu_0}}\ \{f_{\kappa_0} f_{\nu_1}$  $- f_{\kappa_1} f_{\nu_0}$  $\}$
(16) $<\Psi^0_{\kappa_0 a}\vert\hat{H}\vert\Psi^0_{\kappa_0 \kappa_1}>$	
(17) $<\Psi^0_{\kappa_0 a}\vert\hat{H}\vert\Psi^0_{\kappa_0 m}>$	$- f_{\kappa_0}$  $- f_{\kappa_1}$ 

Table 1. (Continued)

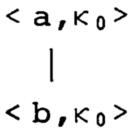
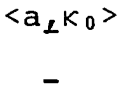
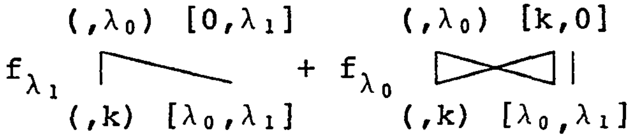
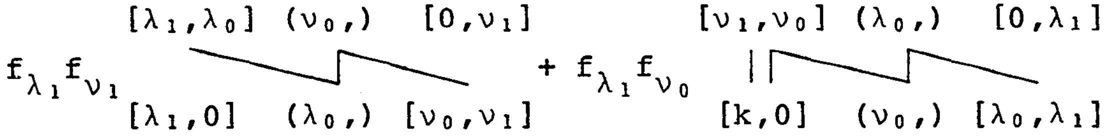
Matrix Element	Orthogonality Diagrams
(18) $\langle\Psi^0_{\kappa_0 a}\|\hat{H}\|\Psi^0_{\kappa_0 b}\rangle$	
(19) $\langle\Psi^0_{\kappa_0 a}\|\hat{H}\|\Psi^0_{\kappa_0 a}\rangle$	
(20) $\langle\Psi^0_{k\lambda_0}\|\hat{H}\|\Phi^0\rangle$	
(21) $\langle\Psi^0_{k\lambda_0}\|\hat{H}\|\Psi^0_{k\nu_0}\rangle$	

Table 1. (Continued)

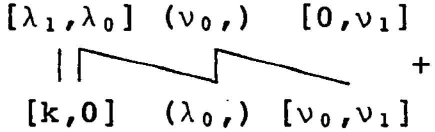
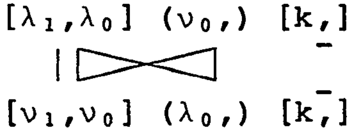
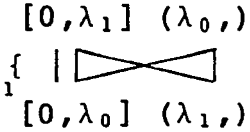
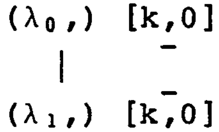
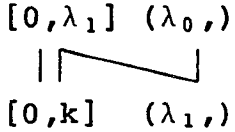
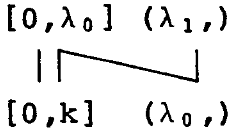
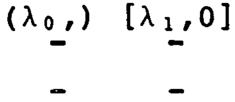
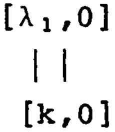
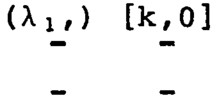
Matrix Element	Orthogonality Diagrams
	$+ f_{\lambda_0} f_{\nu_1}$  $+ f_{\lambda_0} f_{\nu_0}$ 
(22) $\langle \Psi^0{}_{k\lambda_0} \| \hat{H} \| \Psi^0{}_{k\lambda_1} \rangle$	$f_{\lambda_0} f_{\lambda_1} \{$  $+$  $\} + f^2_{\lambda_1}$  $+ f^2_{\lambda_0}$ 
(23) $\langle \Psi^0{}_{k\lambda_0} \| \hat{H} \| \Psi^0{}_{k\lambda_0} \rangle$	$f^2_{\lambda_1}$  $+ 2 f_{\lambda_0} f_{\lambda_1}$  $+ f^2_{\lambda_0}$ 

Table 1. (Continued)

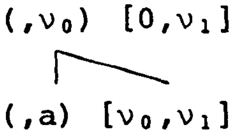
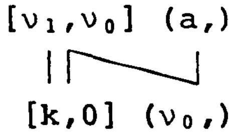
Matrix Element	Orthogonality Diagrams
(24) $\langle\Psi^0_{ka}\vert\hat{H}\vert\Phi^0\rangle$	
(25) $\langle\Psi^0_{ka}\vert\hat{H}\vert\Psi^0_{k\nu_0}\rangle$	f_{ν_1}  + f_{ν_0} 
(26) $\langle\Psi^0_{ka}\vert\hat{H}\vert\Psi^0_{kb}\rangle$	

Table 1. (Continued)

Matrix Element	Orthogonality Diagrams
(27) $<\Psi^0_{ka}\|\hat{H}\|\Psi^0_{ka}>$	(a,)

Geminal Form of the Hamiltonian

Since we are calculating matrix elements between separated-geminal wavefunctions, it is convenient to express the Hamiltonian operator, equation 12, as a sum of pair interactions. This form is

$$\hat{H}(1,2,\cdots,2M) = \sum_{I=1}^{M} \hat{h}_I(I_0,I_1)$$

$$+ \sum_{I=2}^{M} \sum_{J=1}^{I-1} \hat{g}_{IJ}(I_0,I_1,J_0,J_1) + \hat{N}, \tag{48}$$

where

$$\hat{h}_I(1,2) = -\tfrac{1}{2}\nabla_1^2 - \sum_{a=1}^{A} Z_a/R_{1a}$$

$$- \tfrac{1}{2}\nabla_2^2 - \sum_{a=1}^{A} Z_a/R_{2a} + 1/r_{12}, \tag{49-1}$$

$$\hat{g}_{IJ}(1,2,3,4) = 1/r_{13} + 1/r_{14} + 1/r_{23} + 1/r_{24}, \tag{49-2}$$

$$\hat{N} = \sum_{a=2}^{A} \sum_{b=1}^{a-1} Z_a Z_b/R_{ab}. \tag{49-3}$$

The quantities Z_a, R_{ab}, R_{ia}, r_{ij}, and ∇_i^2 were defined in Part I in connection with equation 12.

Integral Expressions for the Three General Diagrams

The standard transformation of the antisymmetrizer (Eyring et al., 1944) gives

$$<\Psi_{rs}|\hat{H}|\Psi_{rs}> = 2^{-M} \{$$

$$\sum_{I=1}^{M} \sum_{P_\mu \in S(1,2M)} <\Omega_1' \cdots \Omega_M'|\hat{h}_I|(-1)^\mu P_\mu \Omega_1 \cdots \Omega_M>$$

$$+ \sum_{I=2}^{M} \sum_{J=1}^{I-1} \sum_{P_\mu \in S(1,2M)} <\Omega_1' \cdots \Omega_M'|\hat{g}_{IJ}|$$

$$(-1)^\mu P_\mu \Omega_1 \cdots \Omega_M > \} . \tag{50}$$

Here we introduced the notation

$$\Omega_I^{rs} = \Omega'_I, \quad \Omega_I^{rt} = \Omega_I , \tag{51}$$

and we will keep it from now on unless it creates confusion.

Equation 50 will be simplified by the antisymmetry of the geminals, equation 40, and any orthogonality among the geminals in the two products. The diagrams in equation 47-1,3 show us that even the most complicated cases still have many orthogonality relations, so the matrix element problem is really not too large.

Diagram 1

This diagram corresponds to the energy of a separated-pair wavefunction. The strong orthogonality and antisymmetry of the geminals reduce equation 50 to

$$\begin{array}{ccccc} - & & & & - \\ - & \bullet & \bullet & \bullet & - \end{array} = \tfrac{1}{2} \sum_{I} \sum_{P_\mu \in S(1,2)} <\Omega_I|\hat{h}|(-1)^\mu P_\mu \Omega_J>$$

$$+ \tfrac{1}{4} \sum_{I<J} \sum_{P_\mu \in S(1,4)} <\Omega_I\Omega_J|\hat{g}_{IJ}|(-1)^\mu P_\mu \Omega_I\Omega_J> \; . \qquad (52)$$

We can write (Miller and Ruedenberg, 1968c)

$$S(1,4) = C \otimes G(1,4) = C \otimes \{1-(1,2)\} \otimes \{1-(3,4)\} \; , \qquad (53\text{-}1)$$

$$C = \{1,(1,3),(1,4),(2,3),(2,4),(1,3)(2,4)\} \; , \qquad (53\text{-}2)$$

$$G(1,4) = \{1-(1,2)\} \otimes \{1-(3,4)\} \; . \qquad (53\text{-}3)$$

Where G(1,4) is the geminal subgroup of S(1,4) and C is the set of left coset generators of S(1,4) from G(1,4). With equation 40

$$\begin{array}{ccccc} - & & & & - \\ & \bullet & \bullet & \bullet & \\ - & & & & - \end{array} = \sum <\Omega_I|\hat{h}_I|\Omega_I>$$

$$+ \sum_{I<J} <\Omega_I\Omega_J|\hat{G}_{IJ}\{1-(1,3)-(1,4)$$

$$-(2,3)-(2,4)+(1,3)(2,4)\}|\Omega_I\Omega_J> . \tag{54}$$

The one-cycles in C are related by similarity transformations from G(1,4). We can see that

$$\begin{aligned}(1,3)+(1,4)+(2,3)+(2,4) &= (1,3)+(3,4)(1,3)(3,4)\\ &\quad +(1,2)(1,3)(1,2)\\ &\quad +(1,2)(3,4)(1,3)(1,2)(3,4)\end{aligned} \tag{55}$$

and the fact that G(1,4) commutes with $\hat{g}_{IJ}(1,2,3,4)$ combine to give

$$\begin{aligned}\overset{-\quad\;\, -}{\underset{-\quad\;\, -}{\cdots}} &= \sum_I <\Omega_I|\hat{h}_J|\Omega_I>\\ &\quad + \sum_{I<J} <\Omega_I\Omega_J|\hat{g}_{IJ}\{1-4(1,3)\}|\Omega_I\Omega_J> .\end{aligned} \tag{56}$$

The term corresponding to (1,3)(2,4) from C is eliminated because Ω_I and Ω_J are strongly orthogonal for I<J. Equation 56 is just the separated-pair energy in terms of the geminals (Hurley *et al.*, 1953; Parks and Parr, 1958; McWeeny, 1959; Miller and Ruedenberg, 1968a; Silver *et. al.*, 1970). The derivation was presented in some detail to introduce the tools needed to evaluate the other diagrams.

Diagrams 2 and 3

These diagrams represent matrix elements between orthogonal functions. This total orthogonality, the remaining strong orthogonality, and geminal antisymmetry can reduce equation 50 to

$$\begin{aligned}
<\Psi^0_{rs}|\hat{H}|\Psi^0_{rt}> &= (1/8) \sum_{P_\mu \in S(1,6)} <\Omega'_1\Omega'_2\Omega'_3| \\
&\hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \hat{g}_{12} + \hat{g}_{13} + \hat{g}_{23}|(-1)^\mu P_\mu \Omega_1\Omega_2\Omega_3> \\
&+ (1/4) \sum_{J>(3)} \sum_{P_\mu \in S(1,8)} <\Omega'_1\Omega'_2\Omega'_3\Omega_J|\hat{g}_{1J} + \hat{g}_{2J} \\
&+ \hat{g}_{3J}|(-1)^\mu P_\mu \Omega_1\Omega_2\Omega_3\Omega_J> . \qquad (57)
\end{aligned}$$

Here we assume that $\Omega_1,\Omega_2,\Omega_3,\Omega'_1,\Omega'_2$, and Ω'_3 are the "affected" geminals. The symmetric groups S(1,6) and S(1,8) can be written as direct products of left coset generators and geminal subgroups to give

$$S(1,6) = C' \otimes G(1,6), \qquad (58\text{-}1)$$

$$S(1,8) = C'' \otimes C' \otimes C \otimes G(1,8), \qquad (58\text{-}2)$$

$$C' = \{1,(1,5),(1,6),(2,5),(2,6),(3,5),(3,6),(4,5),(4,6),$$

$$(1,5)(2,6),(1,5)(3,6),(1,5)(4,6),(2,5)(3,6),$$

$$(2,5)(4,6),(3,5)(4,6)\}, \qquad (58\text{-}3)$$

$$\begin{aligned} C'' = \{&1,(1,7),(1,8),(2,7),(2,8),(3,7),(3,8),\\ &(4,7),(4,8),(5,7),(5,8),(6,7),(6,8),\\ &(1,7)(2,8),(1,7)(3,8),(1,7)(4,8),(1,7)(5,8),\\ &(1,7)(6,8),(2,7)(3,8),(2,7)(4,8),(2,7)(5,8),\\ &(2,7)(6,8),(3,7)(4,8),(3,7)(5,8),(3,7)(6,8),\\ &(4,7)(5,8),(4,7)(6,8),(5,7)(6,8)\}, \end{aligned} \qquad (58\text{-}4)$$

where C is given in equation 53-2. As with diagram 1, the geminal antisymmetry, strong orthogonality, and the commutation relations

$$\begin{aligned} &G(1,6)\{\hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \hat{g}_{12} + \hat{g}_{13} + \hat{g}_{23}\}\\ &= \{\hat{h}_1 + \hat{h}_2 + \hat{h}_3 + \hat{g}_{12} + \hat{g}_{13} + \hat{g}_{23}\}\, G(1,6)\,, \end{aligned} \qquad (59\text{-}1)$$

$$\begin{aligned} &G(1,8)\{\hat{g}_{1J} + \hat{g}_{2J} + \hat{g}_{3J}\}\\ &= \hat{g}_{1J} + \hat{g}_{2J} + \hat{g}_{3J}\}G(1,8) \end{aligned} \qquad (59\text{-}2)$$

unify the summations over symmetric groups in equation 57 to summations over left coset generators, giving

$$\langle \Psi^0_{rs}|\hat{H}|\Psi^0_{rs}\rangle = \sum_{P_\mu \in C'\otimes C} \langle \Omega'_1\Omega'_2\Omega'_3|\hat{h}_1 + \hat{h}_2 + \hat{h}_3$$

$$+ \hat{g}_{12} + \hat{g}_{13} + \hat{g}_{23}|(-1)^\mu P_\mu \Omega_1\Omega_2\Omega_3\rangle$$

$$+ \sum_{J>(3)} \sum_{P_\mu \in C''\otimes C'\otimes C} \langle \Omega'_1\Omega'_2\Omega'_3\Omega'_J|\hat{g}_{1J} + \hat{g}_{2J} + \hat{g}_{3J}$$

$$|(-1)^\mu P_\mu \Omega_1\Omega_2\Omega_3\Omega_J\rangle . \tag{60}$$

This equation now has to be specialized for diagrams 2 and 3. We use similarity transformations from G(1,6) and G(1,8) and the commutation relations in equations 59-1,2 to collect the nonzero terms. The results are

$$\bowtie|\diagdown = \langle \Omega'_1\Omega'_2\Omega'_3|-4\hat{h}_2(1,3) + 8\hat{h}_2(1,3)(4,6)$$

$$+ \hat{g}_{12}\{-4(1,3) + (1,3)(2,4)\}$$

$$+ \hat{g}_{13}\{8(1,3)(4,6) - 4(1,3)(1,5)(2,4)\}$$

$$+ \hat{g}_{23}\{-4(1,3)+8(1,3)(4,6)+8(1,3)(1,5)\}|\Omega_1\Omega_2\Omega_3\rangle$$

$$+ \sum_{J>(3)} \langle \Omega'_1\Omega'_2\Omega'_3\Omega'_J|\hat{g}_{2J}\{-4(1,3)+8(1,3)(4,8)\}$$

$$+ \hat{g}_{3J}\{8(1,3)(4,6)-16(2,4)(3,5)(3,7)\}|\Omega_1\Omega_2\Omega_3\Omega_J\rangle , \tag{61-1}$$

and

$$= \langle \Omega'_1\Omega'_2\Omega'_3 | \hat{h}_2\{1-4(13)\} + \hat{h}_3\{-4(3,5)+8(1,3)(1,5)\}$$

$$+ \hat{g}_{12}\{1-4(13)\} + \hat{g}_{13}\{-4(4,6)+8(1,3)(1,5)\}$$

$$+ \hat{g}_{23}\{1-4(1,3)-4(4,6)+8(1,3)(4,6)+8(1,3)(1,5)\} | \Omega_1\Omega_2\Omega_3 \rangle$$

$$+ \sum_{J>(3)} \langle \Omega'_1\Omega'_2\Omega'_3\Omega'_J | \hat{g}_{2J}\{1-4(1,3)-4(3,7)+8(1,3)(1,7)\}$$

$$+ \hat{g}_{3J}\{-4(3,5)+8(1,3)(1,5)+8(3,5)(3,7)-16(1,3)(1,5)(1,7)\}$$

$$| \Omega_1\Omega_2\Omega_3\Omega_J \rangle . \qquad (61\text{-}2)$$

Simplification of the General Integral Expressions

Equations 56, and 61-1,2 need to be further simplified. We can expand the pair interactions by using equation 49-2, and the definition

$$\rho_{1,2,\cdots,\eta}(1,\eta+1)$$

$$= \begin{cases} 2\int dv_2\cdots dv_\eta \Lambda_1(1,2)\Lambda_2(3,2)\cdots\Lambda_3(n+1,n), & \eta = \text{even} \\ 2\int dv_2\cdots dv_\eta \Lambda_1(1,2)\Lambda_2(3,2)\cdots\Lambda_3(\eta,\eta+1), & \eta = \text{odd}, \end{cases} \qquad (62)$$

where Λ_I is the space geminal in equation 7-3, allows us to integrate over any variables not explicitly appearing in the two-body interactions. The results of these manipulations and substitutions are shown below:

$$\begin{matrix}- & & -\\ & \cdots & \\ - & & -\end{matrix} = \sum_{I} \langle \Lambda_I|\hat{h}_I|\Lambda_I\rangle$$

$$+ \sum_{I<J} \{[\rho_{II}|\rho_{JJ}] - P_{(1,3)}\langle\rho_{II}|1/r_{12}|\rho_{JJ}\rangle\}. \tag{63-1}$$

$$\bowtie|\diagdown = \langle\Lambda'_3|\Lambda_3\rangle\{-2P_{(1,3)}\langle\Lambda'_2|\hat{h}|\rho_{11'2}\rangle$$

$$+ P_{(1,3)(2,4)}[\rho_{1'2}|\rho_{12'}]$$

$$- P_{(1,3)}(\langle\rho_{1'2}|1/r_{12}|\rho_{12'}\rangle + 2\langle\rho_{1'12'}|1/r_{12}|\Lambda_2\rangle)$$

$$- 2 \sum_{J>(3)} (P_{(1,3)}[\rho_{2'11'2}|\rho_{JJ'}]$$

$$- P_{(1,3)(4,8)}\langle\rho_{2'11'2}|1/r_{12}|\rho_{JJ'}\rangle)\}$$

$$+ 4P_{(1,3)(4,6)}\langle\Lambda'_3|\hat{h}|\rho_{32'11'2}\rangle$$

$$- 2\{P_{(1,3)(1,5)(2,4)}[\rho_{1'2}|\rho_{12'33'}] -$$

$$P_{(1,3)(4,6)}(\langle\rho_{1'2}|1/r_{12}|\rho_{12'33'}\rangle$$

$$+2\langle\rho_{1'12'33'}|1/r_{12}|\Lambda_2\rangle) + P_{(1,3)}[\rho_{2'11'2}|\rho_{33'}] -$$

$$P_{(1,3)(4,6)}(\langle\rho_{2'11'2}|1/r_{12}|\rho_{33'}\rangle + \langle\rho_{2'33'}|1/r_{12}|\rho_{11'2}\rangle)$$

$$- P_{(1,3)(1,5)} \langle \rho_{3}{'}_{32}{'} | 1/r_{12} | \rho_{11}{'}_{2} \rangle \}$$

$$+ (4) \sum_{J>(3)} \{ P_{(1,3)(4,6)} [\rho_{3}{'}_{32}{'}_{11}{'}_{2} | \rho_{JJ'}]$$

$$- P_{(1,3)(4,6)(4,8)} \langle \rho_{3}{'}_{32}{'}_{11}{'}_{2} | 1/r_{12} | \rho_{JJ'} \rangle \}, \tag{63-2}$$

and

$$\diagdown\!\diagup\!\diagdown = \langle \Lambda'_1 | \Lambda_1 \rangle \langle \Lambda'_3 | \Lambda_3 \rangle \{ \langle \Lambda'_2 | \hat{h} | \Lambda_2 \rangle + \sum_{J>(3)} ([\rho_{2}{'}_{2} | \rho_{JJ'}]$$

$$- P_{(3,7)} \langle \rho_{2}{'}_{2} | 1/r_{12} | \rho_{JJ'} \rangle) \} + \langle \Lambda'_3 | \Lambda_3 \rangle \{ [\rho_{1}{'}_{1} | \rho_{22}{'}]$$

$$- P_{(1,3)} (\langle \rho_{1}{'}_{1} | 1/r_{12} | \rho_{22}{'} \rangle + 2 \langle \rho_{2}{'}_{21}{'} | 1/r_{12} | \Lambda_1 \rangle)$$

$$- 2 (P_{(1,3)} \langle \Lambda'_2 | \hat{h} | \rho_{11}{'}_{2} \rangle + \sum_{J>(3)} \{ P_{(1,3)} [\rho_{2}{'}_{21}{'}_{1} | \rho_{JJ'}]$$

$$- P_{(1,3)(1,7)} \langle \rho_{2}{'}_{21}{'}_{1} | 1/r_{12} | \rho_{JJ'} \rangle \}) \} + \langle \Lambda'_1 | \Lambda_1 \rangle \{ [\rho_{2}{'}_{2} | \rho_{33}{'}]$$

$$- P_{(4,6)} (\langle \rho_{2}{'}_{2} | 1/r_{12} | \rho_{33}{'} \rangle + 2 \langle \rho_{3}{'}_{32}{'} | 1/r_{12} | \Lambda_2 \rangle)$$

$$- 2 (P_{(4,6)} \langle \Lambda'_3 | \hat{h} | \rho_{22}{'}_{3} \rangle + \sum_{J>(3)} \{ P_{(4,6)} [\rho_{3}{'}_{32}{'}_{2} | \rho_{JJ'}]$$

$$- P_{(4,6)(4,8)} \langle \rho_{3}{'}_{32}{'}_{2} | 1/r_{12} | \rho_{JJ'} \rangle \}) \}$$

$$+ 2 \{ 2 P_{(1,3)(1,5)} \langle \Lambda'_3 | \hat{h} | \rho_{11}{'}_{22}{'}_{3} \rangle - (P_{(1,3)} [\rho_{2}{'}_{21}{'}_{1} | \rho_{33}{'}]$$

$$-p_{(1,3)(1,5)}\{\langle\rho_{2'21'1}|1/r_{12}|\rho_{33'}\rangle + 2\langle\rho_{3'32'21'}|1/r_{12}|\Lambda_1\rangle\})$$

$$-(p_{(4,6)}[\rho_{1'1}|\rho_{22'33'}] - p_{(4,6)(4,2)}\langle\rho_{1'1}|1/r_{12}|\rho_{22'33'}\rangle)$$

$$+ p_{(1,3)(4,6)}\langle\rho_{2'33'}|1/r_{12}|\rho_{11'2}\rangle$$

$$+ p_{(1,3)(1,5)}\langle\rho_{3'32'}|1/r_{12}|\rho_{11'2}\rangle$$

$$+ 2\sum_{J>(3)} (p_{(1,3)(1,5)}[\rho_{3'32'21'1}|\rho_{JJ'}]$$

$$- p_{(1,3)(1,5)(1,7)}\langle\rho_{3'32'21'1}|1/r_{12}|\rho_{JJ'}\rangle)\}. \qquad (63\text{-}3)$$

Here

$$[f|g] = \int dv_1 \int dv_2 f(1)g(2)/r_{12}, \qquad (64)$$

and $p_{(ij\cdots\ell)}$ is the matrix element of the permutation $(ij\cdots\ell)$ between the spin functions of the geminals associated with electrons $i,j,\cdots,\ell$.

Simplifications for the Special Cases

Equations 61-1,3 generate all the diagrams we need. However, a great simplification occurs when we observe that in the diagrams , , , and  the geminals Ω_3 and Ω'_3 are always singlet geminals of the first type shown in equation 36. This means that for these diagrams

$$\rho_{3'3IJ\cdots K} = 0 . \qquad (65)$$

This result is true because for the above diagrams Ω_3 and Ω'_3 are in their natural expansions (Lowdin, 1955).

All the diagrams in the sequence of equation 47-2 are simplified by equation 65; in fact we have

$$\bowtie|\diagdown = 4p_{(1,3)(4,6)}\langle\Lambda'_3|\hat{h}|\rho_{32'11'2}\rangle$$

$$- 2\{p_{(1,3)}[\rho_{2'11'2}|\rho_{33'}] - p_{(1,3)(4,6)}\langle\rho_{2'11'2}|1/r_{12}|\rho_{33'}\rangle\}$$

$$\langle\Lambda'_3|\Lambda_3\rangle\{-2p_{(1,3)}\langle\Lambda'_2|\hat{h}|\rho_{11'2}\rangle + p_{(1,3)(2,4)}[\rho_{1'2}|\rho_{12'}]$$

$$- p_{(1,3)}(\langle\rho_{1'2}|1/r_{12}|\rho_{12'}\rangle + 2\langle\rho_{1'12'}|1/r_{12}|\Lambda_2\rangle)$$

$$- (2)\sum_{J>(3)}(p_{(1,3)}[\rho_{2'11'2}|\rho_{JJ'}]$$

$$- p_{(1,3)(4,8)}\langle\rho_{2'11'2}|1/r_{12}|\rho_{JJ'}\rangle)\} , \qquad (66\text{-}1)$$

and from equation 66-1

$$|\bowtie = -2p_{(1,3)}\langle\Lambda'_1|\hat{h}|\rho_{22'1}\rangle + p_{(1,3)(2,4)}[\rho_{2'1}|\rho_{21'}]$$

$$- p_{(1,3)}(\langle\rho_{2'1}|1/r_{12}|\rho_{21'}\rangle + 2\langle\rho_{2'21'}|1/r_{12}|\Lambda_1\rangle)$$

$$- 2 \sum_{J>(2)} \{ P_{(1,3)} [\rho_{1'22'1} | \rho_{JJ'}]$$

$$- P_{(1,3)(2,6)} \langle \rho_{1'22'1} | 1/r_{12} | \rho_{JJ'} \rangle \} , \qquad (66\text{-}2)$$

$$= - 2 P_{(1,3)} \langle \Lambda'_3 | \Lambda_3 \rangle \langle \rho_{1'12'} | 1/r_{12} | \Lambda_2 \rangle . \qquad (66\text{-}3)$$

The last diagram in this sequence comes from either equation 66-1 or 66-3, and it is given by

$$= - 2 P_{(1,3)} \langle \rho_{2'21'} | 1/r_{12} | \Lambda_1 \rangle . \qquad (66\text{-}4)$$

Two of the diagrams in the sequence of equation 47-3 cannot be simplified by equation 65; they must be calculated from equation 62-3. We find

$$= - 2 P_{(1,3)} \langle \Lambda'_2 | \hat{h} | \rho_{11'2} \rangle + [\rho_{1'1} | \rho_{22'}]$$

$$- P_{(1,3)} (\langle \rho_{1'1} | 1/r_{12} | \rho_{22'} \rangle + 2 \langle \rho_{2'21'} | 1/r_{12} | \Lambda_1 \rangle)$$

$$- (2) \sum_{J>(2)} \{ P_{(1,3)} [\rho_{2'21'1} | \rho_{JJ'}]$$

$$- P_{(1,3)(1,5)} \langle \rho_{2'21'1} | 1/r_{12} | \rho_{JJ'} \rangle \} , \qquad (66\text{-}5)$$

$$= 4 P_{(1,3)(1,5)} \langle \rho_{3'32'21'} | 1/r_{12} | \Lambda_1 \rangle . \qquad (66\text{-}6)$$

By using equation 65 we can simplify the formula for diagram 3 in equations 47-3 and 63-3, so the second sequence of diagrams is given by

$$= \langle\Lambda'_1|\Lambda_1\rangle\{-2P_{(4,6)}\langle\Lambda'_3|\hat{h}|\rho_{22'3}\rangle + [\rho_{2'2}|\rho_{33'}]$$

$$- P_{(4,6)}\langle\rho_{2'2}|1/r_{12}|\rho_{33'}\rangle\} + \langle\Lambda'_3|\Lambda_3\rangle\{[\rho_{1'1}|\rho_{22'}]$$

$$- P_{(1,3)}(\langle\rho_{1'1}|1/r_{12}|\rho_{22'}\rangle + 2\langle\rho_{2'21'}|1/r_{12}|\Lambda_1\rangle)\}$$

$$+ \langle\Lambda'_1|\Lambda_1\rangle\langle\Lambda'_3|\Lambda_3\rangle\{\langle\Lambda'_2|\hat{h}|\Lambda_2\rangle + \sum_{J>(3)}([\rho_{2'2}|\rho_{JJ'}]$$

$$- P_{(3,7)}\langle\rho_{2'2}|1/r_{12}|\rho_{JJ'}\rangle)\} , \qquad (66-7)$$

$$= -2P_{(1,3)}\langle\Lambda'_2|\hat{h}|\rho_{11'2}\rangle + [\rho_{1'1}|\rho_{22'}]$$

$$- P_{(1,3)}\langle\rho_{1'1}|1/r_{12}|\rho_{22'}\rangle + \langle\Lambda'_2|\Lambda_2\rangle\{\langle\Lambda'_1|\hat{h}|\Lambda_1\rangle$$

$$+ \sum_{J>(2)}([\rho_{1'1}|\rho_{JJ'}] - P_{(1,5)}\langle\rho_{1'1}|1/r_{12}|\rho_{JJ'}\rangle)\}, \qquad (66-8)$$

$$= -2P_{(1,3)}\langle\Lambda'_3|\Lambda_3\rangle\langle\rho_{2'21'}|1/r_{12}|\Lambda_1\rangle , \qquad (66-9)$$

$$| = \langle\Lambda'_1|\hat{h}|\Lambda_1\rangle + \sum_{J>(1)}([\rho_{1'1}|\rho_{JJ}]$$

$$- P_{(1,3)}\langle\rho_{1'1}|1/r_{12}|\rho_{JJ'}\rangle) . \qquad (66-10)$$

To go from equations 62-1 and 66-1,10 to the orbital form of the matrix elements requires that we introduce some more notations and definitions. Most of this can be done by considering a simpler problem.

"LITTLE CI" MATRIX IN ORBITAL FORM

Matrix Elements

The "little CI" problems in equation 16-3 determine the geminal expansion coefficients. From equations 16-2,3, and 37, the explicit form of the matrix elements is seen to be

$$\hat{H}^{\kappa}_{\mu\nu} = \langle A\{\Omega_1 \cdots \Omega_{\kappa-1}\phi_{\kappa\mu}\phi_{\kappa\mu}\Theta\ \Omega_{\kappa+1}\cdots\Omega_M\}|H|$$

$$A\{\Omega_1 \cdots \Omega_{\kappa-1}\phi_{\kappa\nu}\phi_{\kappa\nu}\Theta_-\Omega_{\kappa+1}\cdots\Omega_M\}\rangle\ , \qquad (67)$$

and inspection shows that they correspond to the following diagrams

$$\hat{H}^{\kappa}_{\mu\mu} =$$  , (68-1)

$$H^{\kappa}_{01} = \|\,. \qquad (68\text{-}2)$$

Equation 68-1 is just the separated-pair energy, diagram 1 or equation 63-1, and we find using equation 49-3 that

$$\hat{H}^{\kappa}_{\mu\mu} = \langle \phi_{\kappa\mu}\phi_{\kappa\mu}\Theta_-|\hat{h}|\phi_{\kappa\mu}\phi_{\kappa\mu}\Theta_-\rangle$$

$$+ \sum_{J\neq(\kappa)} \langle \phi_{\kappa\mu}\phi_{\kappa\mu}\Theta_-\Omega_J|\hat{g}_{\kappa J}\{1-4(1,3)\,|\phi_{\kappa\mu}\phi_{\kappa\mu}\Theta_-\Omega_J\rangle$$

$$+ \sum_{I\neq(\kappa)} \{<\Omega_I|\hat{h}|\Omega_I> + \sum_{(I)<J\neq(k)} <\Omega_I\Omega_J|\hat{g}_{IJ}\{1-4(1,3)\}$$

$$|\Omega_I\Omega_J> + \hat{N}. \tag{69}$$

Equation 68-2 is a special case of diagram 3 and from equation 66-10, we find

$$\hat{H}^{\kappa}_{01} = <\phi_{\kappa_0}\phi_{\kappa_0}\Theta_-|\hat{h}_{\kappa}|\phi_{\kappa_1}\phi_{\kappa_1}\Theta_-> . \tag{70}$$

The matrix elements $\hat{H}^{\kappa}_{\mu\mu}$ have many terms in common. Since they are the diagonal elements of a "little CI" matrix, we can discard the common terms without affecting the eigenvectors. The orbital expansions from equations 7-3,6 can be introduced into the remaining terms, and the result is the new "little CI" problem

$$\begin{pmatrix} H^{\kappa}_{00} & H^{\kappa}_{01} \\ H^{\kappa}_{10} & H^{\kappa}_{11} \end{pmatrix} \begin{pmatrix} f_{\kappa_0} \\ f_{\kappa_1} \end{pmatrix} = \varepsilon^{\kappa} \begin{pmatrix} f_{\kappa_0} \\ f_{\kappa_1} \end{pmatrix} , \tag{71-1}$$

$$H^{\kappa}_{00} = 2h_{\kappa_0\kappa_0} + (f^2_{\kappa_1} - f^2_{\kappa_0})[\kappa_0\kappa_0|\kappa_0\kappa_0]$$

$$- f^2_{\kappa_1}\, g_{\kappa_1\kappa_1,\kappa_0\kappa_0}$$

$$+ 2G_{\kappa_0\kappa_0} + 2C_{\kappa_0\kappa_0} - E_{\kappa_0\kappa_0} , \tag{71-2}$$

$$H^{\kappa}_{11} = 2h_{\kappa_1\kappa_1} + (f^2_{\kappa_0} - f^2_{\kappa_1})[\kappa_1\kappa_1|\kappa_1\kappa_1]$$

$$- f^2_{\kappa_0} g_{\kappa_1\kappa_1,\kappa_0\kappa_0} + 2G_{\kappa_1\kappa_1} + 2C_{\kappa_1\kappa_1} - E_{\kappa_1\kappa_1} , \qquad (71\text{-}3)$$

$$H^{\kappa}_{01} = [\kappa_0\kappa_1|\kappa_0\kappa_1] . \qquad (71\text{-}4)$$

Here we made use of the permutation matrix element

$$\langle\Theta_-\Theta_-|(13)|\Theta_-\Theta_-\rangle = \tfrac{1}{2} , \qquad (72)$$

and the definitions

$$h_{rs} = \langle\phi_r(1)|-\tfrac{1}{2}\nabla_1^2 - \sum_{a=1}^{A} Z_a/R_{1a}|\phi_s(1)\rangle , \qquad (73\text{-}1)$$

$$g_{rs,tu} = 2[rs|tu]-[ru|ts], \qquad (73\text{-}2)$$

$$G_{rs} = \sum_{\kappa=0}^{N} \sum_{\mu=0}^{1} f^2_{\kappa\mu}\, g_{rs,\kappa\mu\kappa\mu} , \qquad (73\text{-}3)$$

$$C_{rs} = \sum_{\ell=2N+1}^{M} [rs|\ell\ell], \qquad (73\text{-}4)$$

$$E_{rs} = \sum_{\ell=2N+1}^{M} [r\ell|s\ell], \qquad (73\text{-}5)$$

where [rs|tu] is the molecular electron repulsion integral in equation 30. The summation indices used in equations 72-3,5 conform to the conventions we agreed to for distinguishing geminally from singly occupied orbitals as discussed in the text before equation 42.

"Little CI" Eigenvalues

An eigenvalue of the "little CI" in equation 70-1 can be expressed as

$$\varepsilon^{\kappa} = \sum_{\mu=0}^{1} 2f_{\kappa\mu}^{2} \; h_{\kappa\mu\kappa\mu} + \sum_{\mu=0}^{1} \sum_{\nu=0}^{1} f_{\kappa\mu} f_{\kappa\nu} [\kappa\mu\kappa\nu|\kappa\mu\kappa\nu]$$

$$+ \sum_{\mu=0}^{1} f_{\kappa\mu}^{2} \{ (2 \sum_{1=\lambda\neq(\kappa)}^{N} \sum_{\nu=0}^{1} f_{\lambda\nu}^{2} g_{\kappa\mu\kappa\mu,\lambda\nu\lambda\nu})$$

$$+ 2C_{\kappa\mu\kappa\mu} - E_{\kappa\mu\kappa\mu} \} . \qquad (74)$$

This result holds for either of the eigenvalues of the "little CI" matrix, but for the most part we'll be interested in the lowest eigenvalue. ε^{κ} is the energy of the κ(th) geminal in the field of the electrons. As we'll see later, this expression of the eigenvalue can be used to simplify some of the diagonal matrix elements of the "super CI" matrix.

"SUPER CI" MATRIX IN ORBITAL FORM

Definitions

Equations 63-1 and 66-1,10 hold for separated-geminal functions whose geminals are expressed in natural form. The present investigation is concerned with two-term geminals. Introducing these expansions explicitly, and collecting certain terms in the diagonal elements into the pair energies defined by equation 74, we obtain the orbital forms for the "super CI" matrix elements. To this end we require the appropriate values of the permutation matrix elements, they are shown in Table 2.

The following orbital expressions of the matrix elements use the definitions of C_{rs}, E_{rs}, in equations 73-1,5, and ε^{κ} in equation 74. Additionally we introduce the symbols

$$F_{rs} = h_{rs} + G_{rs} + C_{rs} - \tfrac{1}{2}E_{rs} \, , \tag{75-1}$$

$$A_{rs} = h_{rs} + G_{rs} + C_{rs} - E_{rs} \, , \tag{75-2}$$

and restate the summation conventions

$$\sum_{\kappa} \sum_{\mu} = \sum_{\kappa=1}^{N} \sum_{\mu=0}^{1} \, , \tag{75-3}$$

$$\sum_{k} = \sum_{k=2N+1}^{M} \, . \tag{75-4}$$

Table 2. Permutation matrix elements

$$p_{(ij\cdots k)} = \langle \Theta_\alpha \Theta_\beta \Theta_\gamma | (ij\cdots k) \Theta_\alpha \Theta_\beta \Theta_\gamma \rangle$$

α β γ	(1,3)	(1,3)(2,4)	(2,6)	(4,6)	(1,3)(2,6)	(1,3)(4,6)	(1,3)(1,5)
− − −	½	1	½	½	¼	¼	¼
− − +	½	1	½	½	¼	¼	¼
− + −	½	0	½	½	¼	¼	¼
− + +	½	0	½	1	0	½	½
+ + −	1	1	½	½	½	½	½
+ + +	1	1	1	1	1	1	1

"Super CI" Matrix Elements

With these results, the separated-pair energy is (Silver *et al.*, 1970)

$$<\Phi^0|\hat{H}|\Phi^0> = \tfrac{1}{2}\sum_{\kappa}\{\varepsilon^{\kappa} + (\sum_{\mu=0}^{1}\{f^2_{\kappa\mu}(2h_{\kappa\mu\kappa\mu} + [\kappa\mu\kappa\mu|\kappa\mu\kappa\mu])$$

$$+ 2C_{\kappa\mu\kappa\mu} - E_{\kappa\mu\kappa\mu}\}) + 2f_{\kappa_0}f_{\kappa_1}[\kappa_1\kappa_0|\kappa_1\kappa_0]\}$$

$$+ \sum_{k}\{h_{kk} + \tfrac{1}{2}(C_{kk} - E_{kk})\}, \tag{76-1}$$

and the matrix elements become the following:

$$<\Psi^0_{\kappa_0\kappa_1}|\hat{H}|\Phi^0> = \sqrt{2}\,\{(f_{\kappa_0} + f_{\kappa_1})F_{\kappa_1\kappa_0}$$

$$- f_{\kappa_0}f_{\kappa_1}(f_{\kappa_0} - f_{\kappa_1})([\kappa_0\kappa_0|\kappa_0\kappa_1] - [\kappa_1\kappa_1|\kappa_1\kappa_0])\}, \tag{76-2}$$

$$<\Psi^0{}_{\kappa_0\kappa_1}|\hat{H}|\Psi^0{}_{\kappa_0\nu_0}> = 1/\sqrt{f^2_{\kappa_0}f^2_{\nu_1} + f^2_{\kappa_1}f^2_{\nu_0}}\,\{$$

$$(f_{\kappa_0}f^2_{\nu_1} + f_{\kappa_1}f^2_{\nu_0})(F_{\kappa_1\nu_0} + \{f^2_{\kappa_1} - f^2_{\kappa_0}\}[\kappa_1\nu_0|\kappa_0\kappa_0])$$

$$+ (f_{\kappa_0}f^2_{\nu_1}\{1 + f^2_{\kappa_0}\} - f_{\kappa_1}f^2_{\nu_0}\{1 + f^2_{\kappa_1}\})[\kappa_1\kappa_0|\nu_0\kappa_0]$$

$$+ f^2_{\nu_0}f^2_{\nu_1}(f_{\kappa_0} - f_{\kappa_1})(g_{\kappa_1\nu_0,\nu_1\nu_1} - [\kappa_1\nu_0|\nu_0\nu_0])$$

$$+ f_{\kappa_0}f_{\kappa_1}(f_{\kappa_0}f^2_{\nu_0} - f^2_{\kappa_1}f^2_{\nu_1})[\kappa_1\nu_0|\kappa_1\kappa_1]$$

$$- f_{\nu_0} f_{\nu_1} (f_{\kappa_0} - f_{\kappa_1}) [\kappa_1 \nu_1 | \nu_0 \nu_1]\} , \tag{76-3}$$

$$<\Psi^0{}_{\kappa_0 \kappa_1} | \hat{H} | \Psi^0{}_{\kappa_0 \kappa_1}> = F_{\kappa_0 \kappa_0} + F_{\kappa_1 \kappa_1} + 2 [\kappa_1 \kappa_0 | \kappa_1 \kappa_0]$$

$$- [\kappa_1 \kappa_1 | \kappa_0 \kappa_0] - f^2_{\kappa_0} [\kappa_0 \kappa_0 | \kappa_0 \kappa_0] - f^2_{\kappa_1} [\kappa_1 \kappa_1 | \kappa_1 \kappa_1]$$

$$- \varepsilon^{\kappa} + <\Phi^0 | \hat{H} | \Phi^0> , \tag{76-4}$$

$$<\Psi^0{}_{\kappa_0 \lambda_0} | \hat{H} | \Phi^0> = \sqrt{2/(f^2_{\kappa_0} f^2_{\lambda_1} + f^2_{\kappa_0} f^2_{\lambda_0})} \{$$

$$(f^2_{\kappa_0} f^2_{\lambda_1} - f^2_{\kappa_1} f^2_{\lambda_0}) F_{\lambda_0 \kappa_0} - f^2_{\kappa_0} f^2_{\kappa_1} (g_{\lambda_0 \kappa_0 , \kappa_1 \kappa_1} - [\lambda_0 \kappa_0 | \kappa_0 \kappa_0])$$

$$+ f^2_{\lambda_0} f^2_{\lambda_1} (g_{\lambda_0 \kappa_0 \ \lambda_1 \lambda_1} - [\lambda_0 \kappa_0 | \lambda_0 \lambda_0])$$

$$+ f_{\kappa_0} f_{\kappa_1} [\lambda_0 \kappa_1 | \kappa_0 \kappa_1] - f_{\lambda_0} f_{\lambda_1} [\lambda_0 \lambda_1 | \kappa_0 \lambda_1]\} , \tag{76-5}$$

$$<\Psi^0{}_{\kappa_0 \lambda_0} | \hat{H} | \Psi^0{}_{\kappa_0 \nu_0}> = 1/\sqrt{(f^2_{\kappa_0} f^2_{\lambda_1} + f^2_{\kappa_1} f^2_{\lambda_0}) (f^2_{\kappa_0} f^2_{\nu_1} + f^2_{\kappa_1} f^2_{\nu_0})} \{$$

$$(f^2_{\kappa_0} f^2_{\lambda_1} f^2_{\nu_1} - f^2_{\kappa_1} f^2_{\lambda_0} f^2_{\nu_0}) (F_{\lambda_0 \nu_0} + \{f^2_{\kappa_1} - f^2_{\kappa_0}\} [\lambda_0 \nu_0 | \kappa_0 \kappa_0])$$

$$+ (f^2_{\kappa_0} f^2_{\lambda_1} f^2_{\nu_1} \{1 + f^2_{\kappa_0}\} + f^2_{\kappa_1} f^2_{\lambda_0} f^2_{\nu_0} \{1 + f^2_{\kappa_1}\}) [\lambda_0 \kappa_0 | \nu_0 \kappa_0]$$

$$+ f^2_{\lambda_0} f^2_{\lambda_1} (f^2_{\kappa_0} f^2_{\nu_1} + f^2_{\kappa_1} f^2_{\nu_0}) (g_{\lambda_0 \nu_0 , \lambda_1 \lambda_1} - [\lambda_0 \nu_0 | \lambda_0 \lambda_0])$$

$$+ f^2_{\nu_0} f^2_{\nu_1} (f^2_{\kappa_0} f^2_{\lambda_1} + f^2_{\kappa_1} f^2_{\lambda_0}) (g_{\lambda_0 \nu_0 , \nu_1 \nu_1} - [\lambda_0 \nu_0 | \nu_0 \nu_0])$$

$$- f^2_{\kappa_0} f^2_{\kappa_1} (f^2_{\lambda_0} f^2_{\nu_0} + f^2_{\lambda_1} f^2_{\nu_1}) g_{\lambda_0\nu_0,\kappa_1\kappa_1}$$

$$+ f_{\kappa_0} f_{\kappa_1} (f^2_{\lambda_0} f^2_{\nu_1} + f^2_{\lambda_1} f^2_{\nu_0}) [\lambda_0\kappa_1|\nu_0\kappa_1]$$

$$- f_{\lambda_0} f_{\lambda_1} (f^2_{\kappa_0} f^2_{\nu_1} + f^2_{\kappa_1} f^2_{\nu_0}) [\lambda_0\lambda_1|\nu_0\lambda_1]$$

$$- f_{\nu_0} f_{\nu_1} (f^2_{\kappa_0} f^2_{\lambda_1} + f^2_{\kappa_1} f^2_{\lambda_0}) [\lambda_0\nu_1|\nu_0\nu_1]\}, \qquad (76\text{-}6)$$

$$<\Psi^0{}_{\kappa_0\lambda_0}|\hat{H}|\Psi^0{}_{\kappa_0\lambda_1}> = 1/\sqrt{(f^2_{\kappa_0} f^2_{\lambda_1} + f^2_{\kappa_1} f^2_{\lambda_0})(f^2_{\kappa_0} f^2_{\lambda_0} + f^2_{\kappa_1} f^2_{\lambda_1})} \times$$

$$(f_{\lambda_0} f_{\lambda_1}\{ - (f^2_{\kappa_0} - f^2_{\kappa_1}) (F_{\lambda_0\kappa_0} + \{f^2_{\kappa_1} - f^2_{\kappa_0}\}[\lambda_0\lambda_1|\kappa_0\kappa_0])$$

$$+ (1 + 2f^2_{\kappa_0} f^2_{\kappa_1}) [\lambda_0\kappa_0|\lambda_1\kappa_0] + 2f^2_{\kappa_0} f^2_{\kappa_1} g_{\lambda_0\lambda_1,\kappa_1\kappa_1}$$

$$- (f^2_{\kappa_0} f^2_{\lambda_0} + f^2_{\kappa_1} f^2_{\lambda_1}) [\lambda_0\lambda_1|\lambda_1\lambda_1]$$

$$- (f^2_{\kappa_0} f^2_{\lambda_1} + f^2_{\kappa_1} f^2_{\lambda_0}) [\lambda_0\lambda_1|\lambda_0\lambda_0]\}$$

$$+ f_{\kappa_0} f_{\kappa_1} [\lambda_1\kappa_1|\lambda_0\kappa_1]), \qquad (76\text{-}7)$$

$$<\Psi^0{}_{\kappa_0\lambda_0}|\hat{H}|\Psi^0{}_{\kappa_0\lambda_0}> = F_{\kappa_0\kappa_0} + F_{\lambda_0\lambda_0} - f^2_{\kappa_0} [\kappa_0\kappa_0|\kappa_0\kappa_0]$$

$$- f^2_{\lambda_0} [\lambda_0\lambda_0|\lambda_0\lambda_0] + (f^2_{\kappa_1} - f^2_{\kappa_0})(f^2_{\lambda_1} - f^2_{\lambda_0}) [\lambda_0\lambda_0|\kappa_0\kappa_0]$$

$$+ (1 + f^2_{\kappa_0} + f^2_{\lambda_0} - 2f^2_{\kappa_0} f^2_{\lambda_0}) [\lambda_0\kappa_0|\lambda_0\kappa_0]$$

$$+ \{1/(f^2_{\kappa_0} f^2_{\lambda_1} + f^2_{\kappa_1} f^2_{\lambda_0})\}\{-f^2_{\lambda_0} f^2_{\lambda_1} (f^2_{\kappa_0} - f^2_{\kappa_1})^2 g_{\lambda_1\lambda_1,\kappa_0\kappa_0}$$

$$- f^2_{\kappa_0} f^2_{\kappa_1} (f^2_{\lambda_0} - f^2_{\lambda_1})^2 g_{\lambda_0\lambda_0,\kappa_1\kappa_1} - f^2_{\kappa_0} f^2_{\kappa_1} g_{\kappa_1\kappa_1,\kappa_0\kappa_0}$$

$$- f^2_{\lambda_0} f^2_{\lambda_1} g_{\lambda_1\lambda_1\ \lambda_0\lambda_0} - 2 f_{\kappa_0} f_{\kappa_1} f_{\lambda_0} f_{\lambda_1} \times$$

$$(2 f_{\kappa_0} f_{\kappa_1} f_{\lambda_0} f_{\lambda_1} g_{\lambda_1\lambda_1,\kappa_1\kappa_1} + [\lambda_1\kappa_1|\lambda_1\kappa_1])$$

$$+ f^2_{\kappa_0} f^2_{\lambda_1} (2F_{\lambda_1\lambda_1} - \{f^2_{\lambda_1} - f^2_{\lambda_0}\}[\lambda_1\lambda_1|\lambda_1\lambda_1])$$

$$+ f^2_{\kappa_1} f^2_{\lambda_0} (2F_{\kappa_1\kappa_1} - \{f^2_{\kappa_1} - f^2_{\kappa_0}\}[\kappa_1\kappa_1|\kappa_1\kappa_1]))\}$$

$$- \varepsilon^{\kappa} - \varepsilon^{\lambda} + <\Phi^0|\hat{H}|\Phi^0> , \qquad (76\text{-}8)$$

$$<\Psi^0{}_{\kappa_0\ell}|\hat{H}|\Phi^0> = (f^2_{\kappa_0} - f^2_{\kappa_1})(A_{\ell\kappa_0} + E_{\ell\kappa_0})$$

$$- 2f^2_{\kappa_0} f^2_{\kappa_1} (g_{\ell\kappa_0,\kappa_1\kappa_1} - [\ell\kappa_0|\kappa_0\kappa_0])$$

$$+ 2f_{\kappa_0} f_{\kappa_1} [\ell\kappa_1|\kappa_0\kappa_1] + f^2_{\kappa_1} E_{\ell\kappa_0} , \qquad (76\text{-}9)$$

$$<\Psi^0{}_{\kappa_0\ell}|\hat{H}|\Psi^0{}_{\kappa_0\nu_0}> = - 1/\sqrt{2(f^2_{\kappa_0} f^2_{\nu_1} + f^2_{\kappa_1} f^2_{\nu_0})}\{$$

$$(f^2_{\kappa_1} f^2_{\nu_0} - f^2_{\kappa_0} f^2_{\nu_1})(A_{\ell\nu_0} + E_{\ell\nu_0} + \{f^2_{\kappa_1} - f^2_{\kappa_0}\}[\ell\nu_0|\kappa_0\kappa_0])$$

$$- (f^2_{\kappa_1} f^2_{\nu_0}\{1 + f^2_{\kappa_1}\} + f^2_{\kappa_0} f^2_{\nu_1}\{1 + f^2_{\kappa_0}\})[\ell\kappa_0|\nu_0\kappa_0]$$

$$- f^2_{\nu_0} f^2_{\nu_1} (g_{\ell\nu_0,\nu_1\nu_1} - [\ell\nu_0|\nu_0\nu_0]) + f^2_{\kappa_0} f^2_{\kappa_1} g_{\ell\nu_0,\kappa_1\kappa_1}$$

$$+ f_{\nu_0} f_{\nu_1} [\lambda\nu_1|\nu_0\nu_1] + f_{\kappa_0} f_{\kappa_1} [\ell\kappa_1|\nu_0\kappa_1] - f^2_{\kappa_1} f^2_{\nu_0} E_{\ell\nu_0} \}, \quad (76\text{-}10)$$

$$<\Psi^0{}_{\kappa_0\ell}|\hat{H}|\Psi^0{}_{\kappa_0\kappa_1}> = -1/\sqrt{2}\,\{-(f_{\kappa_0} + f_{\kappa_1})(A_{\ell\kappa_1} + E_{\ell\kappa_1} +$$

$$\{f^2_{\kappa_1} - f^2_{\kappa_0}\}[\ell\kappa_1|\kappa_0\kappa_0]) - (f_{\kappa_0}\{1 + f^2_{\kappa_0}\}$$

$$- f_{\kappa_1}\{1 + f^2_{\kappa_1}\})[\lambda\kappa_0|\kappa_1\kappa_0]$$

$$- f_{\kappa_0} f_{\kappa_1}(f_{\kappa_0} - f_{\kappa_1})[\lambda\kappa_1|\kappa_1\kappa_1] + f_{\kappa_1} E_{\ell\kappa_1}\}, \quad (76\text{-}11)$$

$$<\Psi^0{}_{\kappa_0\ell}|\hat{H}|\Psi^0{}_{\kappa_0 m}> = (f^2_{\kappa_0} - f^2_{\kappa_1})(A_{\ell m} + E_{\ell m}$$

$$+ \{f^2_{\kappa_1} - f^2_{\kappa_0}\}[\ell m|\kappa_0\kappa_0]) + (f^4_{\kappa_0} + f^4_{\kappa_1})[\ell\kappa_0|m\kappa_0]$$

$$- 2f^2_{\kappa_0} f^2_{\kappa_1} g_{\ell m,\kappa_1\kappa_1} + 2f_{\kappa_0} f_{\kappa_1}[\ell\kappa_1|m\kappa_1] + f^2_{\kappa_1} E_{\ell m}, \quad (76\text{-}12)$$

$$<\Psi^0{}_{\kappa_0\ell}|\hat{H}|\Psi^0{}_{\kappa_0\ell}> = A_{\kappa_0\kappa_0} - f^2_{\kappa_0}[\kappa_0\kappa_0|\kappa_0\kappa_0]$$

$$+ (f^2_{\kappa_0} - f^2_{\kappa_1})(A_{\ell\ell} + E_{\ell\ell} + \{f^2_{\kappa_1} - f^2_{\kappa_0}\}[\ell\ell|\kappa_0\kappa_0])$$

$$+ f^2_{\kappa_1}(2F_{\kappa_1\kappa_1} + E_{\ell\ell} - \{f^2_{\kappa_1} - f^2_{\kappa_0}\}[\kappa_1\kappa_1|\kappa_1\kappa_1])$$

$$+ (f^4_{\kappa_0} + f^4_{\kappa_1})[\ell\kappa_0|\ell\kappa_0] - 2f^2_{\kappa_0} f^2_{\kappa_1}(g_{\kappa_0\kappa_0,\kappa_1\kappa_1} + g_{\lambda\lambda,\kappa_1\kappa_1})$$

$$+ 2f_{\kappa_0} f_{\kappa_1}[\ell\kappa_1|\ell\kappa_1] - \varepsilon^{\kappa} + <\Phi^0|\hat{H}|\Phi^0>, \quad (76\text{-}13)$$

$$<\Psi^0{}_{\kappa_0 a}|\hat{H}|\Phi^0> = \sqrt{2}\{f_{\kappa_0}(F_{a\kappa_0} - f^2_{\kappa_1}\{g_{a\kappa_0,\kappa_1\kappa_1}$$

$$- [a\kappa_0|\kappa_0\kappa_0]\}) + f_{\kappa_1}[a\kappa_1|\kappa_0\kappa_1]\} , \tag{76-14}$$

$$<\Psi^0{}_{\kappa_0 a}|\hat{H}|\Psi^0{}_{\kappa_0\nu_0}> = 1/\sqrt{f^2_{\kappa_0} f^2_{\nu_1} + f^2_{\kappa_1} f^2_{\nu_0}}\,\{$$

$$f_{\kappa_0} f_{\nu_1}\{f_{\nu_1}(F_{a\nu_0} + \{f^2_{\kappa_1} - f^2_{\kappa_0}\}[a\nu_0|\kappa_0\kappa_0]$$

$$+ \{1 + f^2_{\kappa_0}\}[a\kappa_0|\nu_0\kappa_0] - f^2_{\kappa_1} g_{a\nu_0,\kappa_1\kappa_1}$$

$$+ f^2_{\nu_0}\{g_{a\nu_0,\nu_1\nu_1} - [a\nu_0|\nu_0\nu_0]\})$$

$$- f_{\nu_0}[a\nu_1|\nu_0\nu_1]\} + f_{\kappa_1} f^2_{\nu_0}[a\kappa_1|\nu_0\kappa_1]\} , \tag{76-15}$$

$$<\Psi^0{}_{\kappa_0 a}|\hat{H}|\Psi^0{}_{\kappa_0\kappa_1}> = F_{a\kappa_1} + (f^2_{\kappa_1} - f^2_{\kappa_0})[a\kappa_1|\kappa_0\kappa_0]$$

$$+ (1 + f^2_{\kappa_0})[a\kappa_0|\kappa_1\kappa_0] - f^2_{\kappa_1}[a\kappa_1|\kappa_1\kappa_1], \tag{76-16}$$

$$<\Psi^0{}_{\kappa_0 a}|\hat{H}|\Psi^0{}_{\kappa_0\ell}> = 1/\sqrt{2}\,\{ f_{\kappa_0}(A_{a\ell} + E_{a\ell}$$

$$+ \{f^2_{\kappa_1} - f^2_{\kappa_0}\}[\ell a|\kappa_0\kappa_0] + \{1 + f^2_{\kappa_0}\}[a\kappa_0|\ell\kappa_0]$$

$$- f^2_{\kappa_1} g_{a\ell,\kappa_1\kappa_1}) + f_{\kappa_1}[\ell\kappa_1|a\kappa_1]\}, \tag{76-17}$$

$$<\Psi^0{}_{\kappa_0 a}|\hat{H}|\Psi^0{}_{\kappa_0 b}> = F_{ab} + \{ f^2_{\kappa_1} - f^2_{\kappa_0}\}[ab|\kappa_0\kappa_0]$$

$$+ \{1 + f^2_{\kappa_0}\}[a\kappa_0|b\kappa_0] - f^2_{\kappa_1} g_{ab,\kappa_1\kappa_1} , \tag{76-18}$$

$$\begin{aligned}
&\langle\Psi^0_{\kappa_0 a}|\hat{H}|\Psi^0_{\kappa_0 a}\rangle = F_{aa} + F_{\kappa_0\kappa_0} + (f^2_{\kappa_1} - f^2_{\kappa_0})[aa|\kappa_0\kappa_0] \\
&+ (1 + f^2_{\kappa_0})[a\kappa_0|a\kappa_0] - f^2_{\kappa_1}(g_{aa,\kappa_1\kappa_1} + g_{\kappa_0\kappa_0,\kappa_1\kappa_1}) \\
&- f^2_{\kappa_0}[\kappa_0\kappa_0|\kappa_0\kappa_0] - \varepsilon^{\kappa} + \langle\Phi^0|\hat{H}|\Phi^0\rangle ,
\end{aligned} \tag{76-19}$$

$$\langle\Psi^0_{k\lambda_0}|\hat{H}|\Phi^0\rangle = -\langle\Psi^0_{\lambda_0 k}|\hat{H}|\Phi^0\rangle , \tag{76-20}$$

$$\begin{aligned}
&\langle\Psi^0_{k\lambda_0}|\hat{H}|\Psi^0_{k\nu_0}\rangle = (f^2_{\lambda_1}f^2_{\nu_1} - f^2_{\lambda_0}f^2_{\nu_0})(A_{\lambda_0\nu_0} + E_{\lambda_0\nu_0}) \\
&- (f^2_{\lambda_1}f^2_{\nu_1} + f^2_{\lambda_0}f^2_{\nu_0})([\lambda_0\nu_0|kk] - [\lambda_0 k|\nu_0 k]) \\
&+ f^2_{\lambda_0}f^2_{\lambda_1}(g_{\lambda_0\nu_0,\lambda_1\lambda_1} - [\lambda_0\nu_0|\lambda_0\lambda_0]) \\
&+ f^2_{\nu_0}f^2_{\nu_1}(g_{\lambda_0\nu_0,\nu_1\nu_1} - [\lambda_0\nu_0|\nu_0\nu_0]) \\
&- f_{\lambda_0}f_{\lambda_1}[\lambda_0\lambda_1|\nu_0\lambda_1] - f_{\nu_0}f_{\nu_1}[\lambda_0\nu_1|\nu_0\nu_1] \\
&- (f^2_{\lambda_0}f^2_{\nu_1} + f^2_{\lambda_1}f^2_{\nu_0})[\lambda_0 k|\nu_0 k] - f^2_{\lambda_1}f^2_{\nu_1}E_{\lambda_0\nu_0} ,
\end{aligned} \tag{76-21}$$

$$\begin{aligned}
&\langle\Psi^0_{k\lambda_0}|\hat{H}|\Psi^0_{k\lambda_1}\rangle = f_{\lambda_0}f_{\lambda_1}\{2[\lambda_0\lambda_1|kk] - [\lambda_1\lambda_0|\lambda_0\lambda_0] \\
&- [\lambda_1\lambda_1|\lambda_1\lambda_0] - E_{\lambda_1\lambda_0}\} - [\lambda_0 k|\lambda_1 k] ,
\end{aligned} \tag{76-22}$$

$$\langle\Psi^0_{k\lambda_0}|\hat{H}|\Psi^0_{k\lambda_0}\rangle = \langle\Psi^0_{\lambda_0 k}|\hat{H}|\Psi^0_{\lambda_0 k}\rangle , \tag{76-23}$$

$$<\Psi^{a}_{ka}|\hat{H}|\Phi^{0}> = A_{ak}\ , \tag{76-24}$$

$$<\Psi^{0}_{ka}|\hat{H}|\Psi^{0}_{k\nu_0}> = f^{2}_{\nu_1}(A_{a\nu_0} - [a\nu_0|k\,k] + [ak|\nu_0 k]$$

$$+ f^{2}_{\nu_0}\{g_{a\nu_0,\nu_1\nu_1} - [a\nu_0|\nu_0\nu_0]\})$$

$$- f^{2}_{\nu_0}[ak|\nu_0 k] - f_{\nu_0}f_{\nu_1}[a\nu_1|\nu_0\nu_1]\ , \tag{76-25}$$

$$<\Psi^{0}_{ka}|\hat{H}|\Psi^{0}_{kb}> = A_{ab} - [ab|kk]+[ak|bk]\ , \tag{76-26}$$

$$<\Psi^{0}_{ka}|\hat{H}|\Psi^{0}_{ka}> = A_{aa} - A_{kk}$$

$$- [aa|kk]+[ak|ak]+ < \Phi^{0}|\hat{H}|\Phi^{0}> . \tag{76-27}$$

Equations 76-1,27 complete our calculation of the "super CI" matrix elements for the SPIP function Φ^{0}, but some extensions are possible. A closed shell is obtained from a geminal by setting one expansion coefficient to unity and the other to zero, so the results also cover the "super CI" matrix for a SPIP function made of both geminals and closed shells. Beyond this, an examination of equations 76-1,27 reveals that there is no formal restriction that we consider only systems with an even number of electrons. Assuming that we have an $M = 2\mathit{M}$ electron system, suppose that orbital $2\mathit{M}$ is a singly occupied orbtial, and that it is allowed to become infinitely diffuse. Such an orbital makes no contribution to any of the matrix elements in the "little CI" or the "super CI" problems, so we are in fact treating a $2M-1$ electron system. The system's matrix elements are merely given by equations 76-1,27, where we substitute zero values for all the integrals over the diffuse orbital; the result is the same as formally using equations 76-1,27 for all the MO's except orbital $2M$. Thus we have actually calculated the "little CI" and "super CI" matrices for the general SPIP function Φ^{Γ} in equation 7-1.

PART III. ALGORITHM AND IMPLEMENTATION

INTRODUCTION

In Parts I and II of this work, we developed a general mathematical theory for determining optimized wavefunctions of the separated-pair independent particle (SPIP) type. We shall now outline a concrete algorithm which implements this approach. First, we'll discuss the overall flow of the calculation, then we'll examine in some detail several specific problems that deserve special attention in the course of this procedure.

OVERALL PROCEDURE

Flow Diagram

The complete optimization of a SPIP wavefunction according to the preceding mathematical analysis of this work includes a sequence of calculations best described by a flow diagram. This diagram is shown in Figure 1, where we also indicate equation numbers that refer to the pertinent results from the earlier discussion.

In the subsequent sections we shall comment in more detail on three particular points of the general procedure: namely, the choice of the initial orbitals, the bases for the "super CI" configuration spaces, and some special problems connected with the execution of the molecular electron repulsion integrals transformation.

Initial Orbitals

In any geminal of a SPIP function like equations 7-1,6, we normally have two orbitals; one will have an occupation number only slightly less than two, and the other will have an occupation number only slightly greater than zero. We call these orbitals the major and minor MO's respectively, and we must find a first approximation to them (Box "1" in Figure 1).

The major MO will be closely related to an orbital in the space of orbitals occupied in the Hartree-Fock wavefunc-

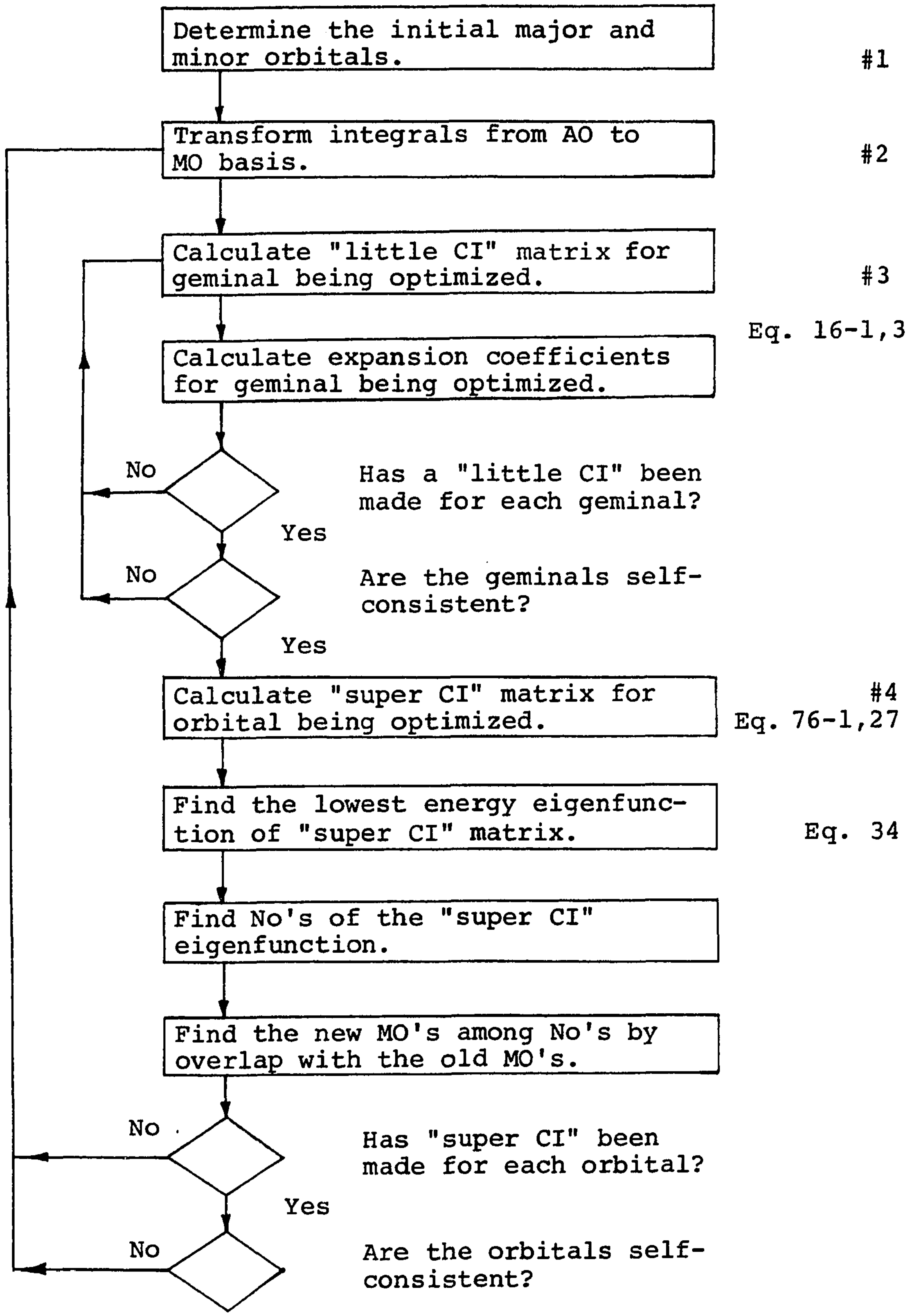


Figure 1. Flow diagram of the SPIP algorithm.

tion, but it is probably much more localized than the canonical MO's usually produced by a Hartree-Fock calculation (Allen and Shull, 1962; McWeeny and Sutcliffe, 1963). Thus, particularly in trying to correlate an orbital among many closed shell orbitals of similar energy, it is reasonable to localize the Hartree-Fock MO's by one of the various methods available (Boys, 1960; Edminston and Ruedenberg, 1963), and then take one of these localized MO's as defining an initial guess to true major SPIP orbital.

To most effectively correlate the electrons in the shell being considered, the minor MO must be localized in the same physical region and have a node through the region of the bond presumably defined by the major MO. Perhaps the easiest way to do this is to use the Boys localization criteria to localize a function in the Hartree-Fock virtual MO space into the region covered by the major orbital, although maximizing the exchange integral between a function in the Hartree-Fock virtual space and the major MO may be an effective and simple alternative. A rather different approach is to project a model of the correlation orbital onto the Hartree-Fock virtual space.

Our experience has indicated that symmetry, if it is present, can be used to find the lowest energy Hartree-Fock virtual orbital which properly fixes the node required for the correlation effect. One calculation of the SPIP procedure's "super CI" problem for the minor orbital is enough to produce an adequate initial guess to this MO.

"Super CI" Configuration Spaces

According to equations 32-1,2 each iteration of the algorithm diagramed in Figure 1 consists of solving a sequence of "super CI" problems ("box 4" in Figure 1) corresponding to each occupied MO ϕ_μ. The "super CI" configuration space corresponding to the MO ϕ_μ consists of the function Φ^Γ and its excitations $\Psi^\Gamma{}_{\mu s}$, where the index (s) is limited by the following constraints:

(a) ϕ_s cannot be doubly occupied in Φ^Γ.

(b) ϕ_μ and ϕ_s cannot both be singly occupied in Φ^Γ.

(c) According to equations 32-1,2 we must have $s>\mu$.

Assuming that Φ^Γ contains Γ closed shells, n orbitals in two-term geminals (TTG's), and M-Γ-n singly occupied orbitals (M is the total number of occupied orbitals), and assuming that in Φ^Γ the closed shells come first, the geminals second, and the singles last, then the "super CI" spaces corresponding to the various orbitals are spanned by the "super CI" configurations shown below:

$\phi_1 \sim \Phi^\Gamma,\ \Psi^\Gamma{}_{1s};\quad s = \Gamma+1,\cdots,\Gamma+n,\Gamma+n+1,\cdots,M,$ virtual,

$\phi_2 \sim \Phi^\Gamma,\ \Psi^\Gamma{}_{2s};\quad s = \Gamma+1,\cdots,\Gamma+n,\Gamma+n+1,\cdots,M,$ virtual,

---

$\phi_\Gamma \sim \Phi^\Gamma, \Psi^\Gamma_{\Gamma,s}$; $s = \Gamma+1,\cdots,\Gamma+n,\Gamma+n+1,\cdots,M$, virtual,

$\phi_{\Gamma+1} \sim \Phi^\Gamma, \Psi^\Gamma_{\Gamma+1,s}$; $s = \Gamma+2,\cdots,\Gamma+n,\Gamma+n+1,\cdots,M$, virtual,

$\phi_{\Gamma+2} \sim \Phi^\Gamma, \Psi^\Gamma_{\Gamma+2,s}$; $s = \Gamma+3,\cdots,\Gamma+n,\Gamma+n+1,\cdots,M$, virtual,

---

$\phi_{\Gamma+n} \sim \Phi^\Gamma, \Psi^\Gamma_{\Gamma+n,s}$; $s = \Gamma+n+1,\cdots,M$, virtual,

$\phi_{\Gamma+n+1} \sim \Phi^\Gamma, \Psi^\Gamma_{\Gamma+n+1,s}$; $s =$ virtual,

---

$\phi_M \sim \Phi^\Gamma, \Psi^\Gamma_{M,s}$; $s =$ virtual.

Note that the spaces involved in each of these "super CI" calculations becomes smaller as one progresses through the algorithm diagramed in Figure 1. As we'll see, this fact has important consequences with respect to the amount of computer time required to make one iteration of the SPIP method.

Integrals Transformation

It is an unfortunate but well known fact that the complete transformation of all two-electron repulsion integrals is a very time consuming process. It therefore can create a real bottleneck in any procedure which, like the present one, is based on a sequence of iterations, each of which requires a recalculation of these integrals because the orbitals change from iteration to iteration (note the position of "box 2" in the flow diagram of Figure 1). Fortunately, the calculation of the matrix elements, indicated in "box 3" and "box 4" of the flow diagram, requires the electron repulsion integrals only in certain combinations, and this circumstance can be used to greatly simplify the integral transformation. The result is a considerable saving of computer time.

To see this we have to go back to the explicit matrix element formulas in equations 76-1,27 of Part II. An examination of these formulas reveals that the electron repulsion integrals appear in just two ways. One way is in the sums defining the matrix G in equation 73-3. G is the two electron part of a matrix representation of a Fock operator (Fock, 1930) and can be calculated by standard procedures using bond-order matrices. The other way is through the specific isolated coulomb and exchange integrals $[rs|\mu\mu]$ and $[r\mu|s\mu]$ where the MO ϕ_μ must satisfy two conditions: its occupation number is non-zero in the SPIP function Φ^{Γ} and less than two in at least one of the "super CI" basis functions Φ^{Γ} and $\Psi^{\Gamma}_{\mu s}$ for fixed (μ).

Let's call the integrals $[rs|\mu\mu]$ and $[r\mu|s\mu]$ where (r) and (s) run over all the MO's, the "integral block" for ϕ_{μ}. How many such blocks have to be calculated for one iteration of our procedure? It is to be noted that, for the "super CI" problem of each orbital occurring during the iteration, certain of these blocks, but not all of them, have to be calculated. This is illustrated in Table 3, where it is assumed that we have Γ closed shells and n orbitals in two-term geminals (TTG's). Each row lists the ϕ_{μ} "integral blocks" needed for the "super CI" problem of the orbital indicated in the first column. A cross or a circle in the μ(th) column of the κ(th) row indicates that "integral block" $[rs|\mu\mu]$ and $[r\mu|s\mu]$ is needed to solve the "super CI" problem for orbital ϕ_{κ}.

Let's consider first the "super CI" problem corresponding to a closed shell orbital ϕ_i, $(i=1,\cdots,\Gamma)$. Since ϕ_i cannot be excited into another closed shell orbital, then all the closed shell oribtals ϕ_j with $j\neq i$ have an occupation number of two in all the "super CI" basis functions and, hence, do not correspond to any isolated "integral blocks". The orbital ϕ_i itself is singly occupied in the excitations Ψ^{Γ}_{is}, and the orbitals in the TTG's have occupation numbers less than two in the unexcited function Φ^{Γ}; as a result, isolated "integral blocks" exist for these orbitals. The blocks are (n+1) in number, and they are indicated by crosses in the appropriate columns of row κ of Table 3; all the rows corresponding to closed shells have these features. There are Γ closed shells, so we have to calculate $(n+1)\Gamma$ isolated "integral blocks" in the course of the optimization of these orbitals.

Let's now consider the "super CI" problem corresponding to a specific orbital, ϕ_{κ}, in one of the TTG's referred to in the last n rows of Table 3. If an orbital, ϕ_i, is a closed shell in the unexcited function Φ^{Γ}, then it is also a closed shell in all of the "super CI" basis functions $\Psi^{\Gamma}_{\kappa s}$, and consequently there is no corresponding "integral block". However, an "integral block" is required for all the orbitals in the TTG's if only because they are not closed shells in Φ^{Γ}; this situation is indicated by the crosses and circles in the last n rows of Table 3.

The crosses and circles indicate a difference which results from a specific feature of the choice of the sequential "super CI" configuration spaces just discussed; namely, the "super CI" problem corresponding to orbital ϕ_{κ} contains only "forward excitations"; i.e., functions $\Psi^{\Gamma}_{\kappa s}$ with $s>\kappa$. Thus the orbitals ϕ_{λ} with $\lambda=1,\cdots,(\kappa-1)$ are not involved in these excitations. The form of the SPIP function then guarantees that they will reappear as natural orbitals (NO's) of the "super CI" density matrix. Hence, they are not changed by this "super CI" problem, which implies that in the integrals $[rs|\lambda\lambda]$ and $[r\lambda|s\lambda]$ only the orbitals ϕ_r and ϕ_s can be changed. This situation leads to a simplification of the transformation needed to calculate such integrals for the "super CI" problem associated with the next orbital. Wherever this simplification is possible is marked by a circle rather than a cross.

The simplification just mentioned becomes evident from the explicit expressions for the integrals in an "isolated integral block". Assuming a basis of L atomic orbitals (AO's), $\chi_1,\cdots,\chi_L$, it is well known that the isolated "integral blocks" can be written as

$$[rs|\mu\mu] = \sum_{a,b} t_{ar}t_{bs} \sum_{c\geq d} 2\Delta_{cd}\, p^{\mu}{}_{cd}[ab|cd], \tag{77-1}$$

$$[r\mu|s\mu] = \sum_{a,b} t_{ar}t_{bs} \sum_{c\geq d} \Delta_{cd}\, p_{cd}([ab|cd]+[ad|cb]), \tag{77-2}$$

where t_{ar}, $p^{\mu}{}_{ab}$, $[ab|cd]$, and Δ_{cd} are defined by

$$\phi_r = \sum_{a} \chi_a t_{ar}\,, \tag{78-1}$$

$$p^{\mu}{}_{ab} = t_{a\mu}\, t_{b\mu}\,, \tag{78-2}$$

$$[ab|cd] = \int dv_1 \int dv_2 \chi_a(1)\chi_b(1)\chi_c(2)\chi_d(2)/|r_1 - r_2| , \quad (78\text{-}3)$$

$$\Delta_{cd} = \begin{cases} \tfrac{1}{2} & c = d \\ 1 & c \neq d . \end{cases} \quad (78\text{-}4)$$

Calculation of the sums over $c \geq d$ in equation 77-1 for all necessary a and b combinations requires approximately $\frac{1}{4}L^4$ multiplications. Subsequent calculation of the similarity transformation implied by the remaining sums over a and b requires at most $2L^3$ multiplications for all r and s combinations. Exactly the same can be said concerning equation 77-2. It is apparent that whenever there is a circle in Table 3, the sums of $c \geq d$ can be taken over from the preceding "super CI" problem, and the recalculation of that "integral block" requires only the $4L^3$ multiplications of the sums over a and b. However, wherever we have a cross in Table 3, the evaluation of the integrals $[rs|\mu\mu]$ and $[r\mu|s\mu]$ requires $\frac{1}{2}L^4 + 4L^3 \approx \frac{1}{2}L^4$ multiplications, so to highest order in L, the block defined by circles can be neglected as regards computation time. Counting the number of crosses in Table 3, we find that, to highest order in L, the total number of multiplications needed to calculate all the isolated "integral blocks" for one complete SPIP interation is given by

$$\# = \tfrac{1}{2}L^4\{(n+1)(M-\tfrac{1}{2}n+1)-2\}, \tag{79}$$

where L is the number of AO basis functions, n is the number of orbitals in TTG's, and M is the total number of occupied orbitals in the SPIP function Φ^{Γ}.

By contrast, the complete 4-index transformation used to calculate all the molecular electron repulsion integrals requires $8L^5/3$ multiplications (Diercksen, 1974).

To compare this load to that required by our method, we form the ratio R between the expression in equation 79 and $8L^5/3$. It can be written as

$$R = f(n,n/M)M/L\ , \tag{80-1}$$

where

$$f(n,t) = (3/16)\{(1-\tfrac{1}{2}t)n+(1+\tfrac{1}{2}t)-t/n\}. \tag{80-2}$$

The fraction (M/L) is the ratio of the number of occupied orbitals to the number of basis orbitals; a fairly typical value for this ratio is about ½. On the other hand, (n/M) is the ratio of the number of orbitals in two term geminals to the total number of occupied orbitals; it can vary between $(n/M) \approx 0$, for a large molecule with a small number of orbitals in two term geminals, to $(n/M) = 1$, for a molecule with no closed shell orbitals at all. Figure 2 shows the factor f(n,t) in equation 80-1 plotted against n for several values of the parameter (n/M). The curves corresponding to the two extreme cases mentioned are

$$f(n,0) = 3(n+1)/16 \quad \text{for } n/M = 0\,, \tag{81-1}$$

$$f(n,1) = 3(n+3-2/n)/32 \quad \text{for } n/M = 1, \tag{81-2}$$

and they define the two solid curves in Figure 2.

To use Figure 2 to assess the economy of the SPIP procedure compared to the general method, do three things: find the value of n, the number of open shells, and its ratio (n/M) to the number of occupied orbitals; locate the curve corresponding to the given value of n/M and find the point directly above the value of n on the horizontal axis; this is the point (f,n), and the value of f can be read from the vertical axis of Figure 2. Suppose $M/L = 0.41$, $n = 4$, $M = 18$, and $L = 44$; for such a case we have $n/M = 0.22$, and $f = 0.86$. This implies that the SPIP integrals calculation requires $f\,M/L = 0.35$ of the time needed for the full 4-index transformation.

Table 3. Enumeration of the integrals needed to fully optimize a general SPIP function Φ^{Γ}

Orbitals to be optimized	Occupied orbitals in Φ^{Γ}															
	1	2	3	•	•	•	$\Gamma-1$	Γ	$\Gamma+1$	$\Gamma+2$	$\Gamma+3$	•	•	•	M−1	M
1	X								X	X	X	X	X	X	X	X
2		X							X	X	X	X	X	X	X	X
3			X						X	X	X	X	X	X	X	X
•				X					X	X	X	X	X	X	X	X
•					X				X	X	X	X	X	X	X	X
•						X			X	X	X	X	X	X	X	X
$\Gamma-1$							X		X	X	X	X	X	X	X	X
Γ								X	X	X	X	X	X	X	X	X
$\Gamma+1$									X	X	X	X	X	X	X	X
$\Gamma+2$									X	X	X	X	X	X	X	X
$\Gamma+3$									0	X	X	X	X	X	X	X
•									0	0	X	X	X	X	X	X
•									0	0	0	X	X	X	X	X
•									0	0	0	0	X	X	X	X
M−1									0	0	0	0	0	X	X	X
M									0	0	0	0	0	0	X	X

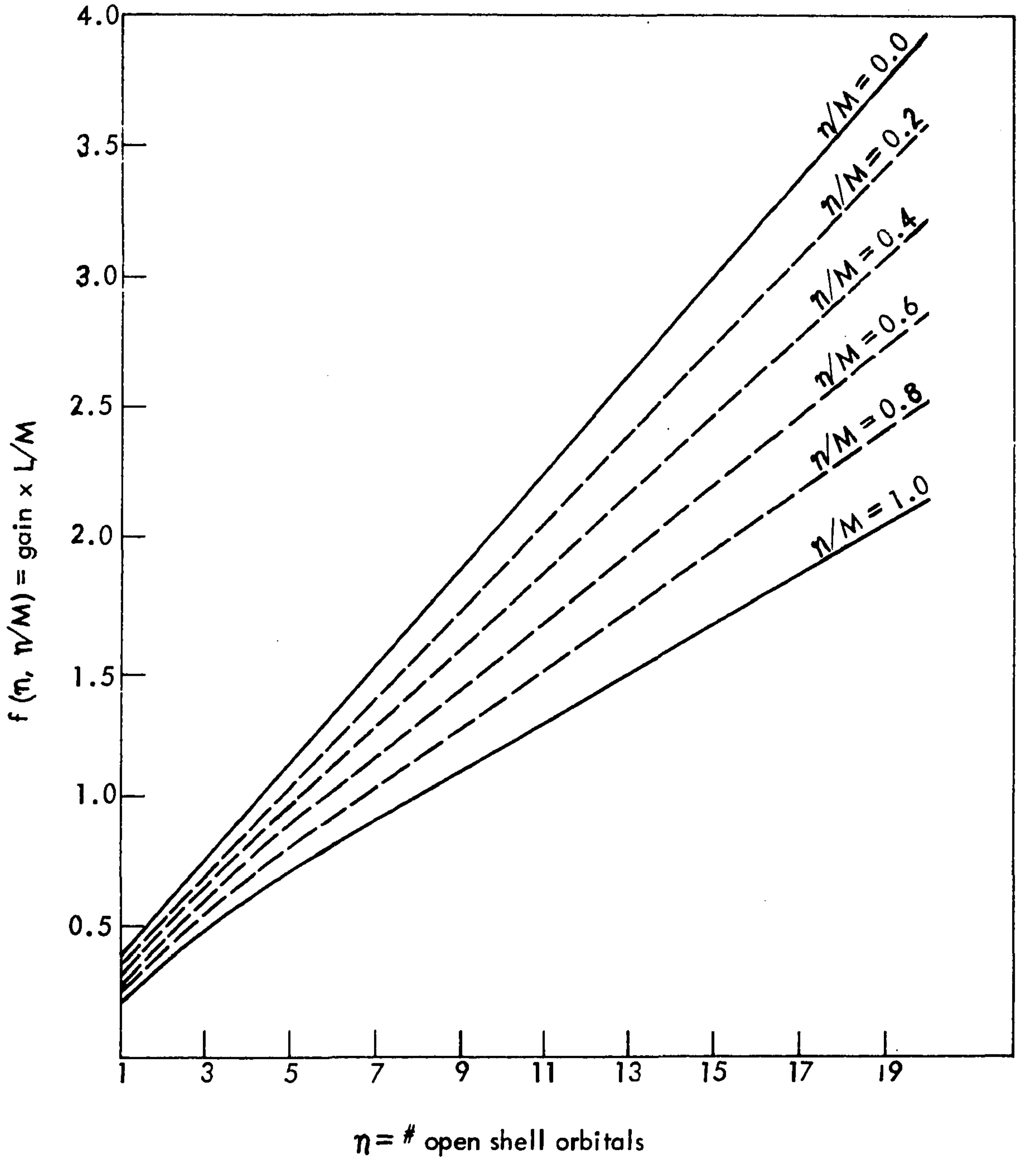


Figure 2. Relation of the gain of the SPIP method as a function of the number of open shell orbitals for several values of the ratio of the number of open to closed shell orbitals.

IMPLEMENTATION

This algorithm was implemented in a set of FORTRAN computer programs for use on the IBM 360/65. The programs were designed to use the BIGGMOLI integrals system developed by R. C. Raffenetti (1973a,b), and the integral files these later programs create match very well with the transformations in equations 77-1,2. Since the BIGGMOLI integral files contain no zero values, we expect the performance of our algorithm to be somewhat enhanced over the predictions of Figure 2.

We have checked this program on a number of polyatomic molecules, and it worked very satisfactorily. Some of these results are reported in Parts IV and V of this dissertation.

PART IV: REACTION ENERGY FOR THE DISSOCIATION OF DIMERS TO FREE RADICAL AND MOLECULAR PRODUCTS

INTRODUCTION

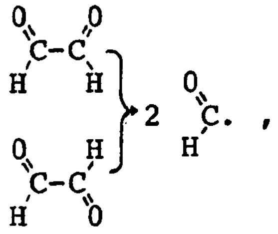
Reaction Energies and Two Types of Dissociation

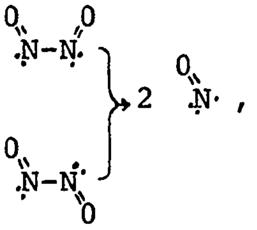
To calculate the energy change accompanying the dissociation of a dimer we need to know the energy of the dimer and its separated monomers; the dimerization energy, Δ, being the difference between the energies of these systems,

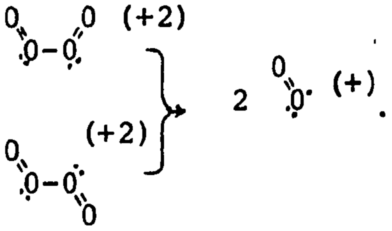
$$\Delta = E(\text{dimer}) - E(\text{monomers}). \tag{82}$$

To accurately calculate this difference we must properly match our models of the various components of the total system; that is, our theory must explicitly allow for the fact that certain physical effects, such as electron correlation, may be different at the two ends of the reaction, and we must construct our models so that any errors inherent in them cancel when we take the difference shown in equation 82.

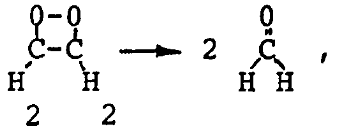
For the correlation effect, this matching can be illustrated with two types of reactions. First, we examine six cases in which a dimer dissociates to free radicals by the cleavage of a single bond; we call the reactants the radical-dimers and the products the radical monomers.

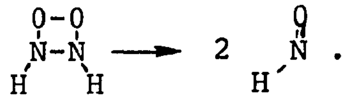
glyoxal,  (83-1)

NO dimer,  (83-2)

O_2^+ dimer,  (83-3)

These reactions will show a correlation contribution to the reaction energy, and the fact that the reactions dissociate the cis and trans forms of a molecule will give us some insight as to how molecular geometry affects electron correlation. The second type of reaction is the dissociation of a cyclic dimer to molecules by the rearrangement of two bonds,

1,2-dioxetane  (84-1) t-HNO dimer



(84-2)

These reactions illustrate how correlation effects balance when we calculate Δ by taking the difference in equation 81. The later reactions have implications with regard to the chemiluminescence of 1,2-dioxetanes in general (Turro and Lechtken, 1973) and tetramethyl-1,2-dioxetane in particular (Turro and Lechtken, 1972), and a detailed study of one mechanism for the reaction in equation 83-1 will be discussed in Part V of this work.

Correlation Defect

The reactions in equations 83-1,3 are characterized by the cleavage of a single bond, so our first perspective in the study of these systems is to focus our attention on the two electrons in the bond broken by the reaction. Let's assume that the effects of bond breakage are of secondary importance for those parts of the system away from the central bond of the dimer or the unpaired electrons in the separated radicals. Collecting these undisturbed spin orbitals into a generalized core function, F, we can write the MO wavefunction for the radical-dimers and their separated monomers as

$$\Phi_R = A\{F\sigma^2\Theta_-\} , \qquad (85\text{-}1)$$

$$\Phi_P = A\{F\,2^{-\frac{1}{2}}(ab+ba)\Theta_-\} , \qquad (85\text{-}2)$$

where σ is a molecular orbital (MO) localized in the region of the central bond of the radical-dimer; Θ_- is the singlet spin function,

$$\Theta_- = \{\alpha\beta-\beta\alpha\}/\sqrt{2} , \qquad (86)$$

and A is an antisymmetrizer. a and b are optimized MO's on the separated systems (SMO's), each being on one of the separated free radical monomers and each containing an unpaired electron. For glyoxal the generalized core function F is a product of closed shell MO products representing the inner shells, oxygen lone pairs, carbon-oxygen sigma and pi bonds, and the carbon-hydrogen sigma bonds. For the other systems in equations 83-1,2 an analogous interpretation of F holds. As usual, we use the left to right order of the factors in a product to determine their arguments.

The SMO's a and b are well-defined functions for the separated radical monomers, and they can be used to define the MO's

$$\sigma = \{a+b\}/\sqrt{2}, \qquad (87\text{-}1)$$

$$\sigma^{*} = \{a-b\}/\sqrt{2}\ . \tag{87-2}$$

Using σ and σ^{*}, we can write equation 85-2 in the alternative form

$$\Phi_{p} = A\{F\ 2^{-\frac{1}{2}}\ (\sigma^{2} - \sigma^{*2})\Theta_{-}\}\ . \tag{88}$$

On the other hand, the MO description of the radical dimer is improved by using separated-pair independent particle (SPIP) wavefunction

$$\Phi = A\{F\Lambda(\sigma,\sigma^{*})\Theta_{-}\}, \tag{89-1}$$

$$\Lambda\ (\sigma,\sigma^{*}) = f_{\sigma}\sigma^{2} + f_{\sigma^{*}}\sigma^{*2}, \tag{89-2}$$

$$f_{\sigma}^{2} + f_{\sigma^{*}}^{2} = 1, \tag{89-3}$$

instead of equation 85-1. The coefficients f_{σ} and $f_{\sigma}*$ define the orbital occupation numbers

$$n_{\kappa} = 2\,f_{\kappa}^{2}\ , \tag{89-4}$$

which corresponds to the number of electrons the SPIP function assigns to orbital ϕ_{κ}.

Equations 89-1,3 define a wavefunction that, when fully optimized, describes the dissociations in equations 83-1,3 for the full course of the reaction: it reduces to the separated radical monomer wavefunction, equation 85-2, at infinite separation, provides a modified MO description of the bond near the molecular equilibrium, and recovers the right-left correlation energy lost by the MO theory. It is apparent from the equal weights given the two configurations in equation 88, that correlation is an important aspect of the separated radical monomer wavefunction; accordingly, its absence from the MO theory of the radical-dimer is called the correlation defect.

Correlation Shift

The dissociation of the cyclic dimers in equations 84-1,2, unlike the dissociations just considered, involve the rearrangement of two bonds rather than the cleavage of one. As a result, we have to examine the reactant and product systems focusing on the four electrons involved in the rearrangement. Accordingly, we write the MO theory wavefunctions for the reactant (the cyclic dimer) and the product molecules as

$$\Phi_R = A\{F\, a_1^2\, a_1^2\ \Theta_{-}\Theta_{-}\}\ , \qquad (90\text{-}1)$$

$$\Phi_P = A\{F\, L^2 R^2\ \Theta_{-}\Theta_{-}\}\ . \qquad (90\text{-}2)$$

For 1,2-dioxetane, see equation 84-1, a_1 and a_2 are MO's representing the oxygen-oxygen and carbon-carbon sigma bonds respectively; the MO's L and R represent the carbon-oxygen *pi* bonds in the left and right separated formaldehyde molecules respectively. The generalized core function F represents all the closed shells in the MO product function that are not much disturbed by the bonding rearrangement. Similar MO wavefunctions can be written for t-HNO dimer and HNO in equation 84-2.

Clearly neither equation 90-1 nor equation 90-2 contains any correlation correction; so if the correlation defect just discussed is of comparable magnitude in both wavefunctions, then taking the difference of their energies results in a cancelation of error called the *correlation balance*. This balance depends on the fact that the oxygen-oxygen and carbon-carbon or nitrogen-nitrogen *sigma* bonds have the same correlation defect as the carbon-oxygen or nitrogen-oxygen *pi* bonds: a conjecture which can be tested by putting right-left correlation into each of these bonds and calculating the energy difference in equation 82 using these improved wavefunctions. The necessary generalization of equations 90-1,2 is afforded by the SPIP functions

$$\Phi''_{R} = \mathrm{A}\{\mathrm{F}\Lambda(\mathrm{a}_1,\mathrm{a}_1^*)\Lambda'(\mathrm{a}_2,\mathrm{a}_2^*)\Theta_-\Theta_-\} , \tag{91-1}$$

$$\Phi''_{\mathrm{P}} = \mathrm{A}\{\mathrm{F}\Lambda''(L,L^*)\Lambda''(R,R^*)\Theta_-\Theta_-\} . \tag{91-2}$$

Here a_1^* and a_2^* are MO's antibonding in the regions of the oxygen-oxygen and carbon-carbon or nitrogen-nitrogen *sigma* bonds respectively, and L^* and R^* are carbon-oxygen or nitrogen-oxygen _pi_ antibonds.

The difference between the reaction energies for the dissociations in equations 84-1,2 as calculated by the wavefunctions in equations 90-1,2 and 91-1,2 is a test of how well the correlation energies balance. This parameter is called the correlation shift because it measures the difference in the correlation defects associated with different molecules.

GEOMETRIES OF THE REACTANTS AND PRODUCTS

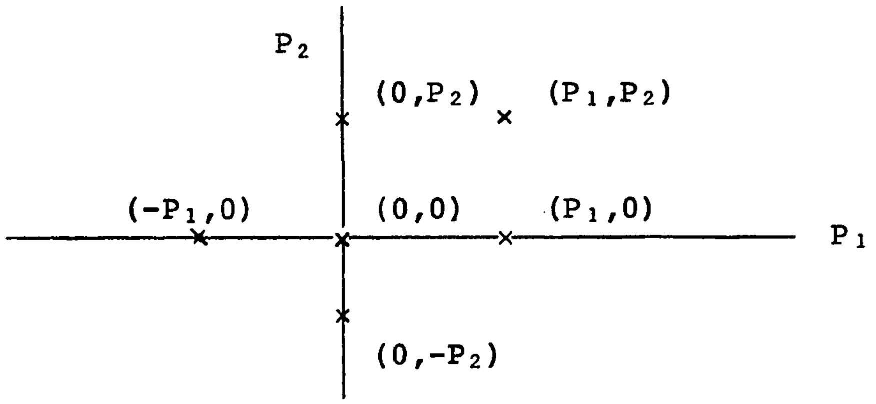
Use of the Hartree-Fock MO Theory

Although the Hartree-Fock approximation cannot generally be used to describe chemical dissociations, it is the most optimal MO theory, and it can nevertheless be used to calculate the equilibrium geometry of molecules. For diatomic molecules, many Hartree-Fock calculations have faithfully reproduced experimental internuclear distances (Cade *et al.*, 1966; Matcha, 1967a,b, 1968a,b; McLean and Yoshimine, 1967). For triatomic systems similar results have been obtained: Ermler and Kern (1971) reproduced the oxygen-hydrogen bond distance in H_2O, but several calculations on CH_2 (Foster and Boys, 1960; Harrison and Allen, 1969; Bender and Schaefer, 1970; O'Neil *et al.*, 1971) indicate that for some systems correlation effects can make important contributions to the angular geometry variables.

For larger polyatomic systems, less experience is available, but work by Pople and his coworkers (Ditchfield *et al.*, 1972) on several small molecules and by Bardo and Ruedenberg (1974a,b) for several molecules containing carbon, hydrogen and oxygen atoms, indicates that the Hartree-Fock approximation can indeed reliably predict the geometries of closed shell molecules. Accordingly, since the molecules being examined here have electronic structures rather closely related to some of the systems treated by Bardo and Ruedenberg, we carried out our geometry optimizations using the Hartree-Fock wavefunction.

Optimization Method

Theoretical geometries of *cis*- and *trans*-glyoxal were determined at the *ab initio* Hartree-Fock level by Sundberg and Cheung (1974). The method used there was a simple quadratic fitting procedure. The geometry parameters were grouped into pairs, and for each pair the total molecular energy was calculated for six points on the energy surface defined by these paramters. Using a good initial guess of the molecule's geometry, we can usually "bracket" the least energy by selecting six points in the pattern shown below:



Here P_1 and P_2 denote the parameters being optimized; the point (0,0) corresponds to the initial geometry and ideally has the lowest energy of any of the points shown. A quadratic equation can be fitted to these points and simple differentiation used to locate the minimum on this approximate surface; the values of the parameters P_1 and P_2 at the quadratic minimum then define our next geometry. Using these optimized parameters, the procedure is executed for each pair of parameters until all the system's structural variables have been optimized. If there is an odd number of parameters, then a similar procedure is used to optimize the last variable by fitting a parabola to three points. The entire procedure can be repeated for several cycles to remove any secondary effects that the alteration of one parameter may have on the others.

In Table 4 we list our molecules, the way we paired their structural parameters for the optimization just described, and the number of cycles made to produce the final geometry.

Atomic Orbital Basis Sets

The wavefunctions were all calculated using even-tempered contracted gaussian atomic orbital (ETCGAO) basis sets (Ruedenberg *et al.*, 1973), but different bases were used to optimize the geometry than were used for the final energy calculations. For the energy calculation, greater care was given to the basis set selection; the atoms need to be described by a set of functions optimized to reflect

Table 4. Parameterization on extent of geometry optimization[a]

Molecule	Parameter pairs and odd parameters	Number of cycles
HCO	$R_{C=O}$, R_{C-H}; $\measuredangle$OCH	2
c-,t-$(HCO)_2$	$R_{C=O}$, R_{C-C}; R_{C-H}, $\measuredangle$CCO; $\measuredangle$CCH	2
NO	$R_{N=O}$	2
c-,t-$(NO)_2$	$R_{N=O}$, R_{N-N}; $\measuredangle$NOO	2
O_2^+	$R_{O=O}$	2
c-,t-$(O_2^+)_2$	$R_{O=O}$, R_{O-O}; $\measuredangle$OOO	2
H_2CO	$R_{C=O}$, R_{C-H}; $\measuredangle$OCH	2
$(H_2CO)_2$	R_{C-O}, R_{O-O}; R_{C-O}, R_{C-H}; $\measuredangle$CCH, $\measuredangle$OCH	3
HNO	$R_{N=O}$, R_{N-H}; $\measuredangle$ONH	2
t-$(HNO)_2$	R_{O-O}, R_{N-N}; R_{N-O}, R_{N-H}; $\measuredangle$NNH; $\measuredangle$ONH, ε	2

[a] $R_{\alpha\cdots\beta}$ is the length of the bond $\alpha\cdots\beta$ in the molecule indicated. $\measuredangle$ ABC is the angle between the atoms A, B, and C.

the bonding environment near them, so we are not generally able to use a universal basis set to describe the dimer and its separated monomers.

We attempted to achieve some of the benefits of an independent optimization of the reactant and product bases by selecting for the various atoms basis sets which had been optimized in simpler molecules with an analogous bonding structure. In Table 5 we list the molecules being studied and the Appendix and Table numbers containing the basis sets used for the geometry optimizations as well as the final energy calculations. Those tables also contain information about the origins of the various bases.

Optimized Geometries

The results of our geometry optimizations are reported in Tables 6 and 7. The meaning of the geometrical parameters listed there is illustrated in Figures 3 and 4. All the theoretical geometries except those for glyoxal were calculated in this work; the glyoxal geometries had been calculated earlier by the methods outlined here.

Several remarks should be made about these calculations. The small [3s/2p] basis for H_2CO shown in Appendix A., Tables 20, 21, and 22 is a truncated version of the [4s/3p] basis used by Bardo and Ruedenberg (1974a,b) to calculate the geometry of this molecule. Their optimization method

Table 5. Appendix and table numbers of the bases used for the geometry optimization and final energy calculation

Molecule	Appendix and table numbers	
	geometry optimization	final energy calculation
HCO	A-26,27,28	A-26,27,28
c-,t-$(HCO)_2$	A-26,27,28	A-26,27,28
NO	A-24,25	B-36,37
c-,t-$(NO)_2$	A-24,25	B-36,37
O_2^+	A-29	B-40
c-,t-$(O_2^+)_2$	A-29	B-40
H_2CO	A-20,21,22	A-20, B-30,31
$(H_2CO)_2$	A-20,21,22	B-32,33,34
HNO	A-23,24,25	B-35,36,37
t-$(HNO)_2$	A-23,24,25	B-38,39,34

(Shah et al., 1964) was more elaborate than our fitting procedure; and though it did use a pairwise partition of the parameter space, the partition was different than the one we advocate in Table 4. The fact that we were able to reproduce their results provides a justification of our parameter partitions, our basic optimization method, and our use of the truncated basis sets shown in Appendix A.

The geometries of the radical (HCO,NO) and molecular (H_2CO,HNO) monomers are in essentially quantitative agreement with the microwave spectra structures (Austin et al., 1974; Halmann and Laulicht, 1965; Takagi and Oka, 1963; Dalby, 1958) also shown in Tables 6 and 7. The agreement is always to at least two significant figures, so our use of the Hartree-Fock approximation in this context is justified.

As seen in Table 6, the agreement of the theoretical and experimental glyoxal structures is encouraging; the major geometric changes associated with the cis-trans isomerization, the angular variables, are significantly reproduced. The trans experimental structure (Kuchitsu et al., 1968, 1969) was an electron diffraction study, but the cis geometry (Currie and Ramsay, 1971; Ramsay and Zauli, 1974) was determined by microwave methods, so these studies are not completely comparable. The fact that the experimental and theoretical results all agree on the direction of the changes in the angular variables confirms that such an effect does occur.

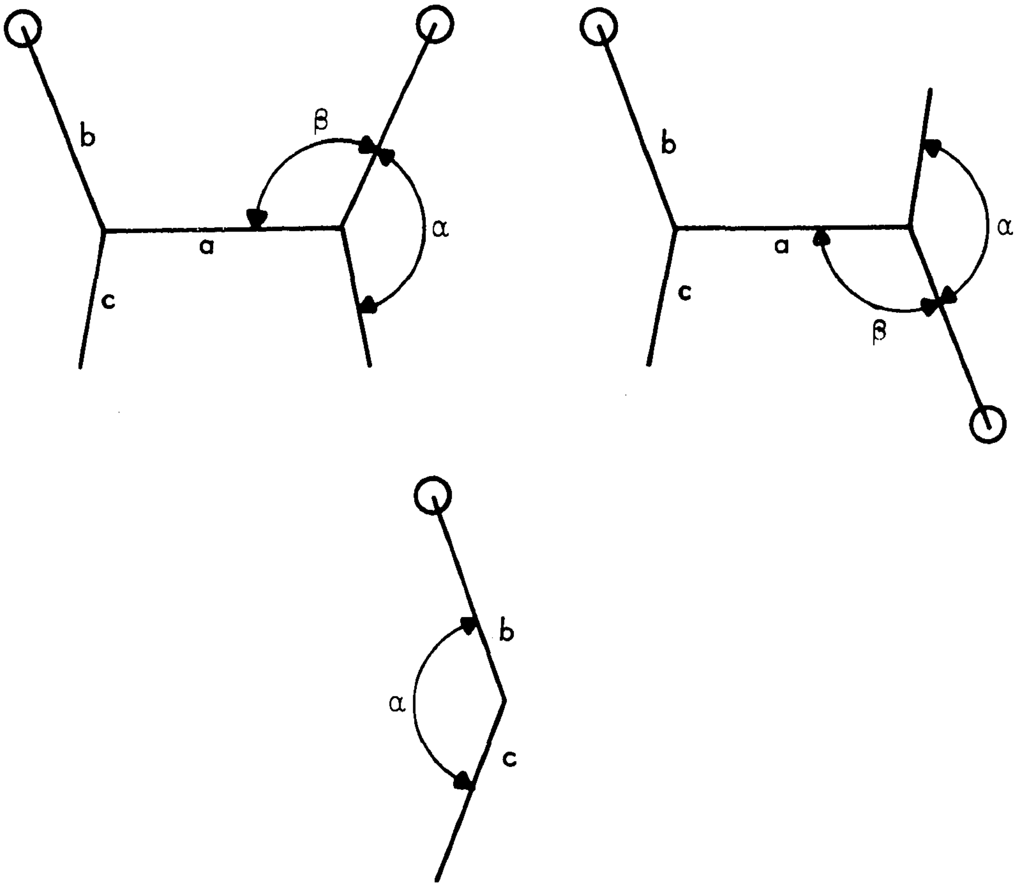


Figure 3. Geometry parameters of the radical-dimers and their radical monomers

Table 6. Theoretical and experimental geometries of the singly bonded dimers and their free radical monomers[a]

	a		b		c		α		β		
molecule	theory	expt.	theory	expt.	theory	expt.	theory	expt.	theory	expt.	ref.
HCO			2.2164	2.2131	2.0665	2.097	127.8	127.4			1
C-$(HCO)_2$	2.8802	2.844	2.2626	2.286	2.0479	2.107	121.8	120.7	122.2	123.8	2
t-$(HCO)_2$	2.8607	2.883	2.2675	2.290	2.0473	2.120	123.4	126.6	120.8	121.2	3
NO			2.1807	2.1746							4
C-$(NO)_2$	3.0501	4.12	2.2275	2.11					111.4		5
t-$(NO)_2$	2.8256		2.2416						109.4		
O_2^+			2.1231								
C-$(O_2^+)_2$	2.9973		2.2101						126.2		
t-$(O_2^+)_2$	2.9348		2.2263						113.1		

---

[a] All bond distances are in a.u. and angles in degrees. The experimental references were by (1), Austin *et al.* (1974); (2), Currie and Ramsay (1971), Ramsay and Zauli (1974); (3), Kuchitsu *et al.* (1968, 1969); (4), Halmann and Laulicht (1965); (5), Lipscomb *et al.* (1961).

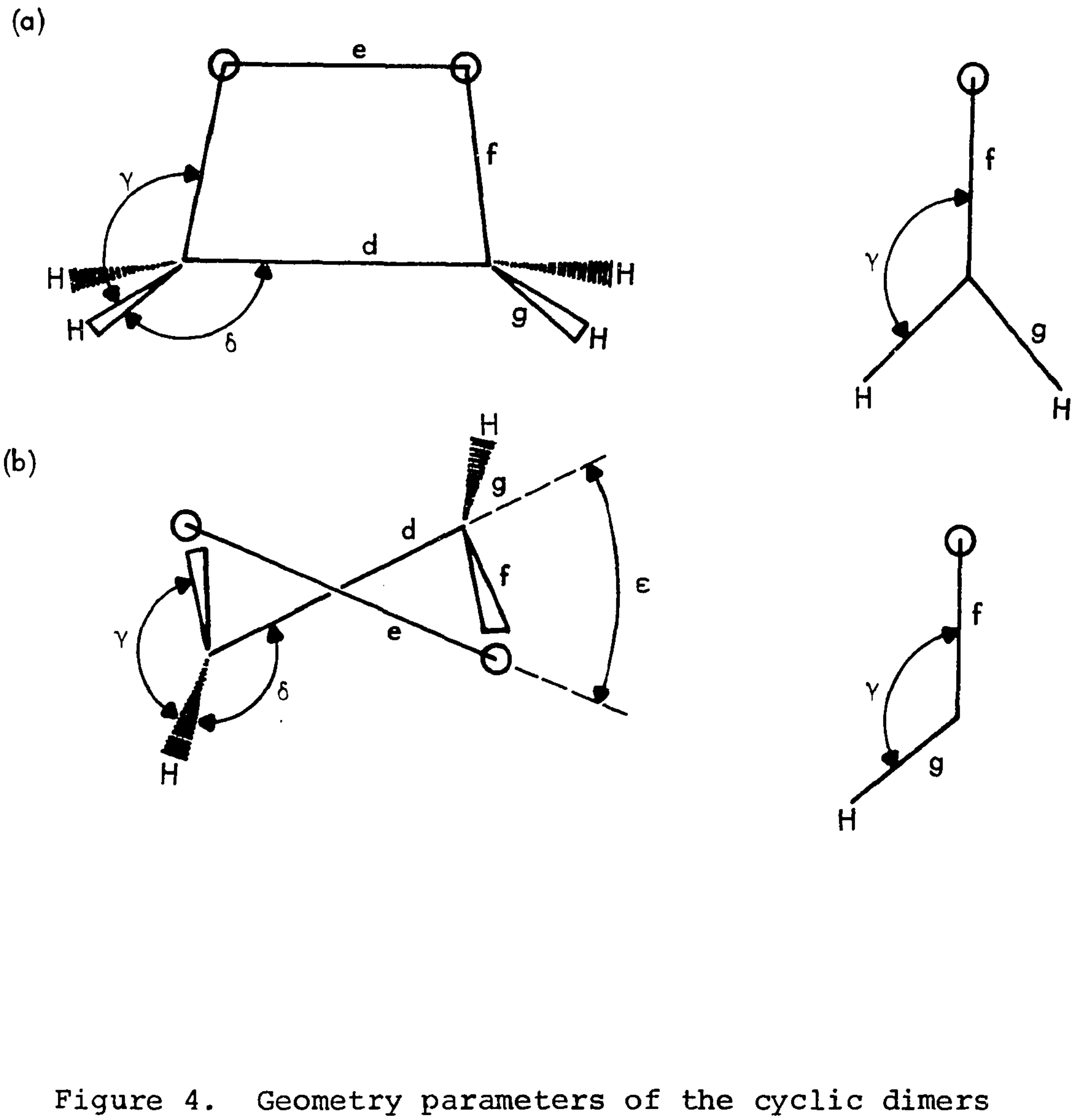


Figure 4. Geometry parameters of the cyclic dimers and molecular monomers (a) 1,2-dioxetane and formaldehyde (b) t-HNO dimer and nitrosyl hydride

Table 7. Theoretical and experimental geometries for the cyclic dimers and their molecular monomers[a]

	d	e	f		g		γ		δ	ε	
molecule	theory	theory	theory	expt.	theory	expt.	theory	expt.	theory	theory	ref.
H_2CO			2.2882	2.2823	2.0278	2.109	122.7	121.7			1
$(H_2CO)_2$	2.8754	2.6934	2.6874		2.0287		112.6		116.6	0.0	
HNO			2.2823	2.2884	1.9372	2.0068	110.5	108.5			2
$t\text{-}(HNO)_2$	2.6788	2.8125	2.7560		1.8890		106.2		109.5	15.34	

[a] All bond distances are in a.u. and angles in degrees. Reference 1 is Takagi and Oka (1963), reference 2 is Dalby (1958).

The experiment bond lengths in cis-$(NO)_2$ were taken from an x-ray study (Lipscomb et al., 1961) which actually indicated that the molecule is slightly trapezoidal. The dimer is at best weakly bound, so it is not surprising to find a large discrepancy in one variable, the nitrogen-nitrogen bond length, between the theoretical isolated molecule and experimental solid state structures. A minimal exponential basis set study (Williams and Murrell, 1971) explored the trapezoidal geometry, but it reported that the trans isomer was the lowest energy form; additionally, it reported structural differences between the cis and trans forms that conform to our results as regards direction but not magnitude. Another study (Skanke and Boggs, 1973) used a contracted gaussian basis to produce an optimized cis geometry similar to the one we report in Table 6.

The last of the cis-trans forms are the O_2^+ dimers. There is no experimental information for these systems, but the dimers are at most only slightly metastable. They represent a completion of the isoelectronic-isostructural series established by glyoxal and NO dimer. Additionally, it may prove useful to acquire information concerning the properties of the triply bonded oxygen ion.

In Table 7 the geometry parameters of the cyclic dimers are close to standard model values (Pople and Gordon, 1967), although all the bonds in both rings are slightly lengthened.

Our 1,2-dioxetane geometry is similar to the Hartree-Fock geometry by Barnett (1974); the most important similarity being the fact that he also predicts a planar ring. t-$(HNO)_2$ has not previously been studied, experimentally or theoretically, but it is a conjectural and perhaps possible molecule.

SPIP CALCULATIONS AND THE REACTION ENERGIES

SPIP Calculation

Having obtained the radical and molecular geometries in Tables 6 and 7, it is a simple matter to execute the Hartree-Fock calculations for all these species using the final basis sets indicated in Table 5 and shown in Appendices A and B. The resulting functions are departure points for the SPIP calculations described below.

The Hartree-Fock (HF) wavefunctions for the separated radical and molecular monomers, equations 85-2 and 90-2, are antisymmetrized products of the HF products for the isolated monomers; the total energy of the separated monomers is twice the energy of one isolated monomer, and thus we really only need the radical monomer function

$$\Phi_M = A\{F'a\alpha\}; \qquad (92\text{-}1)$$

and the molecular monomer function

$$\Phi_{M'} = A\{F'L^2\Theta_-\}. \qquad (92\text{-}2)$$

Here a and L are as previously defined, and F' represents the appropriate core function for the system being considered. Since we never introduce any correlation into the radical monomers, no further calculations using equation 92-1 are needed. For the molecular monomers, however, we need to determine the SPIP function

$$\Phi_M'' = A\{F'\Lambda''(L,L^*)\Theta_-\} \tag{93}$$

to assemble the wavefunction in equation 91-2. To do this requires that we choose initial guesses of the orbitals in equation 93 and execute the SPIP procedure developed in Parts I to III of this work.

The initial orbitals for the core function, F', in equation 93 are taken directly from the HF function in equation 92-2. The initial orbital L in equation 93 is a pi bond, and it is also taken directly from equation 92-2, the antibonding pi orbital, L^*, is the lowest energy HF virtual orbital of the proper symmetry; finally these orbitals are assigned the initial geminal expansion coefficients $f_L = 1.0$ and $f_{L^*} = 0.0$, and the result is taken to define our initial guess of the SPIP function in equation 93. All that remains is to apply the analysis in the preceding to its optimization.

The initial orbitals for the radical-dimer SPIP functions are chosen in the same manner as the orbitals for the molecular monomers. The orbitals for the core function and central sigma bond in equation 89-1,3 are taken from the HF function in equation 85-1; the antibonding orbital, σ^*, is the lowest energy HF virtual orbital of the proper symmetry, and these orbitals are assigned the initial expansion coefficients $f_\sigma = 1.0$ and $f_{\sigma}{*} = 0.0$. The resulting initial SPIP function is to be optimized by the methods of Parts I to III.

Choosing initial orbitals for the cyclic dimer's two geminal SPIP function is a more delicate task. Rather than risk any convergence problems created by simultaneously optimizing two crude initial orbitals, we elected to first calculate the SPIP function

$$\Phi_R{}' = A\{F\Lambda(a_1,a_1^*)a_2^2\,\Theta_-\Theta_-\}. \qquad (94)$$

Its initial orbitals are chosen by exactly the procedure described above: the orbitals in F and the orbitals a_1 and a_2 are taken from the HF function in equation 90-1; the orbital a_1^* is the lowest energy HF virtual orbital of the proper symmetry, and the geminal expansion coefficients are chosen to be $f_{a_1} = 1.0$ and $f_{a_1}{*} = 0.0$. This function is then optimized using the SPIP procedure, and its optimized orbitals are used in an initial guess of the two-geminal function in equation 91-1. As one might suppose, the antibonding orbital a_2^* is the lowest energy SPIP function virtual orbital of the proper symmetry; and the initial geminal expansion coefficients are $f_{a_2} = 1.0$ and $f_{a_2^*} = 0.0$. This is the initial approximation to the two-geminal SPIP function in equation 91-1.

All of these SPIP calculations were executed keeping the inner shells (K shells) of the carbon, nitrogen, and oxygen atoms fixed at their HF values. The other orbitals were optimized until they satisfied the generalized Brillouin theorem (Levy and Berthier, 1968) and they produced an energy stable to eight decimal places. All the occupied orbitals in the Hartree-Fock functions for the radical monomers and the SPIP functions for the radical-dimers are shown in Appendix C, Tables 41 to 49. The occupied orbitals for the Hartree-Fock and SPIP wavefunctions of the molecular monomers and the Hartree-Fock, one-geminal SPIP (equation 94), and two-geminal SPIP functions for the cyclic dimers are shown in Appendix D, Tables 50 to 59.

Correlation Defect in the Radical-Dimers

The Hartree-Fock and SPIP wavefunctions for the six radical-dimers and three radical monomers shown in equations 83-1,3 yield the absolute energies shown in Table 8.

The HF results for these systems are in essential conformity to one's intuitive expectation: the cis form of a dimer will have a higher energy than the trans form. We observe, however, that at the SPIP level, the trans form of NO dimer is the higher energy form. Such a result is surprising, but the NO dimer system has caused confusion before; we remarked that Williams and Murrell (1971) made a calculation establishing the trans isomer as the lower

Table 8. Absolute energies of the radical-dimers and radical-monomers[a]

molecule	monomer	cis-dimer	cis-dimer	trans-dimer	trans-dimer
	(HF)	(HF)	(SPIP)	(HF)	(SPIP)
glyoxal	-113.1083	-226.3171	-226.3322	-226.3246	-226.3396
NO dimer	-129.1778	-258.2809	-258.3205	-258.2870	-258.3197
O_2^+ dimer	-149.0693	-297.7663	-297.8465	-297.7823	-297.8552

[a] Energy in a.u.

energy form; however, a subsequent gaussian basis set calculation (Vladimeroff, 1972) at the Williams and Murrell geometry inverted the cis>trans energy order. It is possible that an examination of the correlation defect and geometry changes concerned with this system can elucidate the origins of this inversion.

In Table 9, we show the reaction energies and correlation defect for six reactions in equations 83-1,3. Along with these energies, we show the occupation numbers associated with the orbitals in the geminal describing the central sigma bond of the radical-dimers. These energy differences show two things clearly: (1) we see that the correlation defect is important, amounting to roughly 15% of the dissociation energy of glyoxal; (2) the defect always stabilizes the cis more than the trans isomer of a given system. Here is the mechanism to invert the HF cis>trans energy order: In all these systems, the correlation defect stabilizes the cis more than the trans isomer, but in NO dimer this favoritism is greater than the difference in the HF energies of the two isomers. To see this, look at Table 10 where we display the trans-cis splitting for the radical-dimers in the HF and SPIP approximations; we also record the differences between the correlation defects (trans-cis), the correlation shift. Observe that the shift in NO dimer and O_2^+ dimer is about the same; so the inversion in NO dimer is created by the near

Table 9. Occupation numbers, reaction energies, and correlation defect for the radical-dimers[a]

molecule	SPIP n_σ	SPIP $n_\sigma{}^*$	Δ E (HF)	Δ E (SPIP)	defect
c-$(HCO)_2$	1.9833	0.0167	-0.1005	-0.1156	-0.0151
t-$(HCO)_2$	1.9838	0.0162	-0.1080	-0.1230	-0.0150
c-$(NO)_2$	1.9168	0.0832	0.0747	0.0352	-0.0395
t-$(NO)_2$	1.9463	0.0537	0.0687	0.0360	-0.0327
c-(O_2^+)	1.7482	0.2518	0.3723	0.2922	-0.0801
t-(O_2^+)	1.8030	0.1970	0.3564	0.2835	-0.0729

[a] Energy in a.u. one a.u. = 627.0 kcal/mole.

Table 10. Trans-cis splitting and the correlation shifts for the radical-dimers[a]

molecule	trans-cis HF	splitting SPIP	correl. shift
glyoxal	-0.0075	-0.0074	0.0001
NO dimer	-0.0061	0.0009	0.0068
O_2^+ dimer	-0.0160	-0.0087	0.0072

[a] Given are the differences trans-cis.

degeneracy of its cis and trans isomers; only the rather large splitting in O_2^+ dimer prevents an inversion there.

Having isolated this effect, we ask about a mechanism to explain its origin. An explanation emerges from an examination of the geometries in Table 6. There we see that, on going from the cis to trans isomer of any molecule the major structural changes concern the length of the central bond and the magnitude of the CCO, NNO, and OOO angles. We see, however, that the change in the NNO angle is rather small; almost all the geometric response this molecule makes to the isomerization is a change in the NN sigma bond length. This structural change produces a shift in the correlation defect; and with the near degeneracy of the cis and trans isomers, it inverts their energy order.

The relative strength of the central sigma bond in the various radical-dimers is plain from the dimerization energies in Table 9, but Figures 5 to 7 provide a graphic illustration of the bonding character. We show contour plots of the two natural orbitals in the geminal of equations 89-1,3 for each of the radical-dimers. We also show one of the singly occupied GVB (Hay, Hunt, and Goddard, 1972a,b,c) orbitals generated by the transformation in equations 9-1,3. The GVB orbitals become the free radical SMO's on infinite separation, so the extent to which they localize on one

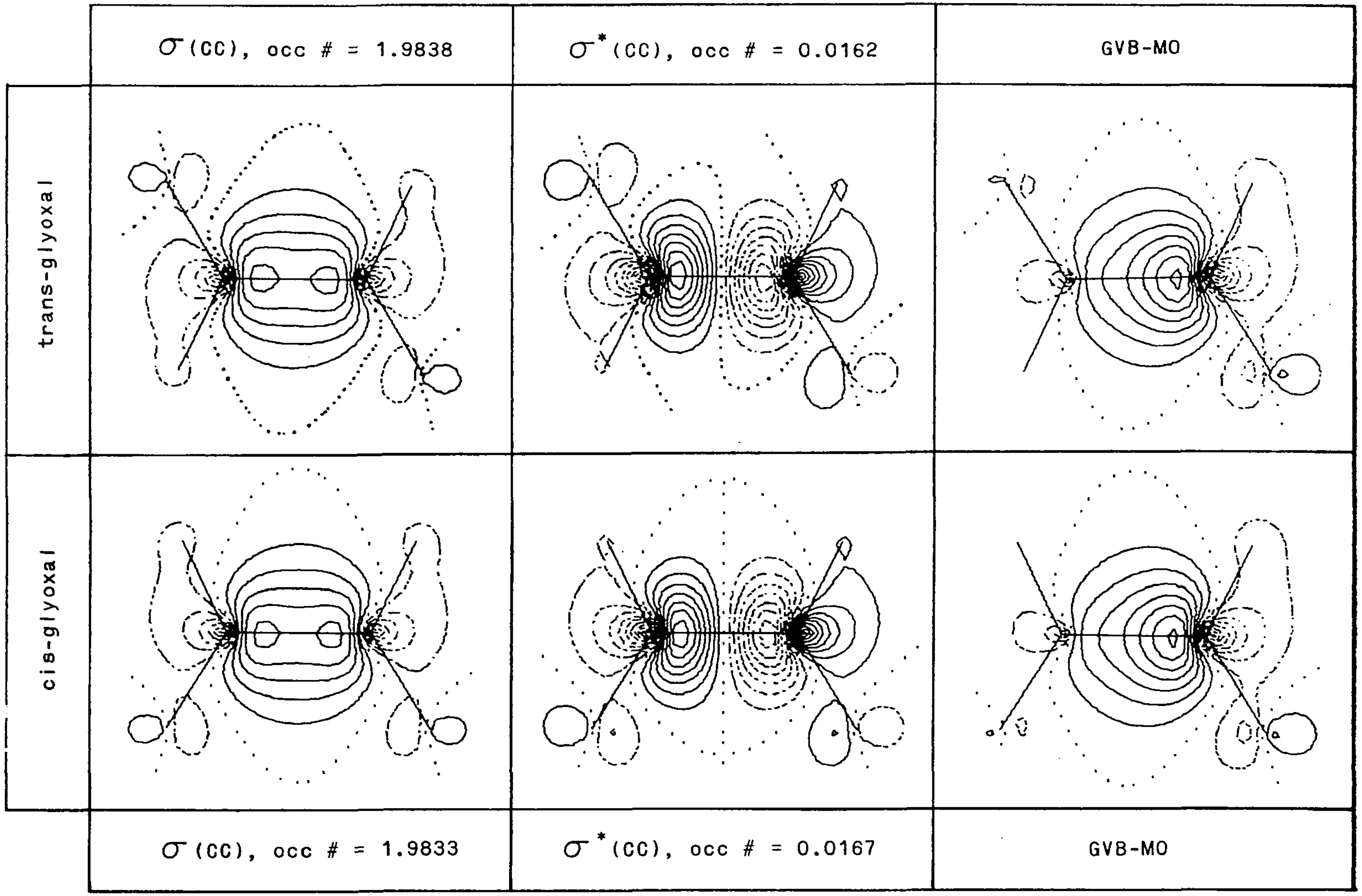


Figure 5. Major and minor natural orbitals and GVB orbitals for glyoxal.

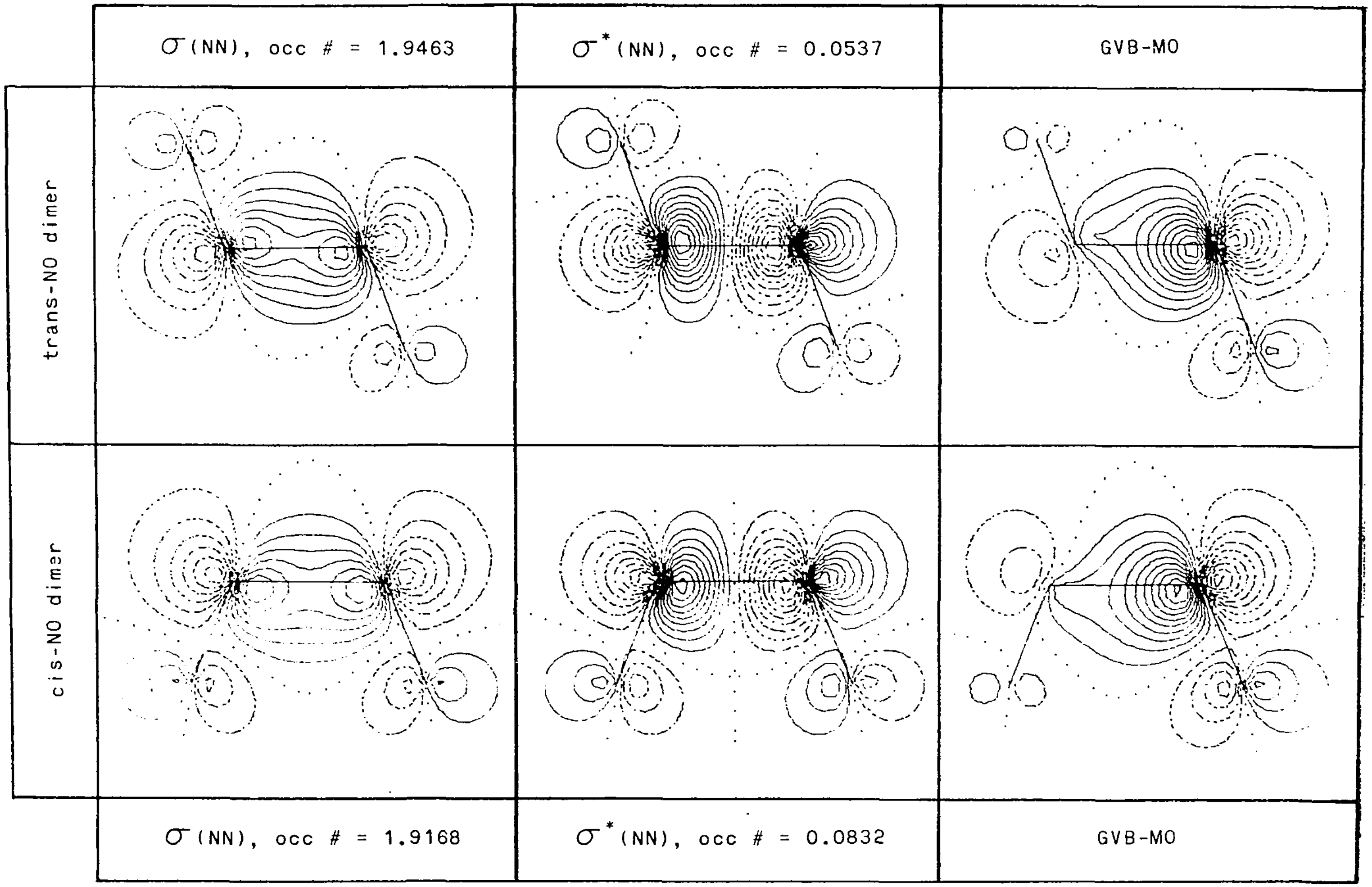


Figure 6. Major and minor natural orbitals and GVB orbitals for NO dimer.

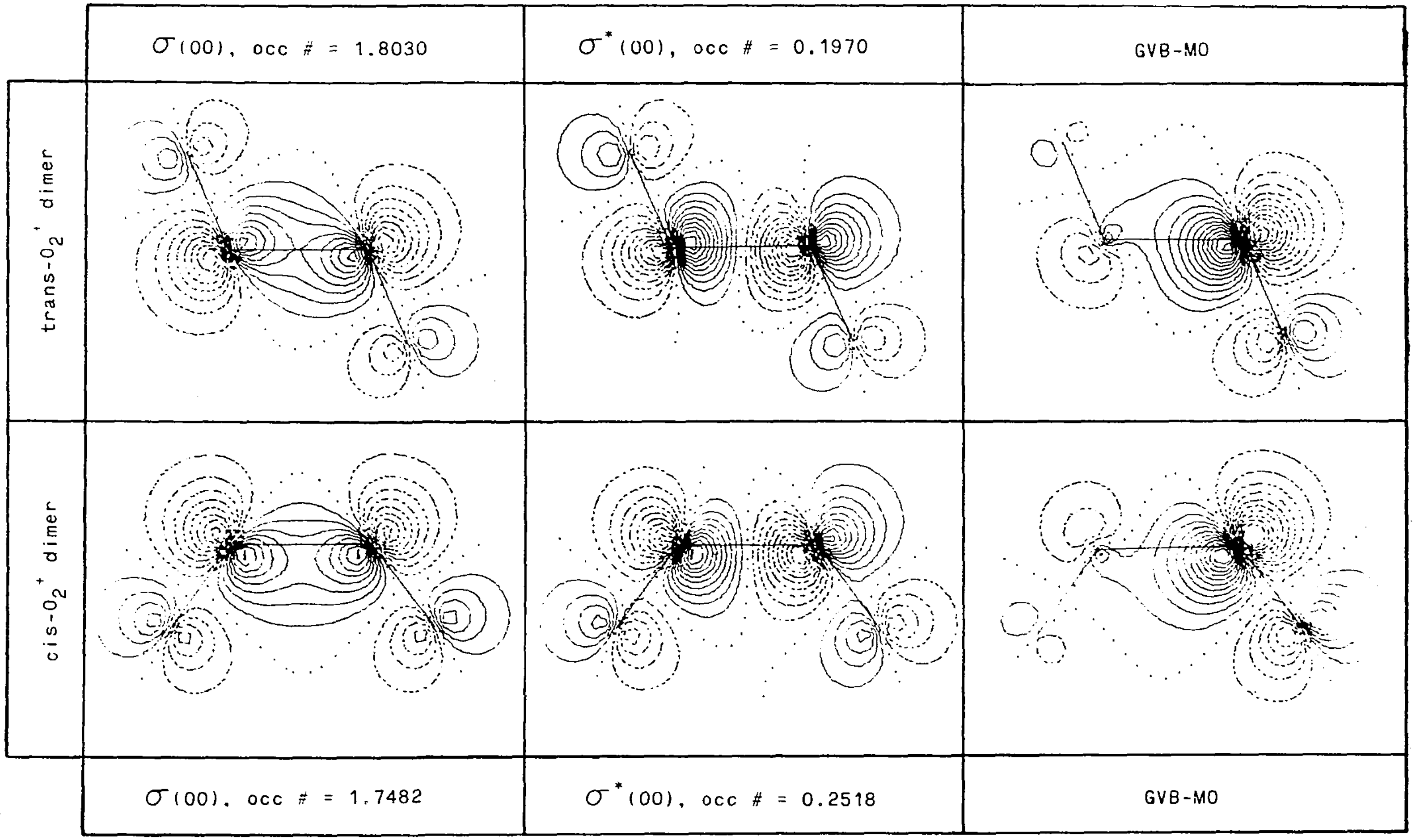


Figure 7. Major and minor natural orbitals and GVB orbitals for O_2^+ dimer.

fragment is a reflection of the weakness of the bond; clearly the bond in NO dimer is very weak, and the bond in O_2^+ dimer hardly exists at all.

Correlation Shift in the Cyclic Dimers

The HF and SPIP functions (equations 91-1 and 93) for the cyclic dimers and molecular monomers shown in equations 84-1,2 yield the absolute energies shown in Table 11.

These values can be combined to yield the reaction energies, and by taking the difference between the reaction energies of the HF and SPIP wavefunctions we obtain the correlation shift. It is a reflection of the fact that the electrons in different bonds of a molecule correlate one another differently. For 1,2-dioxetane it is approximately the difference between the correlation energies of an oxygen-oxygen and a carbon-carbon _sigma_ bond and of two carbon-oxygen _pi_ bonds. A positive or negative value indicates greater or lesser correlation in the molecular monomers than in the ring. These values are shown in Table 12; Table 13 displays the occupation numbers of the SPIP functions. These data confirm one another; the correlation shift is in favor of the molecular monomers, and for both systems the minor orbital occupation numbers for the _pi_* orbitals in the molecular monomers is greater than either minor orbital occupation number in the cyclic dimers.

Table 11. Absolute energies of the cyclic dimers and molecular monomers[a]

reaction system	monomer (HF)	dimer (HF)	monomer (SPIP)	dimer (SPIP)
$(H_2CO)_2$	-113.8171	-227.5429	-113.8578	-227.6049
$(HNO)_2$	-129.7283	-259.3871	-129.7821	-259.4651

[a] Energy in a.u.

Table 12. Reaction energies and the correlation shift for the cyclic dimers[a]

reaction system	Δ (HF)	Δ (SPIP)	shift
$(H_2CO)_2$	0.0913	0.1107	0.0194
$(HNO)_2$	0.0694	0.0992	0.0298

[a] Energy in a.u.

Table 13. Occupation numbers of the orbitals in the geminals of the molecular monomer and cyclic dimer SPIP functions

reaction system	n_L	$n_L{}^*$	n_{a_1}	$n_a{}^*$	n_{a_2}	$n_a{}^*$
$(H_2CO)_2$	1.9001	0.0999	1.9255	0.0745	1.9808	0.0192
$(HNO)_2$	1.8636	0.1364	1.8960	0.1040	1.9720	0.0280

The reaction energy for the thermal dissociation of 1,2-dioxetane has been thermochemically estimated (O'Neal and Richardson, 1970, 1971) to be 53 kcal/mole; a simple combination of standard bond energies (Cottrell, 1958) gives 43 kcal/mole. These estimates are more in line with our HF estimate of 57 kcal/mole than our SPIP value of 70 kcal/mole, but the energy for the dissociation of tetramethyl-1,2-dioxetane to acetone has been measured (Lechtken and Hoehne, 1973) and is 70 kcal/mole for the solid and 61 kcal/mole in a solution, so we are left in a quandry. However, the bond energy estimate for the dissociation of t-$(HNO)_2$, to HNO is 110 kcal/mole; a value far more exothermic than either the HF or SPIP prediction; so it seems, at least for t-$(HNO)_2$, that our SPIP wavefunction does not overestimate the correlation shift in favor of the separated system. Accordingly, we accept the beyond Hartree-Fock separated-pair independent particle reaction energies, but a calculation on tetramethyl-1,2-dioxetane is needed to settle the issue. Beyond question, however, is the fact that the correlation shift can make a nontrivial contribution to the reaction energy.

Zero Point Energy

Although our primary concern up to this point has been associated with the effect of electron correlation on reaction energies, there are other phenomena that can make a non-trivial contribution to these quantities. Among the most important such considerations is any change in the zero point vibrational energy: the ground state energy associated with the oscillatory motions of the heavy nuclei on the adiabatic potential surface (London, 1929) defined by the molecular electronic wavefunction.

Like the correlation effect, the zero point energy associated with the radical-dimers creates a defect, and the zero point energy associated with the cyclic dimers becomes involved in a balance.

For the radical-dimers, the vibrational degree of freedom along the reaction coordinate has a positive zero point energy which goes to zero at infinite separation (Glasstone *et al.*, 1941). This produces a defect in the reaction energy

$$\Delta' = \Delta + \tfrac{1}{2} h \nu_r ,$$

where Δ is the reaction energy calculated with the electronic wavefunctions; h is Plank's constant, and ν_r is the fundamental vibrational frequency for stretching the dimer along the central bond.

Similar arguments show the zero point shift for 1,2-dioxetane to have the form

$$\Delta' = \Delta + \tfrac{1}{2} h \{\nu_{oo} + \nu_{cc} + 2\nu_{co} - 2\nu_{co'}\} ,$$

where ν_{OO}, ν_{CC}, and, ν_{CO} represent the fundamental stretching frequencies for the oxygen-oxygen, carbon-carbon, and carbon-oxygen sigma bonds in 1,2-dioxetane, and ν'_{CO} represents the fundamental stretching frequency for the carbon-oxygen double bond in formaldehyde.

The fundamental frequency varies inversely as the square root of the vibrating masses, so we expect the vibration energy associated with massive oscillators to be smaller than that for lighter ones. For H_2 (Schwartz and Schaad, 1967) the zero point energy is 6.3 kcal/mole, but for Li_2 (Herzberg, 1950) it is 0.5 kcal/mole. The relationship is not perfect because different bonds are associated with different force constants; but broadly speaking, we can expect the zero point energy for bonds between second row atoms to be less than 3.1 kcal/mole. Using the fundamental stretching frequencies from Roberts and Caserio (1964) we find zero point energies for the carbon-carbon and carbon-oxygen sigma bonds and the carbon-oxygen double bond to be about 0.6 kcal/mole, 1.2 kcal/mole, and 2.5 kcal/mole respectively. Using the same zero point energy for the nitrogen-nitrogen and oxygen-oxygen sigma bonds and for the carbon-oxygen and nitrogen-oxygen double bonds, we infer that neglect of the zero point energy leads us to overestimate the reaction energy for the dissociation of the radical-dimers by about 0.6 kcal/mole; for the dissociation of the cyclic dimers, we expect to underestimate the reaction energy by 1.2 kcal/mole. So, neglecting the zero point energy completely will be a second-order error.

PART V: A SPIP AND MCSCF STUDY OF THE THERMOLYSIS OF 1,2-DIOXETANE

INTRODUCTION

The thermolysis of 1,2-dioxetane to formaldehyde is an interesting and controversial reaction, the major source of the excitement being the fact that several 1,2-dioxetanes are known to thermolyize to chemiluminescent products (Turro and Lechtken, 1972, 1973; Lechtken *et al.*, 1973; Turro *et al.*, 1974; Wilson *et al.*, 1973; Steinmetzer *et al.*, 1974; Yang and Carr, 1974; Darling and Foote, 1974). Since the mechanisms of these decompositions are rather speculative, the 1,2-dioxetane system is a valuable topic on which theoreticians and experimentalists can interact.

Both concerted and biradical pathways have been suggested for these reactions, and the mechanisms have been supported with correlation diagrams (Kearns, 1971; McCapra, 1968; Turro and Lechtken, 1973; Barnett, 1974) and semiempirical calculations (Evleth and Feler, 1973; Roberts, 1974). These calculations used minimal beyond Hartree-Fock (HF) methods to calculate activation energies far above the 25 kcal/mole suggested by experiment (Kopecky and Mumford, 1969; O'Neal and Richardson, 1970, 1971; Richardson *et al.*, 1972; Wilson and Schaap, 1971; Turro and Lechtken, 1973). This discrepancy can be assigned to correlation effect neglected by the wavefunctions, or it can be attributed to unrefined geometries along the reaction paths.

Dewar and Kirschner (1974) approached this problem using a MINDO/3-configuration interaction (Bingham _et_ _al_., 1975a,b, c,d; Bingham and Dewar, 1972) study of the molecule's singlet and triplet energy surfaces. They found that these surfaces intersected 38.3 kcal/mole above the molecular ground state, and their calculations would imply dissociation to excited products from a molecular transition state. Eaker and Hinze (unpublished) used a semiempirical multiconfiguration self-consistent field (MCSCF) method (Eaker and Hinze, 1974) to study a similar reaction path. They found an activation energy of 24 kcal/mole, and using the O'Neal and Richardson (1970, 1971) thermochemical dissociation energy of 55 kcal/mole, they predicted no chemiluminescence. In contrast, the calculation of Roberts (1974) predicted dissociation to chemiluminescent products from a biradical intermediate.

In an effort to elucidate the structure of the transition state and evaluate the activation energy, we began an _ab_ _initio_ study of the thermolysis of 1,2-dioxetane. Here we report some of our results for the dissociation of the molecular ground state to the ground state of the separated formaldehydes. The study was made using wavefunctions considerably beyond the HF approximation, and their presentation affords us the opportunity to expound several fundamental ideas that may be useful in the study of other reactions.

ORBITAL AND CONFIGURATIONAL REACTION SPACES

Core and Reaction Orbital Spaces

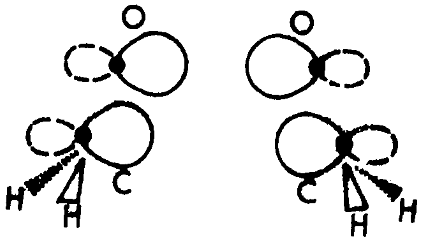
As we remarked in Part IV, the thermolysis of 1,2-dioxetane is a rearrangement of two sigma bonds to two pi bonds. This rearrangement involves four electrons, and its description is facilitated by a decomposition of the space of occupied molecular orbitals into two sets:

(1) "Generalized core orbitals "(CMO's) that describe those closed shells not much disturbed by bonding rearrangement and used to make up the generalized core function F that we used in Part IV, equations 90-1,2 and 91-1,2.

(2) "Reaction molecular orbitals" (RMO's) that are linear combinations of those minimal basis set reaction hybrid orbitals (RHO's) that undergo essential physical deformations during the reaction.

We assume, without loss of generality, that the CMO's and RMO's are two orthogonal sets, and we furthermore make the reasonable assumption that the CMO's are orthogonal to the RMO's.

In 1,2-dioxetane the RMO's are orbitals in the four dimensional space spanned by four AO's (or RMO's), one on each of the heavy atoms; and they are schematically indicated below:



The actual orbitals are more complicated than the simple figures above; for example, orthogonality will make each RHO a multicenter function localized primarily near, rather than wholly on, one of the heavy atoms. Giving each RHO a name corresponding to the atom it's localized around, we call them ℓ_o, ℓ_c, r_o, and r_c (ℓ means left, r means right, o means oxygen, and c means carbon). Since the ground state of 1,2-dioxetane has C_{2v} symmetry, from Part IV, this four dimensional space can be broken into two subspaces which transform like the A_1 and B_2 irreducible representations of C_{2v}; and accordingly in this space we can find four symmetry adapted RMO's

$$a_1 = t_o\{\ell_o + r_o\} + t_c\{\ell_c + r_c\}, \tag{96-1}$$

$$a_2 = t'_o\{\ell_o + r_o\} + t'_c\{\ell_o + r_c\}, \tag{96-2}$$

and

$$b_1 = s_o\{\ell_o - r_o\} + s_c\,\{\ell_c - r_c\}\,, \tag{96-3}$$

$$b_2 = s_o'\{\ell_o - r_o\} + s_c'\,\{\ell_c - r_c\}\,, \tag{96-4}$$

where t_o, t_o', t_c, t_c', s_o, s_o', s_c, and s_c' are expansion coefficients. With an appropriate choice of the orbitals ℓ_o, ℓ_c, r_o, and r_c and the expansion coefficients, the MO's a_1, a_2, b_1, and b_2 span the RMO space; and the best possible choice defines the multiconfiguration self-consistent field (MCSCF) variationally optimized orbitals. To find these orbitals, however, we must make a study of the space of configuration functions needed to describe the reaction.

"Complete Configurational Reaction Space"

Having divided the space of occupied MO's into CMO's and RMO's, we can form a special set of configurations by choosing each member to be an antisymmetrized product of the CMO closed shells, the generalized core function F, and one of the possible RMO orbital products times a spin function. All these configurations span the "complete configurational reaction space" (CCRS). In the present case all the configurations must have A_1 symmetry and be singlet functions; consequently each configuration must contain an even number of b-type orbitals; each RMO orbital product must be combined with one or both of the spin functions

$$\Theta_{--} = \{\alpha\beta - \beta\alpha\}\{\alpha\beta - \beta\alpha\}/2, \tag{97-1}$$

$$\Theta_{++} = \{\alpha\alpha\beta\beta + \beta\beta\alpha\alpha - (\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)/2\}/\sqrt{3}\ , \tag{97-3}$$

where α and β are the usual spinors, and the left to right order of the factors in a product of functions determines their arguments. These limitations and the Pauli exclusion principle combine to restrict the CCRS for the symmetric dissociation (C_{2V} or C_2 symmetry) of 1,2-dioxetane to the following twelve configurations:

$$\Psi_1 = A\{F\ a_1^2\ b_1^2\ \Theta_{--}\} = |11,11\rangle = |1,1\rangle\ , \tag{98-1}$$

$$\Psi_2 = A\{F\ a_2^2\ b_2^2\ \Theta_{--}\} = |22,22\rangle = |2,2\rangle\ , \tag{98-2}$$

$$\Psi_3 = A\{F\ a_1^2\ b_2^2\ \Theta_{--}\} = |11,22\rangle = |1,2\rangle\ , \tag{98-3}$$

$$\Psi_4 = A\{F\ a_2^2\ b_1^2\ \Theta_{--}\} = |22,11\rangle = |2,1\rangle\ , \tag{98-4}$$

$$\Psi_5 = A\{F\ a_1a_2b_1b_2\ \Theta_{--}\} = |12,12\rangle = |3,3\rangle\ , \tag{98-5}$$

$$\Psi_6 = A\{F\ a_1^2\ b_1b_2\ \Theta_{--}\} = |11,12\rangle = |1,3\rangle, \tag{98-6}$$

$$\Psi_7 = A\{F\ a_2^2\ b_1b_2\ \Theta_{--}\} = |22,12\rangle = |2,3\rangle\ , \tag{98-7}$$

$$\Psi_8 = A\{F\ a_1a_2b_1^2\ \Theta_{--}\} = |12,11\rangle = |3,1\rangle\ , \tag{98-8}$$

$$\Psi_9 = A\{F\ a_1 a_2 b_2^2\ \Theta_{--}\} = |_{12,22}\rangle = |_{3,2}\rangle\ , \tag{98-9}$$

$$\Psi_{10} = A\{F\ a_1^2\ a_2^2\ \Theta_{--}\} = |a\rangle\ , \tag{98-10}$$

$$\Psi_{11} = A\{F\ b_1^2\ b_2^2\ \Theta_{--}\} = |b\rangle\ , \tag{98-11}$$

$$\Psi_{12}\quad A\{F\ a_1 a_2 b_1 b_2\ \Theta_{++}\} = |T\rangle\ , \tag{98-12}$$

which also introduces two shorthand notations for the orbital products in the configurations and shows our convention of writing the a-type orbitals before the b-type. The configurations $|a\rangle$ and $|_{2,2}\rangle$ correspond to the Hartree-Fock descriptions of 1,2-dioxetane and the separated formaldehyde molecules respectively.

The first eleven configurations are singlet coupled; they join two singlet products together to make a singlet; but the last configuration is triplet coupled; it joins two triplet products to form a singlet. Taken together they make the "complete configurational reaction space" (CCRS) appropriate for our discussion, and the wavefunction for 1,2-dioxetane at any stage of its symmetric dissociation is approximated by the configuration interaction (CI) function

$$\Psi = \sum_{\kappa=1}^{12} C_\kappa \Psi_\kappa\ . \tag{99}$$

Invariance of the "Complete Configurational Reaction Space"

Let's be given a set of MCSCF orbitals a_1, a_2, b_1, and b_2 and the transformation

$$\begin{pmatrix} a_1 \\ a_2 \\ b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 & 0 \\ -\sin\alpha & \cos\alpha & 0 & 0 \\ 0 & 0 & \cos\beta & \sin\beta \\ 0 & 0 & -\sin\beta & \cos\beta \end{pmatrix} \begin{pmatrix} \bar{a}_1 \\ \bar{a}_2 \\ \bar{b}_1 \\ \bar{b}_2 \end{pmatrix} . \tag{100}$$

A reasonable question is: what is the transformation connecting $\Psi_1, \cdots, \Psi_{12}$ to the configurations $\Psi_1, \cdots, \Psi_{12}$ which are formed from the orbitals $\bar{a}_1$, $\bar{a}_2$, $\bar{b}_1$ and $\bar{b}_2$ in a manner analogous to equations 98-1,12. It is readily seen that the last three of these equations are invariant:

$$|a\rangle = |\bar{a}\rangle, \quad |b\rangle = |\bar{b}\rangle, \quad |T\rangle = |\bar{T}\rangle . \tag{101}$$

To find the transformation of the first nine configurations we proceed stepwise. First, direct substitution shows that the "hybrid" configurations

$$|\bar{i}\,\bar{j}, k\ell\rangle = A\{F\ \bar{a}_i \bar{a}_j b_k b_\ell\ \Theta_{--}\} \tag{102}$$

are related to the original configurations by the following orthogonal transformation

$$\begin{pmatrix} |11k\ell\rangle \\ |22k\ell\rangle \\ |12k\ell\rangle \end{pmatrix} = \begin{pmatrix} \cos^2\alpha & \sin^2\alpha & \sin(2\alpha)/\sqrt{2} \\ \sin^2\alpha & \cos^2\alpha & -\sin(2\alpha)/\sqrt{2} \\ -\sin(2\alpha)/\sqrt{2} & \sin(2\alpha)/\sqrt{2} & \cos(2\alpha) \end{pmatrix} \begin{pmatrix} |\bar{1}\bar{1}k\ell\rangle \\ |\bar{2}\bar{2}k\ell\rangle \\ |\bar{1}\bar{2}k\ell\rangle \end{pmatrix} . \qquad (103)$$

Employing our second configurational shorthand notation, equations 98-1,2, we rewrite the transformation in equation 103 as

$$|i, k\rangle = \sum_{j=1}^{3} D_{i\bar{j}}(\alpha)\,|\bar{j}, k\rangle \ , \qquad (104)$$

where the coefficients $D_{i\bar{j}}$ are obtained by comparison with equation 103. An analogous treatment of the second pair of indices gives the final transformation

$$|i,k\rangle = \sum_{j=1}^{3}\ \sum_{\ell=1}^{3} D_{i\bar{j}}(\alpha)\,D_{k\bar{\ell}}(\beta)\,|\bar{j},\bar{\ell}\rangle \ , \qquad (105)$$

and we see that $\Psi_1,\cdots,\Psi_9$ and $\bar{\Psi}_1,\cdots,\bar{\Psi}_9$ are related by the Kronecker product of two orthogonal transformations. Since this transformation is itself orthogonal, we have at once that the configurations $\bar{\Psi}_1,\cdots,\bar{\Psi}_{12}$ span exactly the same space as $\Psi_1,\cdots,\Psi_{12}$, and as a result they too are a basis of the "complete configurational reaction space" (CCRS).

Natural Reaction Orbitals

The CCRS invariance just discussed reveals an arbitrariness in the orbitals produced by an MCSCF calculation of a general function from this space; namely, the RMO's are determined to within only an orthogonal transformation. A similar arbitrariness exists among the doubly occupied CMO's; but here, as with a HF wavefunction, the arbitrariness is rather subtly different. A HF function's first order density matrix is proportional to a unit matrix in the space of its occupied MO's as is the first-order density matrix of our MCSCF function in the space of its CMO's; however, the first order density matrix of an MCSCF function is in general not diagonal in the space of its RMO's. Rather this portion of the matrix contains precisely as many off diagonal elements as there are arbitrary parameters in the orthogonal transformation specifying the RMO's, so we can require that our MCSCF function from the CCRS produce a diagonal density matrix, and as a result we produce unique MCSCF orbitals. These orbitals are special natural orbitals (Lowdin, 1955), which we call the "natural reaction" orbitals or NRO's.

For four RMO's we should specify six conditions to find the NRO's, but the C_2 or C_{2V} symmetry of 1,2-dioxetane reduces this problem to that of determining the angles (α) and (β) shown in equation 100. The first-order density matrix for 1,2-dioxetane can be shown to be

$$\rho(1,2) = \sum_{i=1}^{2} \sum_{j=1}^{2} \{p^a_{ij}\, a_i(1) a_j(2) + p^b_{ij}\, b_i(1) b_j(2)\} , \quad (106)$$

where the bond-order matrices are related to the expansion coefficients $C_1, \cdots, C_{12}$ of the function in equation 99 in terms of the configurations in equations 98-1,12 by the following

$$p^a_{11} = 2(C^2_1 + C^2_3 + C^2_6 + C^2_{10}) + (C^2_5 + C^2_8 + C^2_9 + C^2_{12}) , \quad (107\text{-}1)$$

$$p^b_{22} = 2(C^2_2 + C^2_4 + C^2_7 + C^2_{10}) , + (C^2_5 + C^2_8 + C^2_9 + C^2_{12}) , \quad (107\text{-}2)$$

$$p^a_{12} = p^a_{21} = \sqrt{2}\, \{C_5(C_6 + C_7) + C_8(C_1 + C_4) + C_9(C_2 + C_3)\} , \quad (107\text{-}3)$$

$$p^b_{11} = 2(C^2_1 + C^2_4 + C^2_8 + C^2_{11}) + (C^2_5 + C^2_6 + C^2_7 + C^2_{12}) , \quad (107\text{-}4)$$

$$P^b_{22} = 2(C_2^2 + C_3^2 + C_9^2 + C_{11}^2)$$

$$+ (C_5^2 + C_6^2 + C_7^2 + C_{12}^2), \qquad (107\text{-}5)$$

$$P^b_{12} = P^b_{21} = \sqrt{2}\,\{C_5(C_8 + C_9)$$

$$+ C_6(C_1 + C_3) + C_7(C_2 + C_4)\}. \qquad (107\text{-}6)$$

It is apparent that the density matrix is diagonal if $C_6 = C_7 = C_8 = C_9 = 0$: i.e., if the configurations in which the a-type orbitals are doubles and the b-type orbitals are singles and vice versa are eliminated. The space of the remaining eight configurations is not invariant to transformations among the NRO's, and its MCSCF orbitals are unique. As we'll see, they are similar to the NRO's of the CCRS because in fact C_6, C_7, C_8, and C_9 turn out to be small.

AN APPROXIMATION TO THE RMO'S FOR 1,2-DIOXETANE

SPIP Models of the Reactant and Products

As we have seen from Part IV, a reasonable approximation to the wavefunction for 1,2-dioxetane is the separated-pair independent particle (SPIP) model

$$\Phi = A\{F\Lambda(a_o,b_o)\Lambda'(a_c,b_c)\Theta_{--}\} \, , \tag{108}$$

where

$$\Lambda(a,b) = f_a a^2 + f_b b^2 \, , \tag{109-1}$$

$$f_a^2 + f_b^2 = 1, \tag{109-2}$$

and the MO's a_o, b_o, a_c, and b_c are the bonding and antibonding orbitals localized in the regions of the oxygen-oxygen and carbon-carbon <u>sigma</u> bonds respectively. It is expedient to make the identification

$$a_1 = a_o, \quad a_2 = a_c, \quad b_1 = b_c, \quad b_2 = b_o \tag{110}$$

and use these orbitals to write the CI expansion of Φ. Using equations 108, 109-1,2 and 98-1,12 we find

$$\Phi = f_{ao}f_{ac}|a\rangle + f_{bo}f_{bc}|b\rangle + f_{ao}f_{bc}|1,1\rangle + f_{bo}f_{ac}|2,2\rangle. \tag{111}$$

On the other hand, the most general wavefunction for two separated formaldehyde molecules in the CCRS is of the form

$$\Phi_{\infty} = A\{F\,\Lambda''(L,L^{*})\Lambda''(R,R^{*})\Theta_{--}\}\ , \qquad (112)$$

where L,L^{*}, R,R^{*} are the bonding and antibonding pi orbitals on the left and right formaldehyde molecules respectively. These orbitals can be related to a set of symmetry adapted orbitals by

$$a = (L+R)/\sqrt{2},\quad a^{*} = (L^{*}+R^{*})/\sqrt{2}\ , \qquad (113\text{-}1)$$

$$b = (L-R)/\sqrt{2},\quad b^{*} = (L^{*}-R^{*})/\sqrt{2}\ . \qquad (113\text{-}2)$$

The identification

$$a_2 = a,\quad a_1 = a^{*},\quad b_2 = b,\quad b_1 = b^{*} \qquad (114)$$

allows us to use equations 98-1,12 to write the CI expansion

$$\Phi_{\infty} = f_L^2|{}_{2,2}> + f_L^2{}^{*}|{}_{1,1}> - \tfrac{1}{2}\ f_L f_L{}^{*}\{|a> + |b>$$

$$+ |{}_{1,2}> + |{}_{2,1}> + |{}_{3,3}> + \sqrt{3}\ T>\}\ . \qquad (115)$$

Since Ψ_6, Ψ_7, Ψ_8, and Ψ_9 do not occur in the wavefunction Φ, we infer that they make no essential contribution to the CCRS wavefunction at the molecular equilibrium. Since furthermore, these configurations are absent for the separated molecules, even in the CCRS, we conjecture that they can be omitted along the whole reaction path without affecting the quality of the wavefunction. The RMO's resulting from such a simplified wavefunction should be good approximation to the NRO's of the total CCRS. An MCSCF calculation of this type is, however, still impractical in our laboratory at the present time. Fortunately a further approximation is reasonable.

SPIP Model of the RMO's

It is evident that the SPIP function Φ_∞ cannot give any reasonable description of 1,2-dioxetane near its molecular equilibrium; Φ_∞ gives significant and inappropriate weight to the configurations in the braces of equation 115. The SPIP function Φ, however, can provide a reasonable approximation to the molecular wavefunction at the dissociation limit; Φ can give prominence to the configuration $|2,2>$ which is the HF wavefunction for the separated formaldehyde molecules.

Therefore, we choose to make a SPIP calculation along the reaction path to generate the NRO's shown in equation 110. Having found these NRO's we then make a full MCSCF calculation using <u>all</u> twelve configurations in equations 98-1,12 but limit the orbital variations to occur only in the orbital space spanned by the CMO's and NRO's. This procedure places a restriction on the MCSCF optimization, but by keeping the number of MO's small, it is an economical method; and near the equilibrium it is a good approximation. As we'll see, the space of RMO's generated by the SPIP function Φ is also an excellent approximation at the dissociation limit.

Simplest SPIP Model of the Reaction

The two-geminal SPIP function Φ of equation 108 is not the simplest model function which embodies a continuous description for the transition from the 1,2-dioxetane molecule to the separated formaldehydes. The simplest wavefunction which does this is the one-geminal SPIP function

$$\hat{\Phi} \; A\{F \; \Lambda \; (a_o, b_o) a_c \Theta_{--}\} \, . \qquad (116)$$

By making the identifications

$$a_o = a_1 , \quad a_c = a_2 , \quad b_o = b_2 \qquad (117)$$

we can write it as the CI expansion

$$\hat{\Phi} = f_{a_1} |a> + f_{b_2} |_{2,2}> \, . \qquad (118)$$

Clearly the function $\hat{\Phi}$ describes the transition from a modestly correlated model of 1,2-dioxetane to a slightly correlated Hartree-Fock model of the separated formaldehyde molecules. Although this function does not provide enough information to approximate all four RMO's, it is adequate to optimize the reaction path, and its simplicity and economical calculation make it a natural choice for this purpose.

DETERMINATION OF THE REACTION PATH

Atomic Orbital Basis Sets

As with the geometry optimizations in Part IV, we use a rather restricted basis to optimize all the variables needed to define a reasonable reaction path. This basis set is actually the small formaldehyde basis shown in Appendix A Tables 20, 21, and 22. After the optimizations are completed we'll recalculate the wavefunction for points along the reaction path using the larger formaldehyde basis shown in Appendices A and B, Tables 20, 30, and 31.

Calculation of the One-Geminal SPIP Function

The dissociation is examined preserving the C_{2V} symmetry of the molecule, and we'll calculate the reaction path using the carbon-carbon sigma bond length as the reaction parameter. The optimizations are made with the one-geminal SPIP function $\hat{\Phi}$ from equation 116, and this function is determined by the following procedures.

1. The HF functions of the type $|a>$ and $|_{2,2}>$ from equations 98-1,12 are calculated.
2. The orbitals from $|a>$ and $|_{2,2}>$ are then used to assemble an initial approximation to the SPIP function $\hat{\Phi}$; the technique is essentially that outlined in Part IV except that special care is given to the selection

of the CMO's for those points on the reaction path nearest to the energy maximum. At these points we select the A_1 type MO's from the HF function $|a\rangle$ and the other MO's from the HF function $|_{2,2}\rangle$.

(3) The SPIP function $\hat{\Phi}$ can then be found by applying the analysis of Parts I to III to the optimization of orbitals a_1, a_2, and b_2.

Optimization of the Reaction Path

The function $\hat{\Phi}$ is used to optimize the structural variables of the molecule (the oxygen-oxygen and carbon-oxygen bond lengths and the carbon-carbon-hydrogen and hydrogen-carbon-hydrogen angles) as functions of the reaction parameter (the carbon-carbon bond length). One variable, the carbon-hydrogen bond length, was kept fixed at the molecular value for the whole calculation. The optimization procedure is simply the quadratic fitting method discussed in Part IV, and it can be applied in the following way:

(1) At the molecular equilibrium we accept the Hartree-Fock geometry from Part IV.

(2) For a large separation (a carbon-carbon bond length, R_{CC}, of 8.8754 a.u.) the structural variables are optimized using

the one-geminal SPIP function $\hat{\Phi}$. After one optimization cycle the geometry was found to be that of two separated formaldehyde molecules, so this geometry was accepted without further refinement.

(3) The method of geometry optimization for all the other points was the same as that used in step 2; namely, using the SPIP function $\hat{\Phi}$. The points on the reaction path are chosen by creeping in small increments from the point determined in step 1 outward, and from the point determined in step 2 inward. In this manner changes in the reaction parameter remain small, and each optimization requires only one cycle through the fitting procedure outlined in Part IV.

The result of this effort is listed on Table 14, where we see the optimized geometries of 1,2-dioxetane for ten values of the reaction parameter. The major variables, the carbon-oxygen distance (R_{CO}) and the oxygen-oxygen distance (R_{OO}), are shown as functions of the reaction parameter in Figure 8. The minor variables, the oxygen-carbon-hydrogen angle ($\measuredangle$OCH) and the hydrogen-carbon-hydrogen angle ($\measuredangle$HCH) are similarly shown in Figure 9. Two dramatic aspects of the dissociation are evident, the rapid shrinkage of the carbon-oxygen bond and the rapid opening of the oxygen-oxygen bond.

Table 14. Geometries of 1,2-dioxetane along the reaction path parameterized by the carbon-carbon sigma bond distance R_{CC}[a]

point	R_{CC}	R_{CO}	R_{OO}	∢HCH	∢OCH
1	2.8754	2.6874	2.6934	109.0°	112.6°
2	3.3754	2.6851	2.9200	111.0°	114.7°
3	3.8754	2.6804	3.2532	113.4°	115.8°
4	3.9872	2.6800	3.3434	114.0°	115.8°
5	4.0369	2.6725	3.4434	114.5°	116.0°
6	4.0754	2.6685	3.5725	114.5°	116.0°
7	4.1754	2.4162	5.0489	115.6°	121.6°
8	4.3754	2.2972	5.6917	114.6°	122.3°
9	5.8754	2.2854	6.1695	114.2°	122.9°
10	8.8754	2.2803	8.9004	114.6°	122.7°

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[a] Bond distances in a.u. and R_{CH} = 2.0287 a.u.

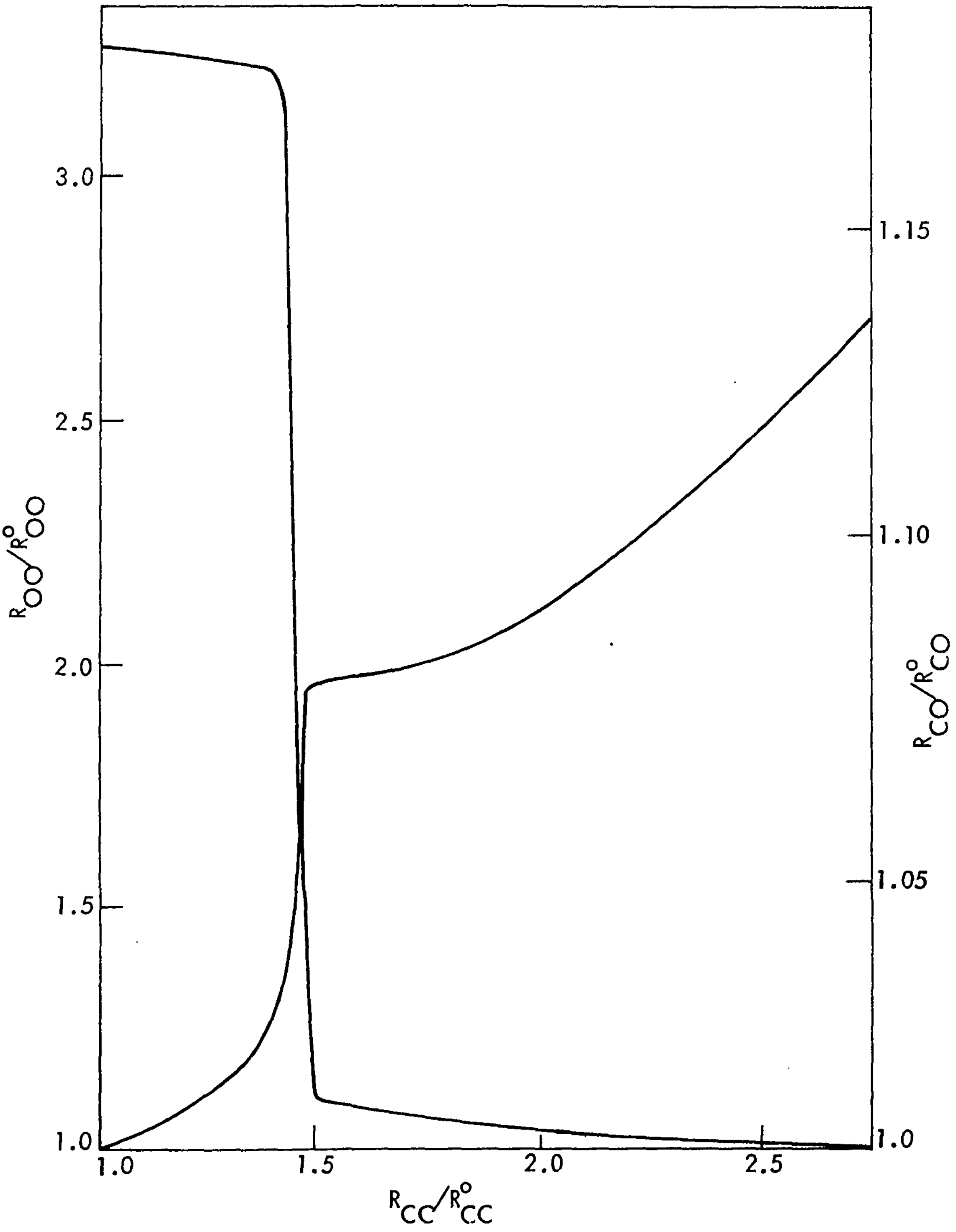


Figure 8. Major bond lengths along reaction path

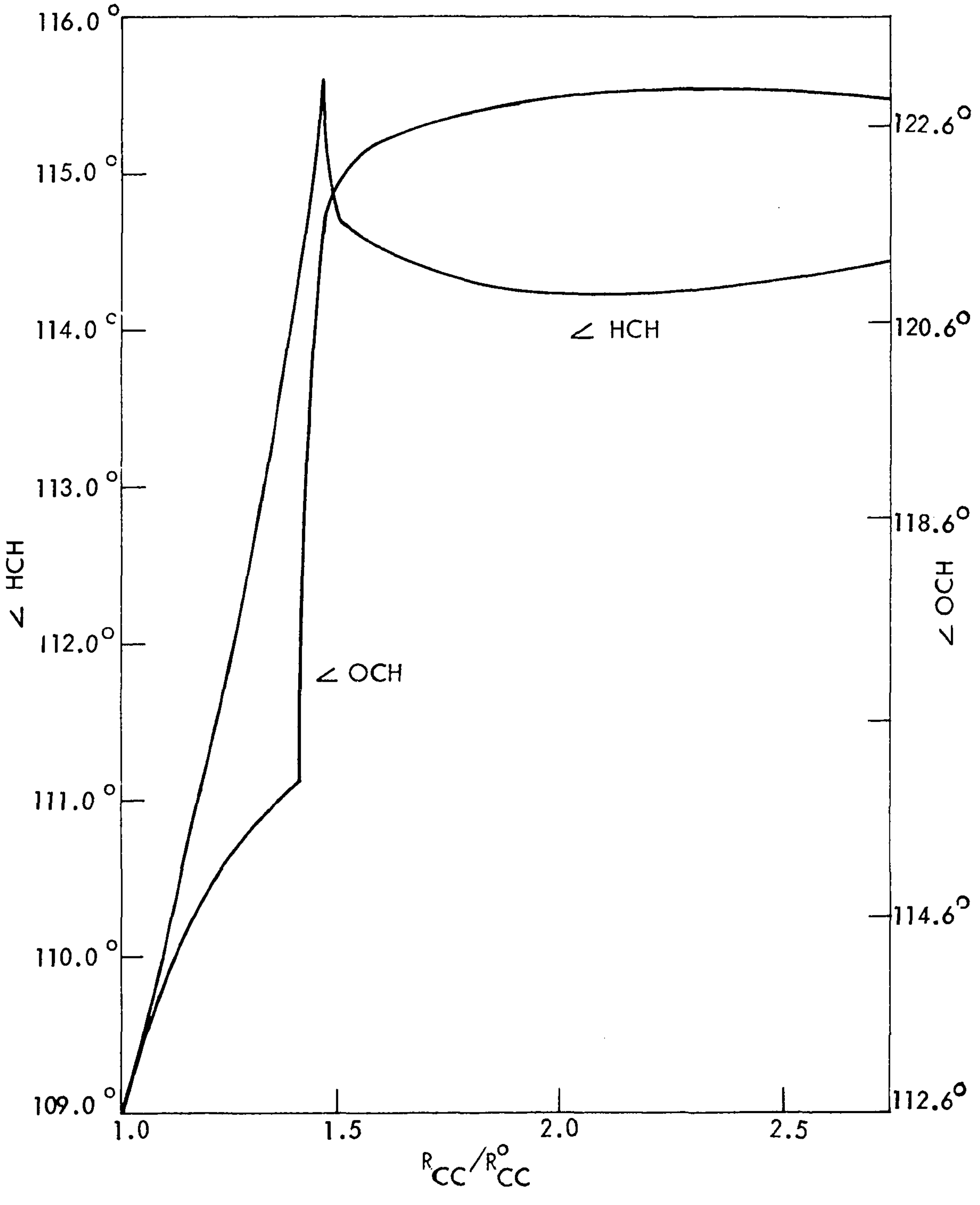


Figure 9. Bond angles along the reaction path

CALCULATION OF THE DISSOCIATION

Calculating the SPIP Functions

Having obtained the reaction path shown in Table 14, we can refine the entire curve using the larger contracted orbital formaldehyde basis set shown in Appendices A and B, Tables 20, 30, and 31. The execution of the one-geminal SPIP calculation follows the general outline of the last section. However, having made the previous calculation, we are able to make a more judicious choice of the core orbitals for the functions describing the points nearest the barrier maximum: namely, for the two points nearest the energy maximum, we choose the B_2 orbitals from the HF function $|_{2,2}\rangle$ and the other orbitals from $|a\rangle$.

The two-geminal SPIP function, Φ, see equation 108, can be approximated by selecting the initial orbitals a_1, a_2, and b_2 from the one-geminal function $\hat{\Phi}$, and using lowest energy virtual orbital of the proper symmetry as an initial b_1 MO. With initial expansion coefficients of $f_{a1} = 1.0$ and $f_{b2} = 0.0$, we can optimize the orbitals a_2, a_1, b_1, and b_2 in Φ using the analysis of Parts I to III of this work.

Orbital Energies, Hartree-Fock Energies, SPIP Energies, and the Origins of the Activation Energy

It is evident from the form of the HF functions $|a\rangle$ and $|_{2,2}\rangle$ that $|a\rangle$ cannot possibly dissociate into $|_{2,2}\rangle$; in fact, from the considerations in Part IV, we know that $|a\rangle$ dissociates to a mixture of covalent and ionic states that poorly describe the separated formaldehyde molecules. On the other hand, the HF function $|_{2,2}\rangle$ correlates with an excited state on association. Thus at some intermediate value of the reaction parameter, these curves cross, and the rapid change of the wavefunction from a form dominated by $|a\rangle$ to one dominated by $|_{2,2}\rangle$ forces the system to "switch dissociation surfaces" and thereby avoid the crossing created by Hartree-Fock approximation. The one-geminal SPIP function is the simplest formula capable of doing this, and it was formally used for this purpose in the early work of Evans and his associates (Evans and Polanyi, 1938; Evans and Warhurst, 1938, 1939; Glasstone et al., 1941).

In Table 15 we show the energies of the orbitals a_1 and b_2 in the HF functions $|a\rangle$ and $|_{2,2}\rangle$ respectively, and along with them we show the total molecular energy of the HF functions. The crossing of the orbital energies is shown in Figure 10, and the crossing of the HF energies is shown in Figure 24. The total energies and occupation numbers of the orbitals in the one- and two-geminal SPIP functions are shown in Tables 16 and 17 and displayed in Figures 11, 12, and 24. From these data we can make several inferences: namely,

(1) The barrier maximum occurs at $R_{CC} = 4.04$ a.u. which is quite close to where the HF energies cross: i.e., 4.10 a.u. The HF orbital energies (ε_{a_1} from |a> and ε_{b_2} from |2,2>) and the occupation numbers n_{a_1} and n_{b_2} in either SPIP function also cross near $R_{CC} = 4.10$ a.u.

(2) The essential changes in the HF energies, in ε_{a_1} and ε_{b_2}, and in n_{a_1}, and n_{b_2} occur between $R_{CC} = 4.08$ and $R_{CC} = 4.18$ a.u.; definitely on the separated formaldehyde slope of the barrier.

(3) References to Figures 8 and 9 show that the dramatic geometric changes in the system also occur between $R_{CC} = 4.08$ and 4.18 a.u.; again on the separated formalydehyde slope of the barrier.

(4) The two-geminal SPIP function recovers a correlation effect that is important only on the molecular side of the activation barrier; by construction, this effect is right-left correlation of the carbon-carbon bond, and this bond only exists on the molecular side of the activation barrier. In fact the two-geminal SPIP function recovers 0.043 a.u. of correlation energy in 1,2-dioxetane and only 0.015 a.u. from the separated formaldehyde molecules, but from the work in Part Part IV we know that there is 0.081 a.u. of right-left correlation to be recovered in the <u>pi</u> bonds of the separated system.

Clearly, the fundamental aspects of the barrier are understood but its quantitative features need to be refined to correct the correlation imbalance.

Table 15. Energies of the highest occupied orbitals in and total energies of the Hartree-Fock wavefunctions for 1,2-dioxetane ($|a\rangle$) and two formaldehyde molecules ($|_{2,2}\rangle$)[a]

Point	$\varepsilon(a_1)$ from$|a\rangle$	$\varepsilon(b_2)$ from$|_{2,2}\rangle$	E from$|a\rangle$	E from$|_{2,2}\rangle$
1	-0.4988	-0.1407	-227.5388	-226.8152
2	-0.4339	-0.2172	-227.5111	-227.0736
3	-0.3708	-0.2895	-227.4363	-227.2715
4	-0.3581	-0.3038	-227.4158	-227.3051
5	-0.3493	-0.3166	-227.3996	-227.3332
6	-0.3419	-0.3304	-227.3815	-227.3591
7	-0.2475	-0.4575	-227.1420	-227.5681
8	-0.2141	-0.5027	-227.0151	-227.5982
9	-0.1682	-0.5234	-226.9085	-227.6260
10	-0.1184	-0.5383	-226.7808	-227.6323

[a] Energies in a.u. and dashed line corresponds to crossing of orbital energies.

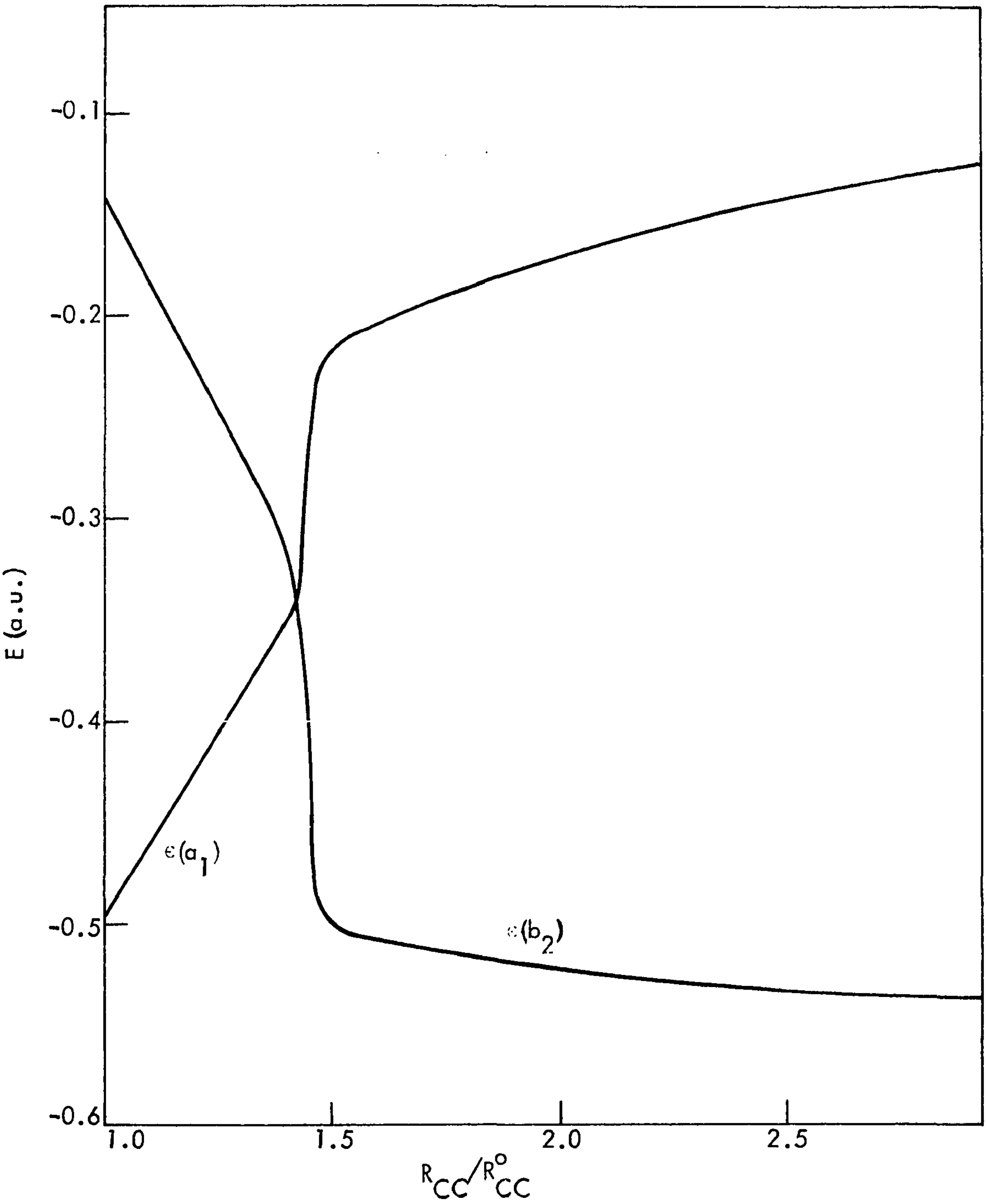


Figure 10. Orbital energies from the dimer and dissociation product HF functions

Table 16. Energy and occupation numbers of the one-geminal SPIP function $\hat{\Phi}^{a}$

Point	OCC # a_1	OCC # b_2	E from $\hat{\Phi}$
1	1.9441	0.0559	-227.5728
2	1.8978	0.1022	-227.5601
3	1.7783	0.2217	-227.5136
4	1.7328	0.2672	-227.5020
5	1.6745	0.3255	-227.4964
6	1.5300	0.4700	-227.4973
7	0.0831	1.9169	-227.5903
8	0.0439	1.9561	-227.6138
9	0.0223	1.9777	-227.6360
10	0.0154	1.9846	-227.6402

[a] Energies in a.u.

Table 17. Energy and occupation numbers of the two-geminal SPIP function Φ^a

Point	OCC # a_1	OCC # b_2	OCC # a_2	OCC # b_1	E from Φ
1	1.9442	0.0558	1.9884	0.0116	-227.5815
2	1.9006	0.0994	1.9631	0.0369	-227.5783
3	1.7988	0.2012	1.9110	0.0890	-227.5436
4	1.7631	0.2369	1.8959	0.1041	-227.5345
5	1.7159	0.2841	1.8924	0.1076	-227.5292
6	1.5982	0.4018	1.8976	0.1024	-227.5289
7	0.0845	1.9155	1.9910	0.0090	-227.5953
8	0.0439	1.9561	1.9916	0.0084	-227.6187
9	0.0220	1.9780	1.9878	0.0122	-227.6424
10	0.0152	1.9848	1.9857	0.0143	-227.6477

[a] Energies in a.u.

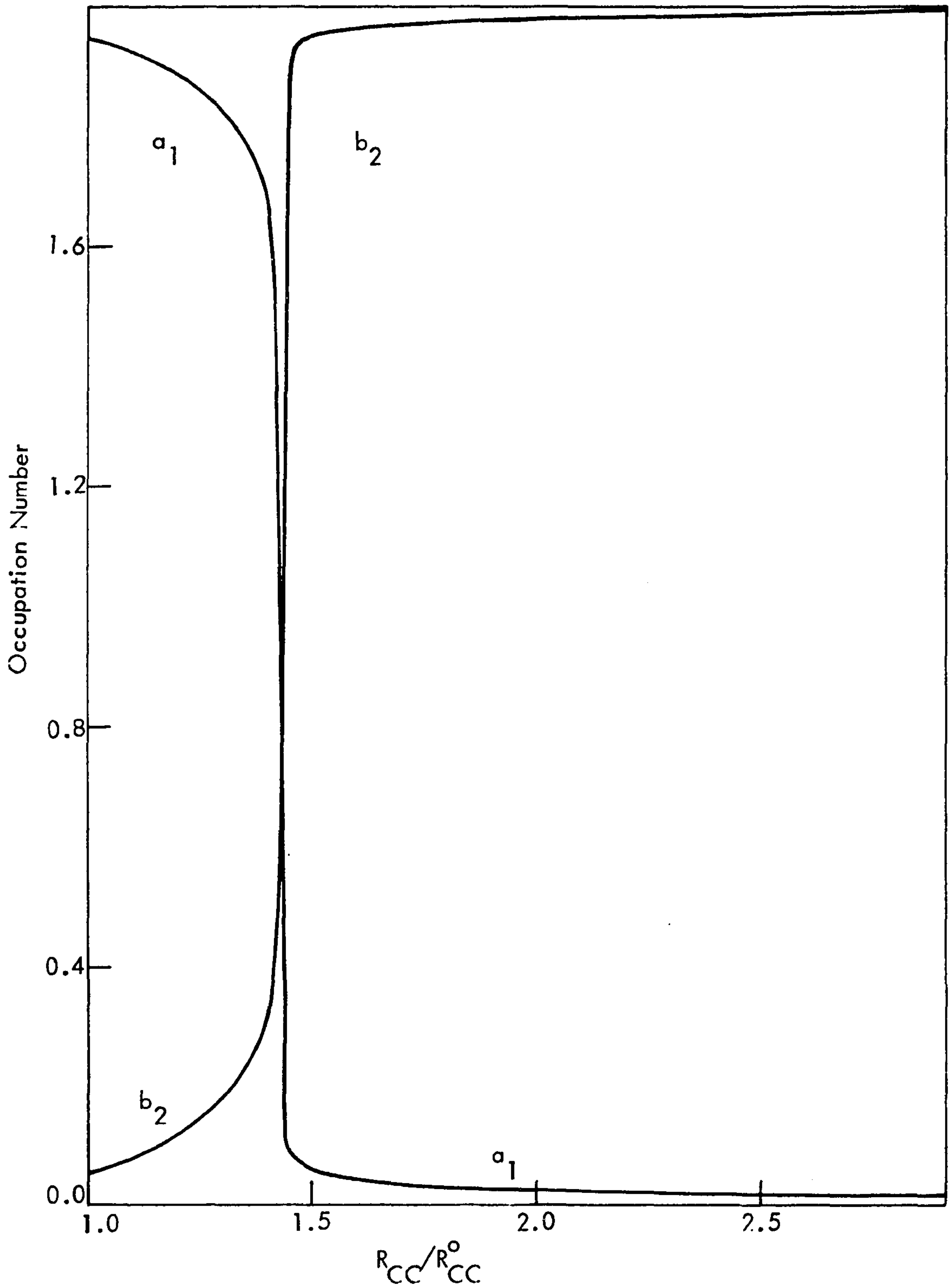


Figure 11. Occupation numbers from the one-geminal SPIP function $\hat{\Phi}$

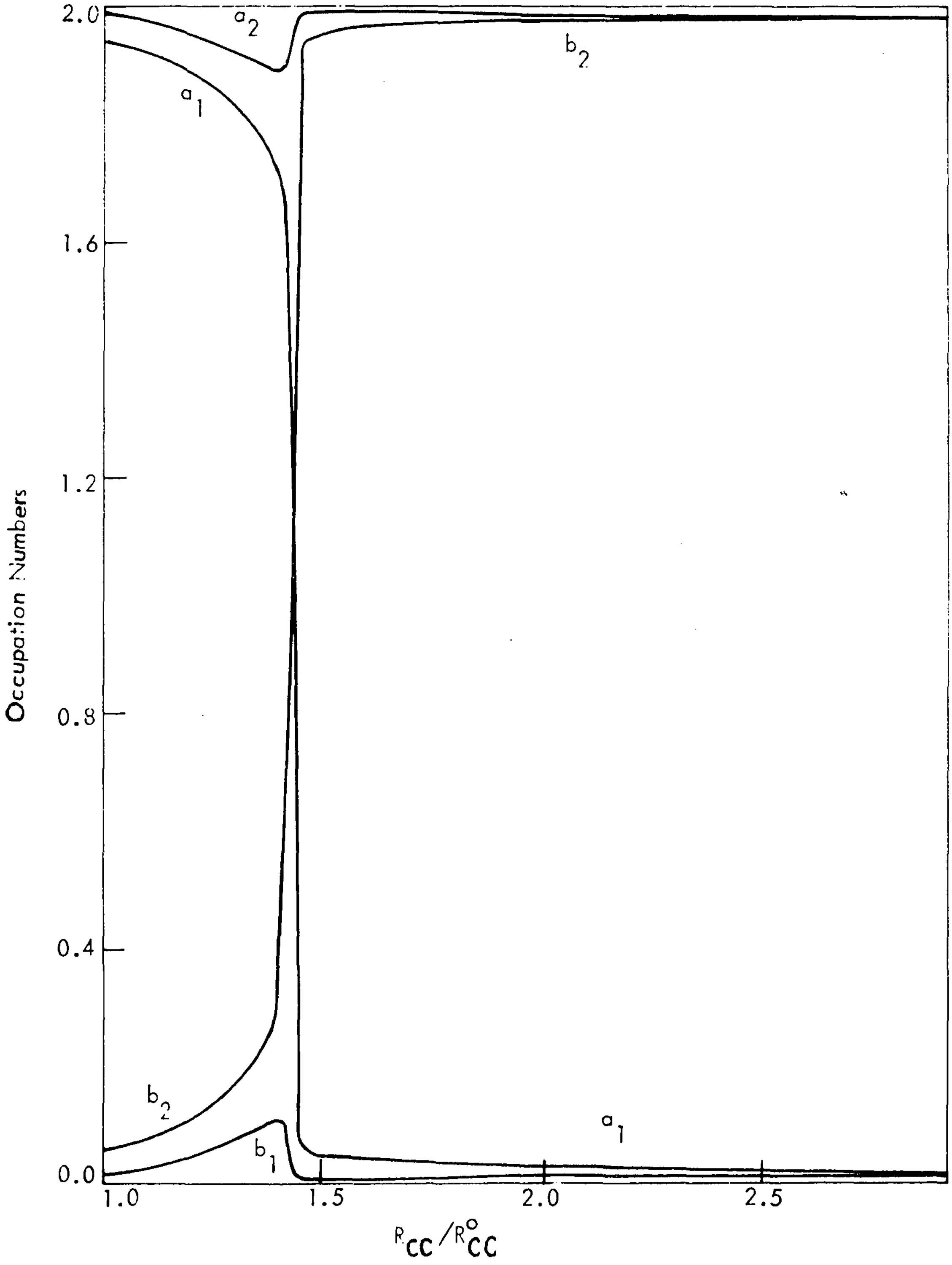


Figure 12. Occupation numbers from the two-geminal SPIP function Φ

Dissociation as Described with the CCRS

To obtain the correlation balance we calculate an MCSCF function in the CCRS spanned by the configurations in equation 98-1,12; however, as discussed in the second section of this part, we limit the orbital variations to occur only in the orbital space spanned by the reaction molecular orbitals (RMO's: a_1, a_2, b_1, and b_2) and the core orbitals (CMO's) of the two-geminal SPIP function Φ. Using the analysis of the preceding in connection with equation 106 we find the natural reaction orbitals (NRO's) and expand the wavefunction in terms of configurations made up from NRO's.

The orbitals are given in Appendix E, Tables 61 to 69 and are shown as functions of the reaction parameter in the contour plots in Figures 13 to 22. These plots give insight into the nature of the NRO's. At the equilibrium we have two symmetric halves joined by two sigma bonds; this is clear from the left panels in Figure 13, where the two heavily occupied MO's indeed represent an oxygen-oxygen and a carbon-carbon sigma bond. Similarly, the bonding assignment at infinite separation is clear; there are two distinct formaldehyde pi bonds delocalized between the carbon and oxygen atoms.

The intermediate plots illustrate how the orbitals change to create the barrier. As one dissociates the molecule it can be seen in the upper left panels of Figures 13 to 17 that the orbital representing the oxygen-oxygen *sigma* bond delocalizes to cover all four heavy atoms, but this delocalization makes the orbital antibonding with respect to the carbon-oxygen bonds. Such a process causes an increase in the energy of the system (creates a barrier) so the orbital becomes depopulated as the dissociation proceeds, and the orbital receiving this population (upper right panel in Figures 13 to 17) is not only bonding in the carbon-oxygen region but also it is antibonding in the oxygen-oxygen region. Thus the dissociation is accompanied by a large amount of right-left correlation, and as a consequence, referring to Figure 14, the barrier is neither steep nor high. In contrast, the association of the separated formaldehyde molecule can be seen by looking backwards through Figures 22 to 17. There we see a strong non-bonded repulsion associated with the antisymmetric combination of *pi* bonds in the upper right panel of these Figures; this orbital simply becomes antibonding in the region between the two halves of the dimer, and a barrier to association is created. A natural response to such a situation would be for the upper right orbital to weaken its *pi* bonds and shift its population to another orbital; we see, however, that the most favorable orbital available to receive population (the oxygen-oxygen bond in the upper left panel) is antibonding

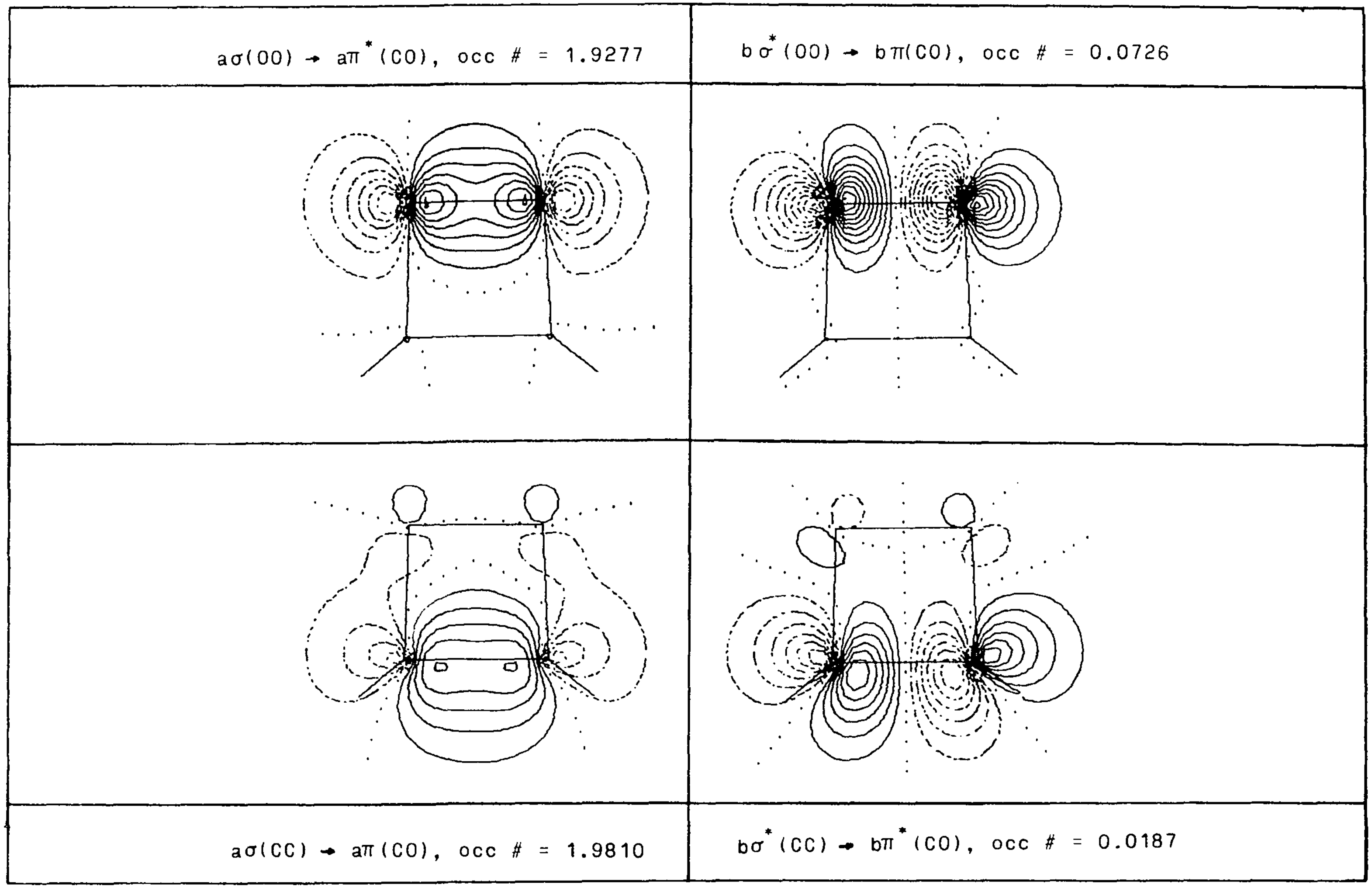
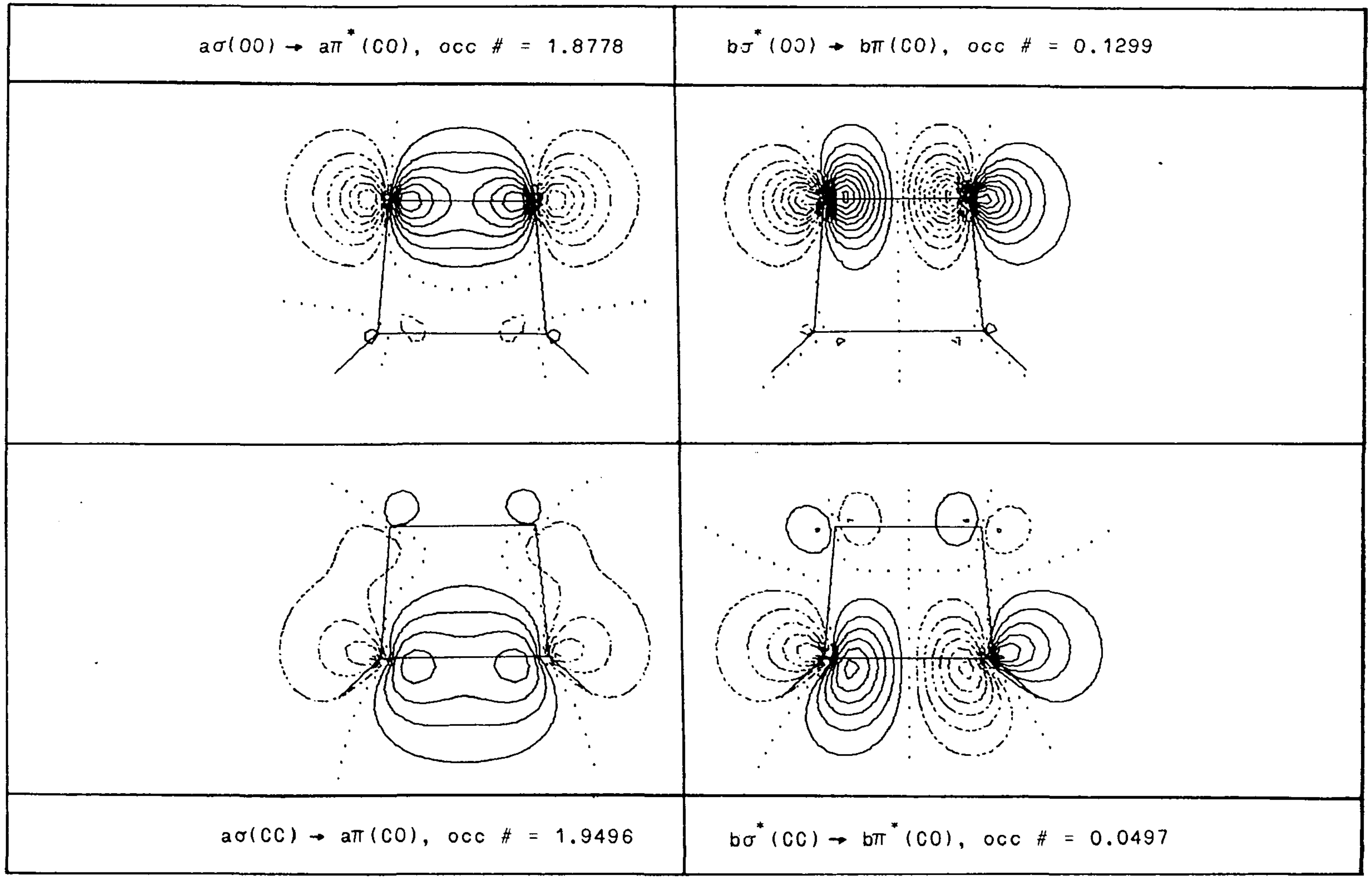


Figure 13. NRO's for 1,2-dioxetane at R_{CC} = 2.8754 a. u. (molecular equilibrium).



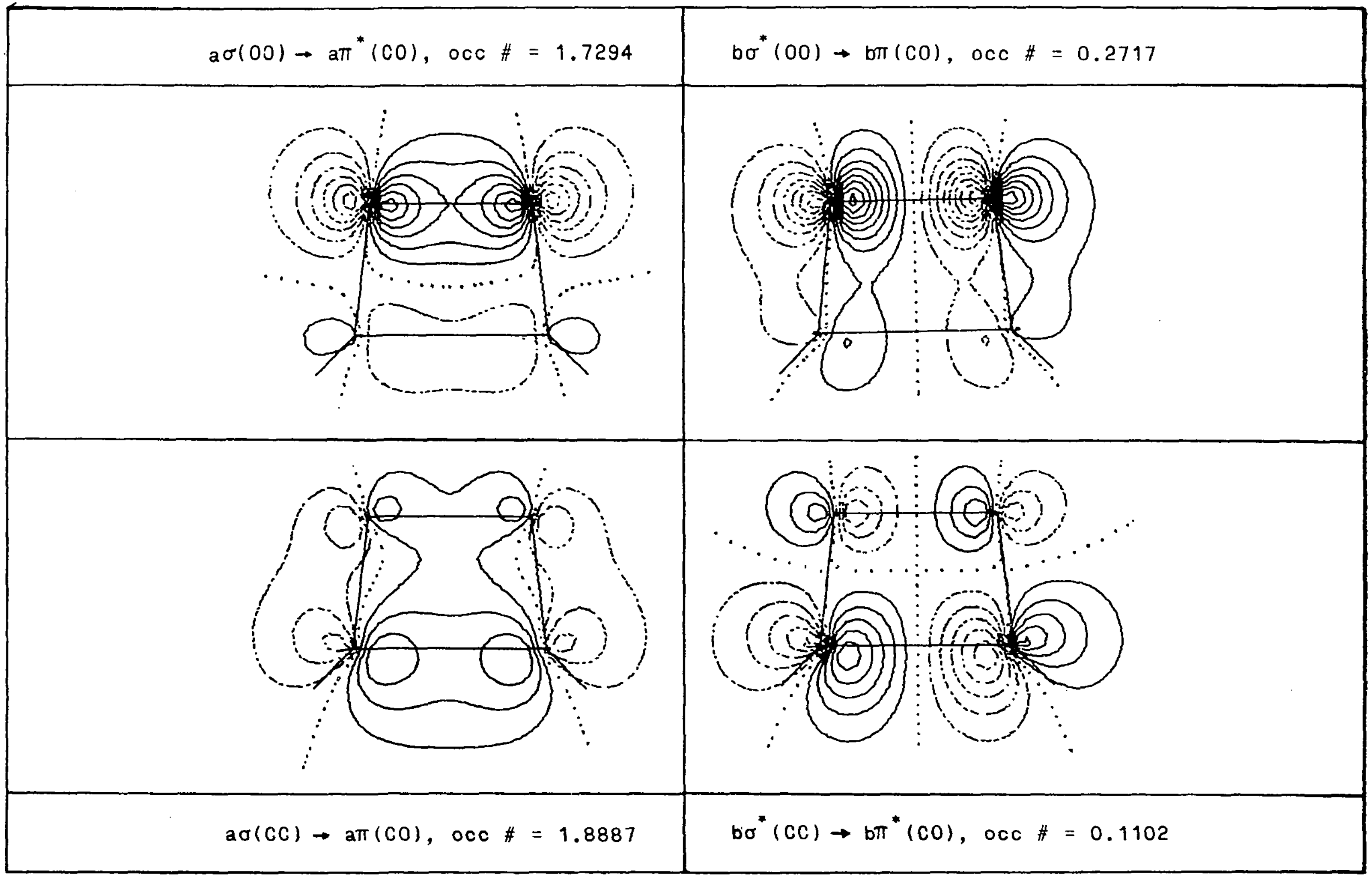
$a\sigma(OO) \rightarrow a\pi^*(CO)$, occ # = 1.8778

$b\sigma^*(OO) \rightarrow b\pi(CO)$, occ # = 0.1299

$a\sigma(CC) \rightarrow a\pi(CO)$, occ # = 1.9496

$b\sigma^*(CC) \rightarrow b\pi^*(CO)$, occ # = 0.0497

Figure 14. NRO's for 1,2-dioxetane at R_{CC} = 3.3754 a.u.



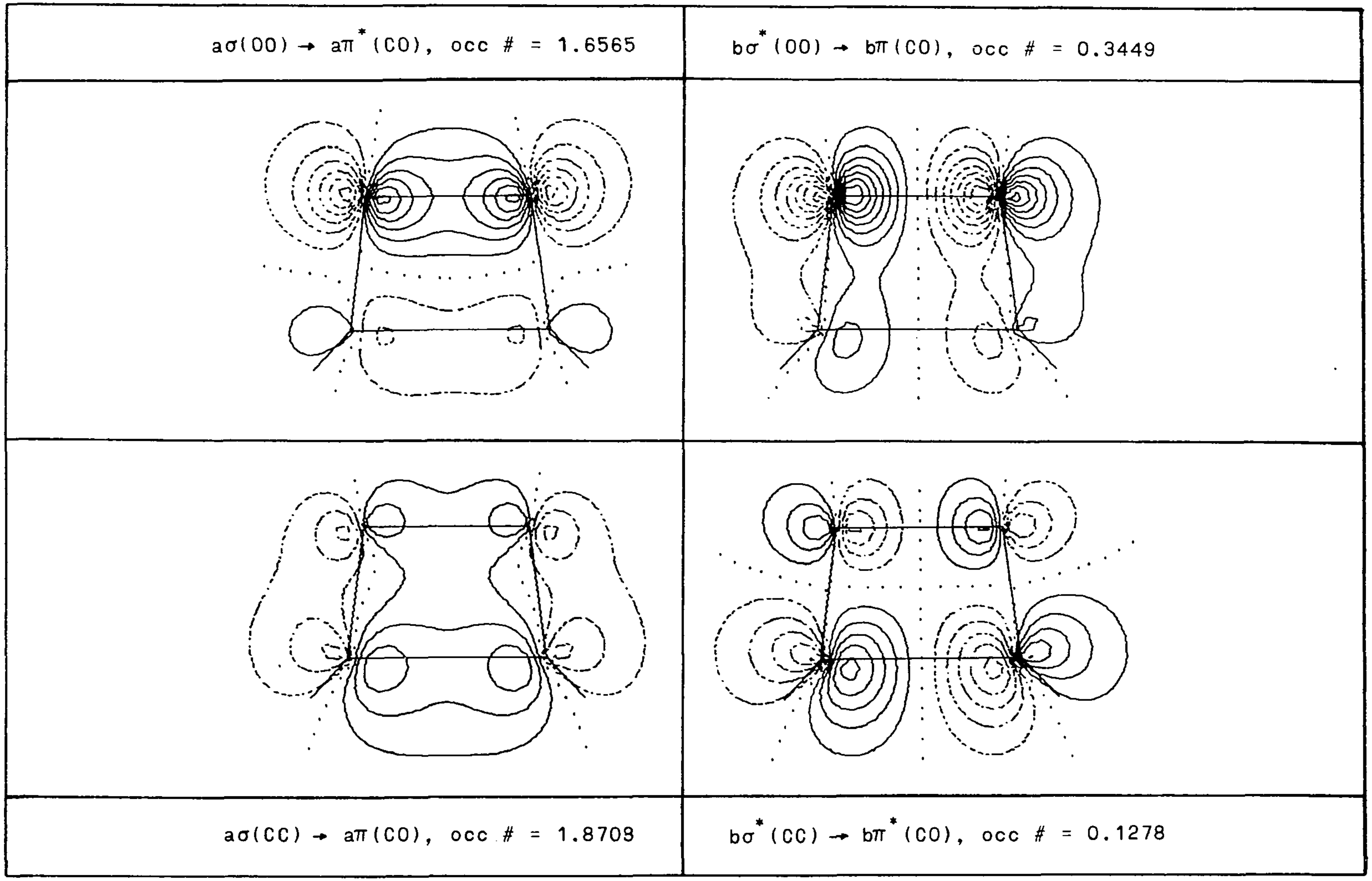
$a\sigma(OO) \rightarrow a\pi^*(CO)$, occ # = 1.7294

$b\sigma^*(OO) \rightarrow b\pi(CO)$, occ # = 0.2717

$a\sigma(CC) \rightarrow a\pi(CO)$, occ # = 1.8887

$b\sigma^*(CC) \rightarrow b\pi^*(CO)$, occ # = 0.1102

Figure 15. NRO's for 1,2-dioxetane at R_{CC} = 3.8754 a.u.



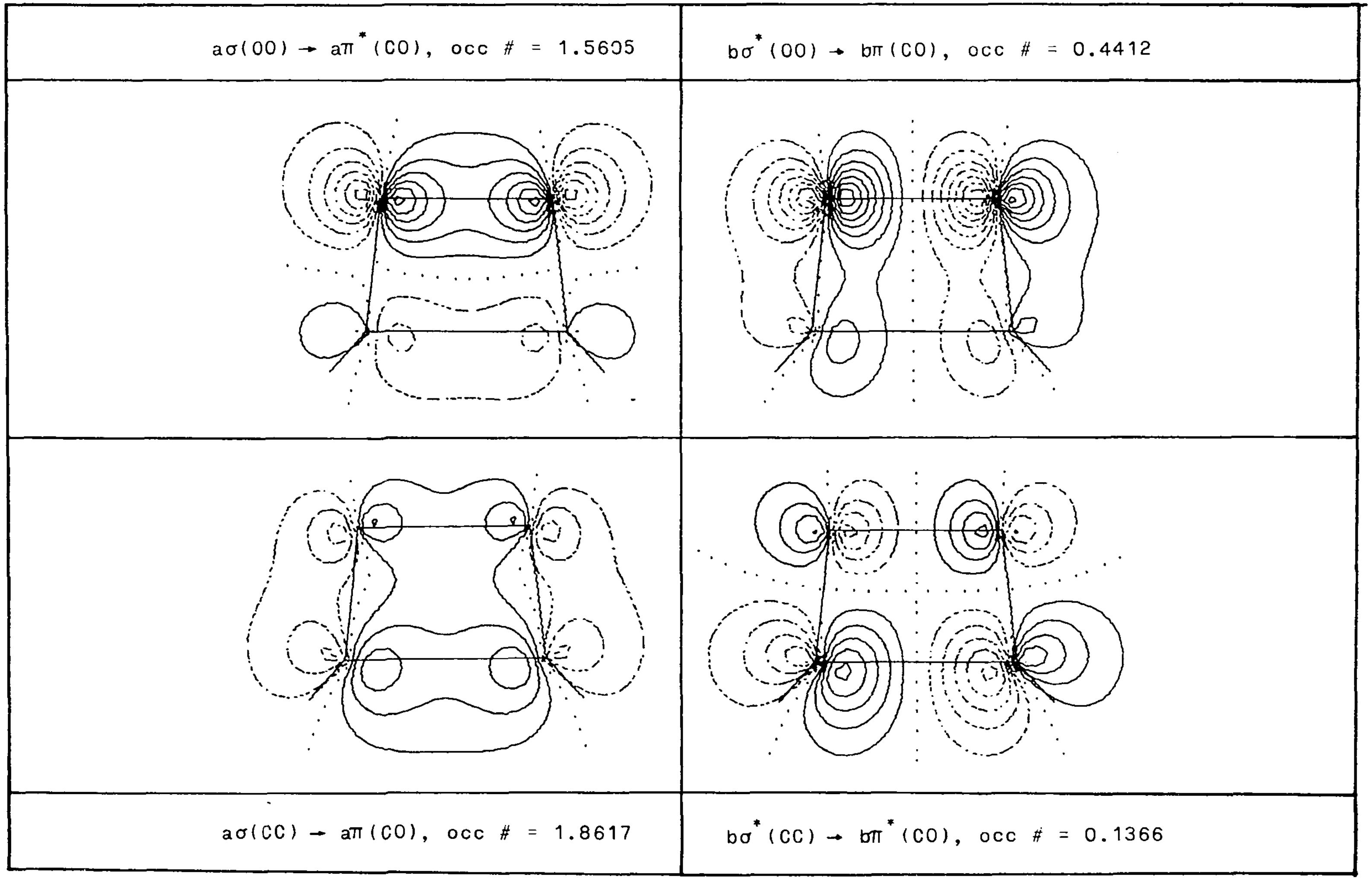
$a\sigma(\mathrm{OO}) \rightarrow a\pi^{*}(\mathrm{CO})$, occ # = 1.6565

$b\sigma^{*}(\mathrm{OO}) \rightarrow b\pi(\mathrm{CO})$, occ # = 0.3449

$a\sigma(\mathrm{CC}) \rightarrow a\pi(\mathrm{CO})$, occ # = 1.8708

$b\sigma^{*}(\mathrm{CC}) \rightarrow b\pi^{*}(\mathrm{CO})$, occ # = 0.1278

Figure 16. NRO's for 1,2-dioxetane at R_{CC} = 3.9872 a.u.



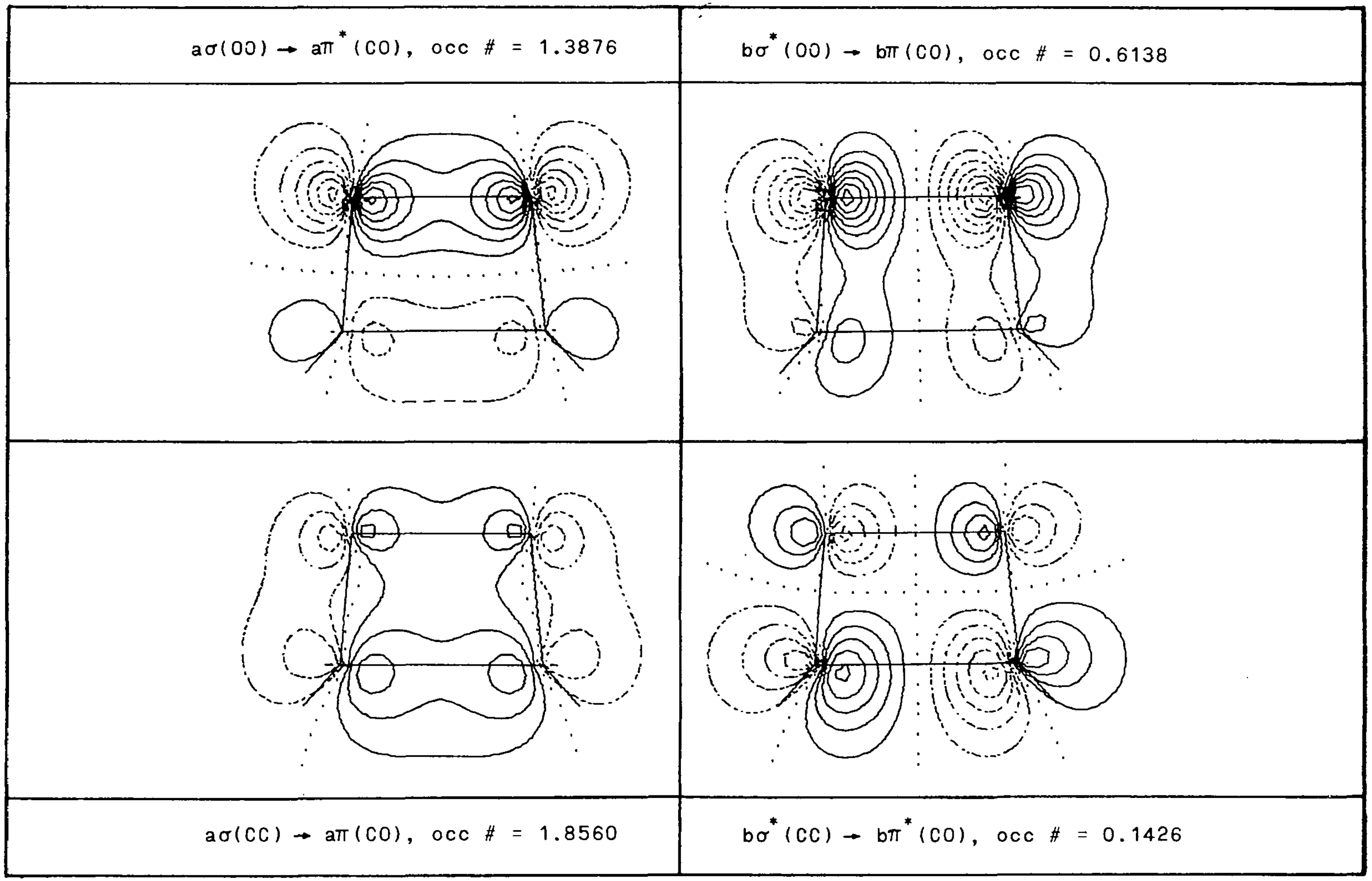
$a\sigma(OO) \rightarrow a\pi^*(CO)$, occ # = 1.5605

$b\sigma^*(OO) \rightarrow b\pi(CO)$, occ # = 0.4412

$a\sigma(CC) \rightarrow a\pi(CO)$, occ # = 1.8617

$b\sigma^*(CC) \rightarrow b\pi^*(CO)$, occ # = 0.1366

Figure 17. NRO's for 1,2-dioxetane at R_{CC} = 4.0369 a.u. (barrier maximum)



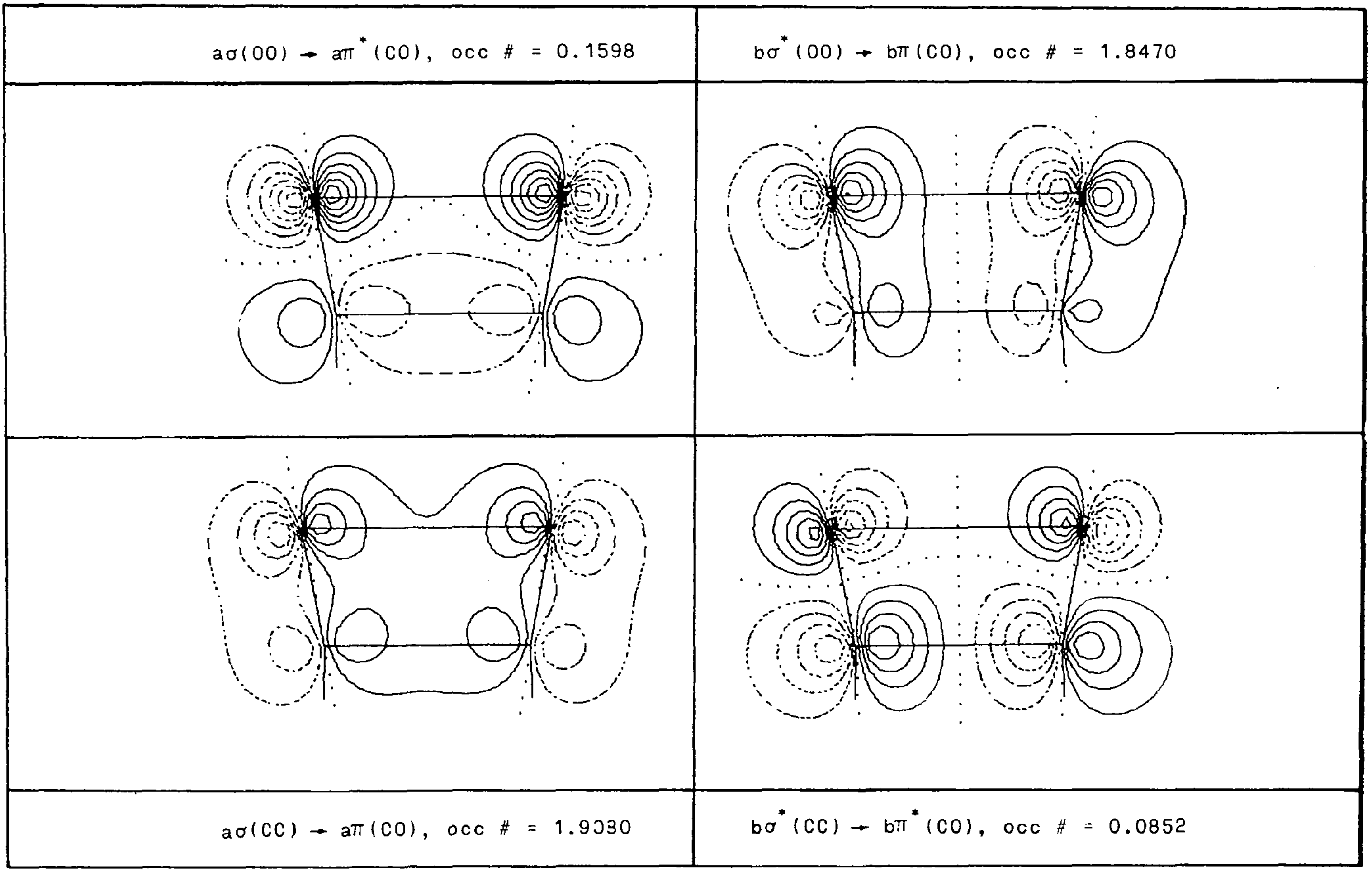
$a\sigma(OO) \rightarrow a\pi^*(CO)$, occ # = 1.3876

$b\sigma^*(OO) \rightarrow b\pi(CO)$, occ # = 0.6138

$a\sigma(CC) \rightarrow a\pi(CO)$, occ # = 1.8560

$b\sigma^*(CC) \rightarrow b\pi^*(CO)$, occ # = 0.1426

Figure 18. NRO's for 1,2-dioxetane at R_{CC} = 4.0754 a.u.



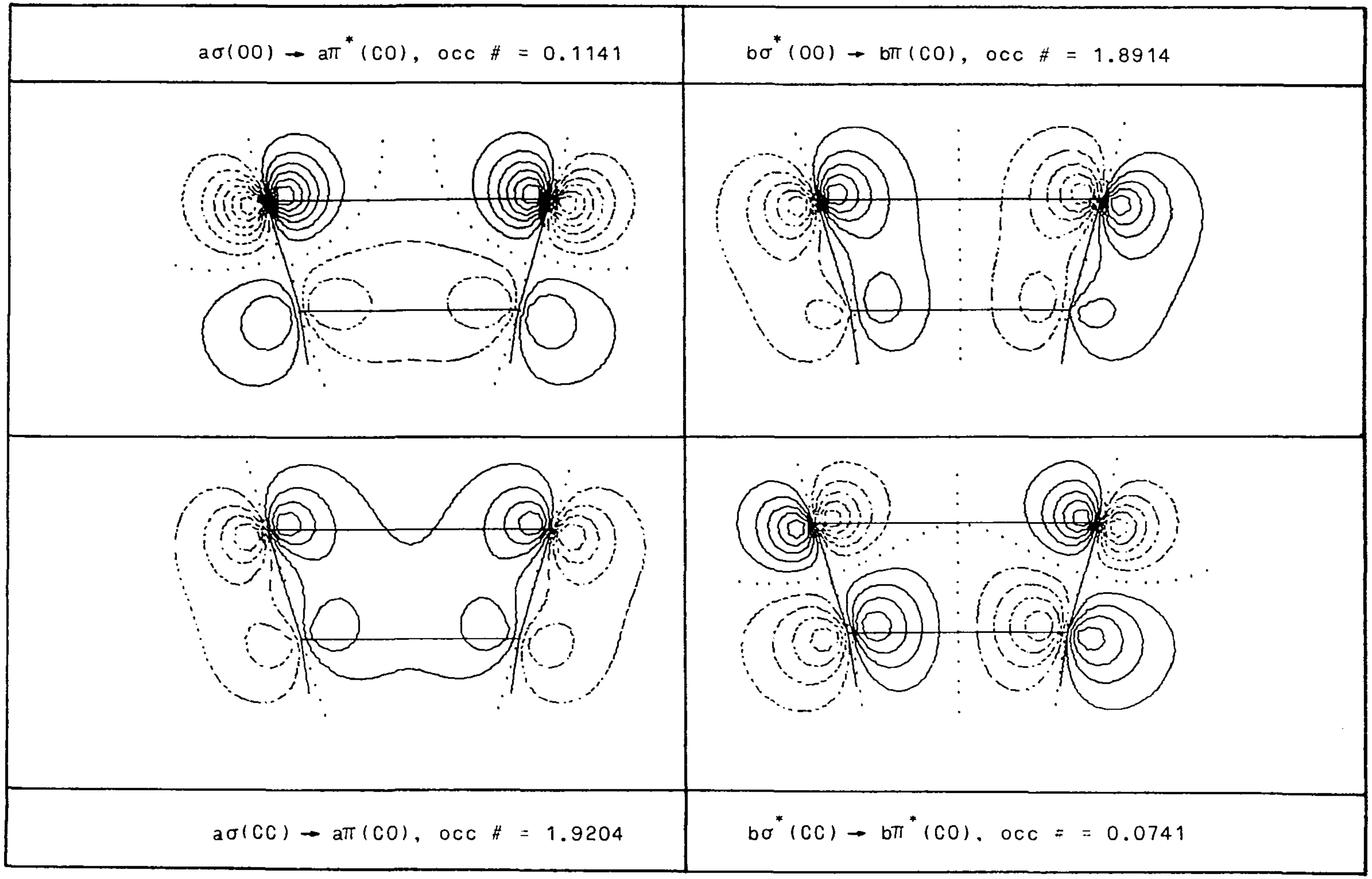
$a\sigma(OO) \rightarrow a\pi^*(CO)$, occ # = 0.1598

$b\sigma^*(OO) \rightarrow b\pi(CO)$, occ # = 1.8470

$a\sigma(CC) \rightarrow a\pi(CO)$, occ # = 1.9030

$b\sigma^*(CC) \rightarrow b\pi^*(CO)$, occ # = 0.0852

Figure 19. NRO's for 1,2-dioxetane at R_{CC} = 4.1754 a.u.



$a\sigma(OO) \rightarrow a\pi^*(CO)$, occ # = 0.1141

$b\sigma^*(OO) \rightarrow b\pi(CO)$, occ # = 1.8914

$a\sigma(CC) \rightarrow a\pi(CO)$, occ # = 1.9204

$b\sigma^*(CC) \rightarrow b\pi^*(CO)$, occ # = 0.0741

Figure 20. NRO's for 1,2-dioxetane at R_{CC} = 4.3754 a.u.

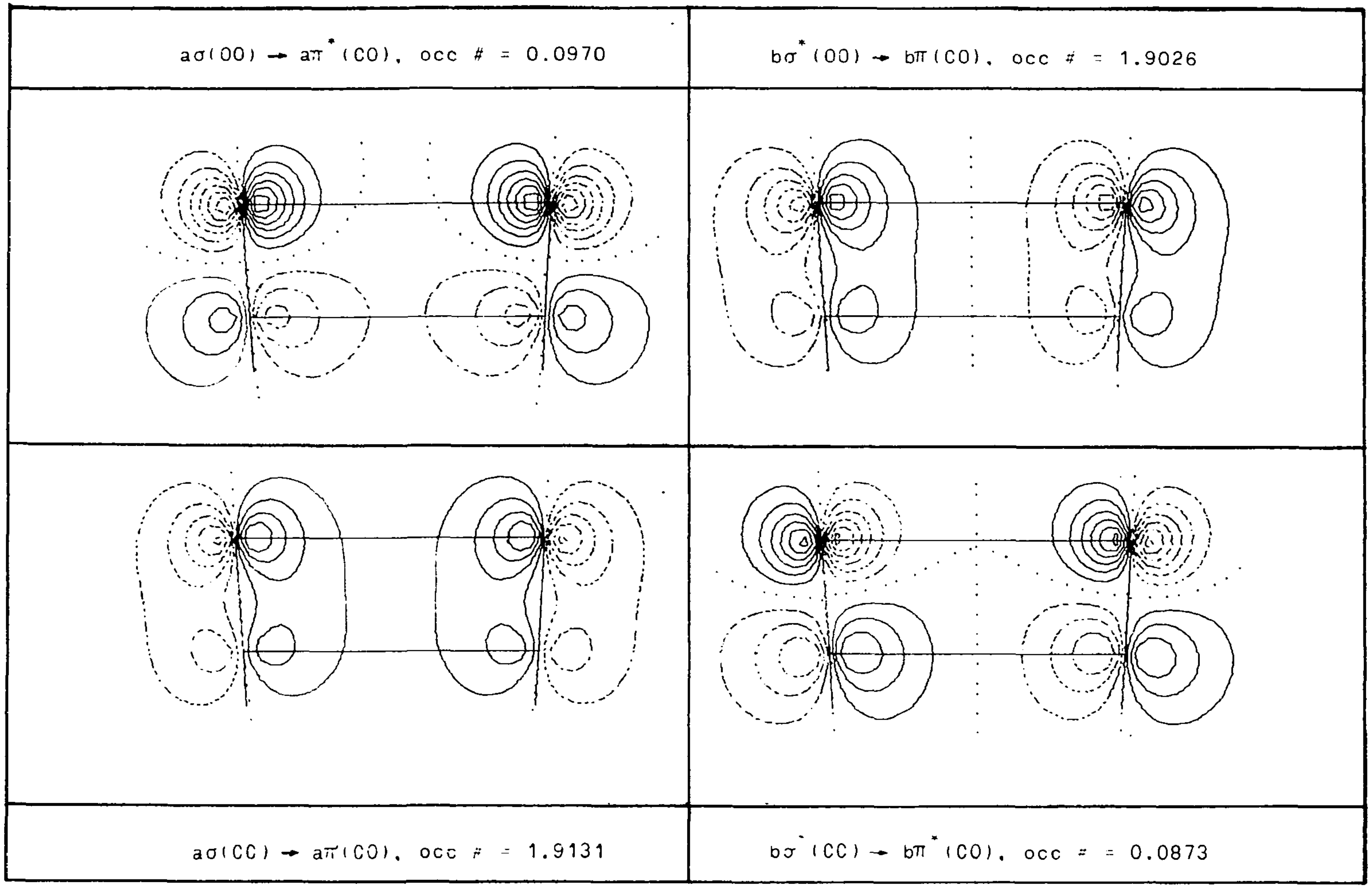
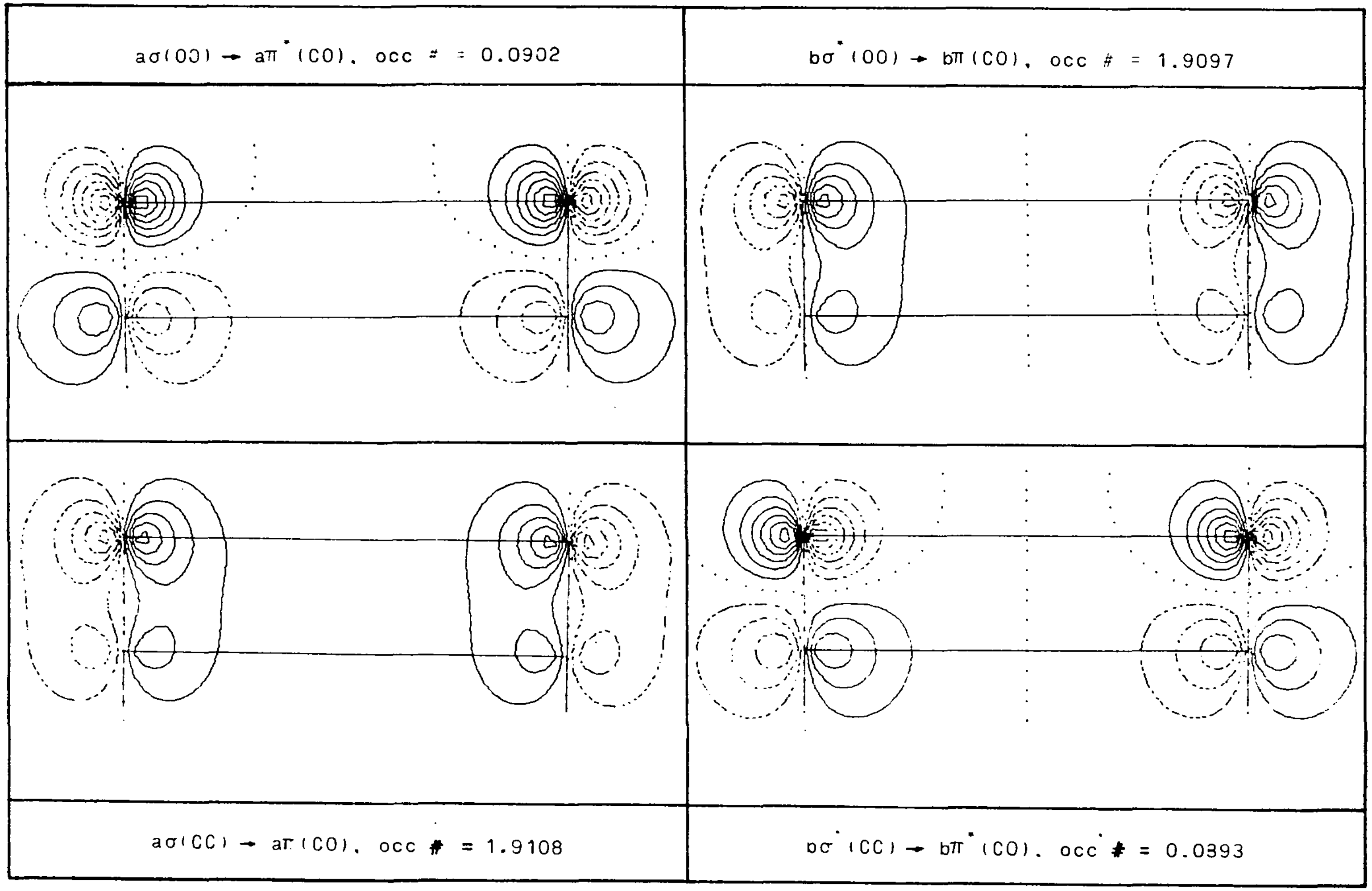


Figure 21. NRO's for 1,2-dioxetane at R_{CC} = 5.8754 a.u.



$a\sigma(OO) \rightarrow a\pi^*(CO)$, occ # = 0.0902

$b\sigma^*(OO) \rightarrow b\pi(CO)$, occ # = 1.9097

$a\sigma(CC) \rightarrow a\pi(CO)$, occ # = 1.9108

$b\sigma^*(CC) \rightarrow b\pi^*(CO)$, occ # = 0.0893

Figure 22. NRO's for 1,2-dioxetane at R_{CC} = 8.8754 a.u.

with respect to carbon-oxygen region, so this orbital is also energetically unfavorable. As a result the carbon-oxygen *pi* bonds cannot disappear until the oxygen-oxygen sigma bond is formed so that the depopulated upper right orbital can favorably recover correlation. Consequently, the association barrier is steep as well as high. The carbon-carbon *sigma* bond (the lower left panel in Figure 13) is always bonding, and it is always highly occupied; tracing the reaction from 1,2-dioxetane to the separated formaldehyde molecules we see that it rapidly delocalizes to become a symmetric combination of two *pi* bonds.

The configurational expansion coefficients are given in Table 19. The MCSCF coefficients for two separated formaldehyde molecules are given by equation 112 or its configuration interaction expansion in equation 115; these coefficients can be evaluated using the occupation numbers for an isolated formaldehyde molecules from Table 13 of Part IV, and they are shown as point ∞ in Table 24. One sees that point 10 in Table 19 has very nearly the same MCSCF expansion as point ∞, so our wavefunction really does dissociate to two separated formaldehyde molecules. The energy and occupation numbers are shown in Table 18 and displayed in Figures 23 and 24. We note that on dissociation, the MCSCF function recovers 0.079 a.u. of the 0.081 a.u. of right-left correlation energy in two formaldehyde *pi* bond systems. As a

Table 18. Energy and occupation numbers of the multiconfiguration self-consistent field wavefunction Ψ

Point	OCC # a_1	OCC # b_2	OCC # a_2	OCC # b_1	E from Ψ
1	1.9277	0.0726	1.9810	0.0187	-227.5979
2	1.8778	0.1229	1.9496	0.0497	-227.5959
3	1.7294	0.2717	1.8887	0.1102	-227.5636
4	1.6565	0.3449	1.8708	0.1278	-227.5565
5	1.5605	0.4412	1.8617	0.1366	-227.5540
6	1.3876	0.6138	1.8560	0.1426	-227.5548
7	0.1598	1.8470	1.9080	0.0852	-227.6583
8	0.1141	1.8914	1.9204	0.0741	-227.6779
9	0.0970	1.9026	1.9131	0.0873	-227.7063
10	0.0902	1.9097	1.9108	0.0893	-227.7111

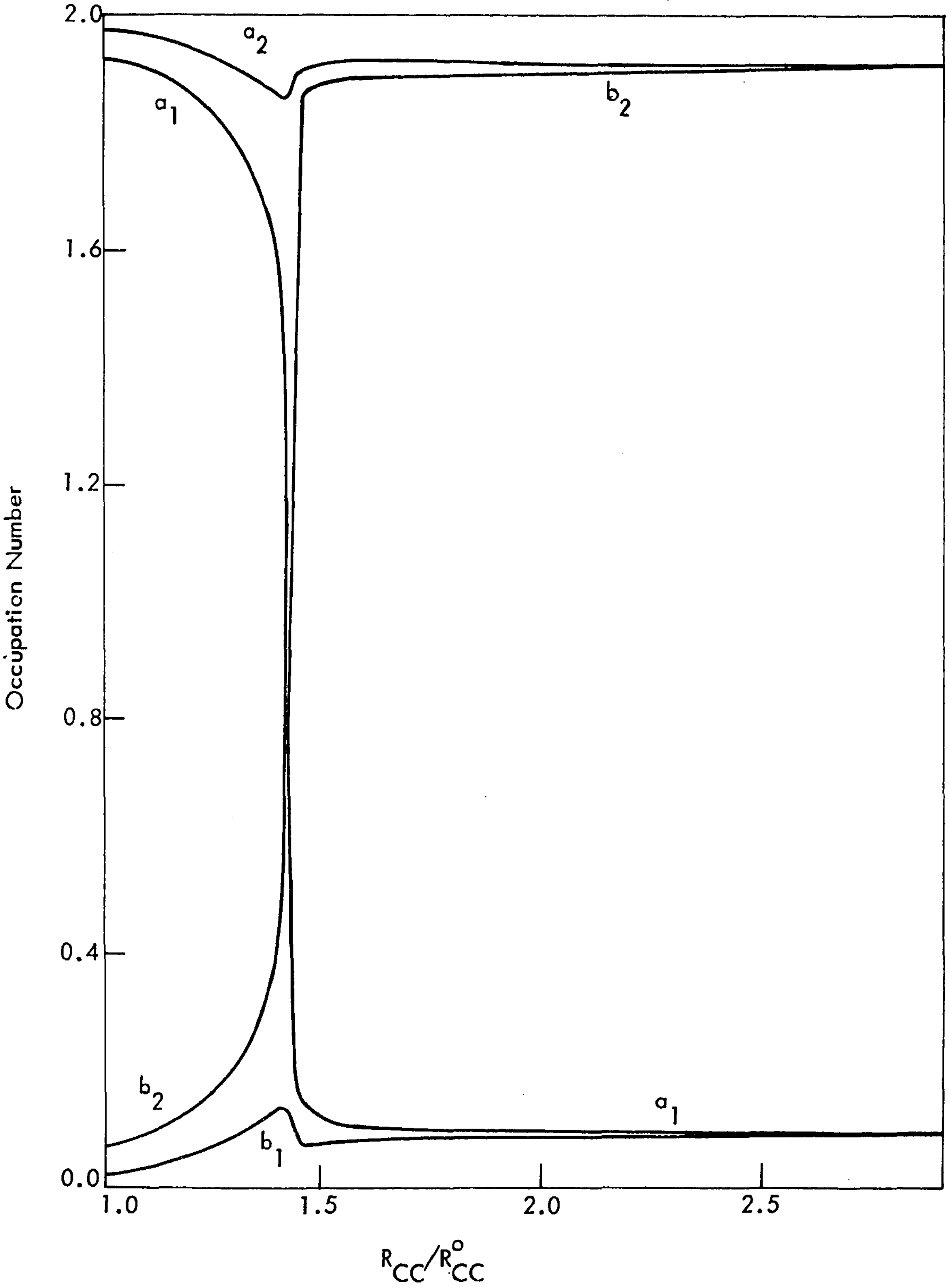


Figure 23. Occupation numbers for the MCSCF function Ψ

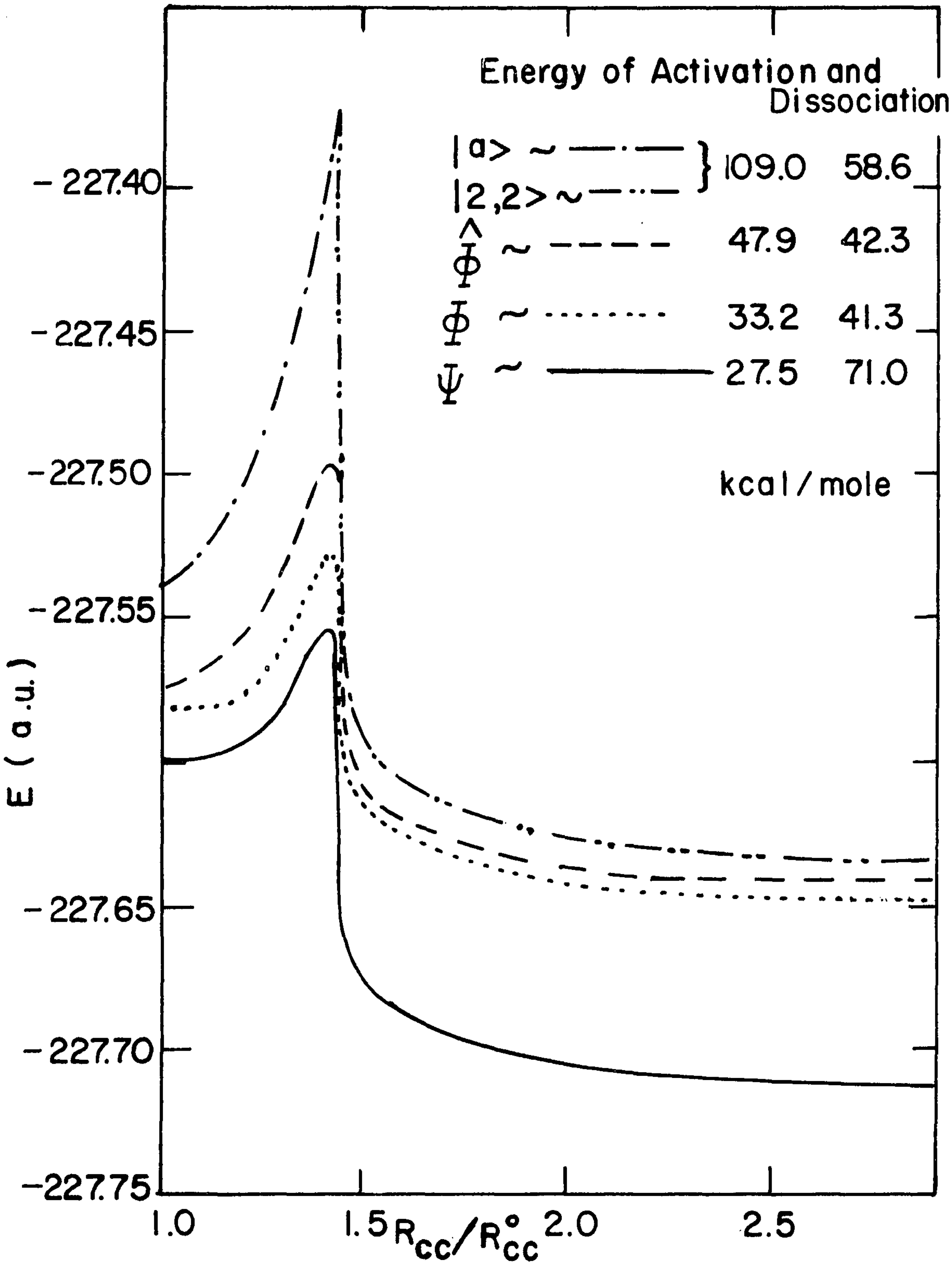


Figure 24. Total molecular energies for several wavefunctions

Table 19. Expansion Coefficients of the MCSCF wavefunction

Point	$\vert 1,1\rangle$	$\vert 1,2\rangle$	$\vert 1,3\rangle$	$\vert 2,1\rangle$	$\vert 2,2\rangle$	$\vert 2,3\rangle$
1	-0.0923	-0.0031	0.0208	-0.0013	-0.1884	-0.0104
2	-0.1358	-0.0143	0.0551	-0.0114	-0.2372	-0.0346
3	-0.1369	-0.0609	-0.0935	-0.0580	-0.3222	-0.0609
4	-0.1283	-0.0730	-0.0866	-0.0695	-0.3586	0.0548
5	-0.1241	-0.0707	-0.0757	-0.0662	-0.4128	0.0444
6	-0.1193	-0.0553	0.0574	-0.0507	-0.5013	-0.0291
7	0.0518	-0.1041	-0.0114	-0.0857	0.9383	0.0021
8	0.0433	-0.1028	-0.0083	-0.0882	0.9529	0.0011
9	0.0455	-0.1048	-0.0028	-0.1057	0.9539	0.0005
10	0.0448	-0.1039	0.0001	-0.1041	0.9551	-0.0001
∞	0.0499	-0.1089	0.0	-0.1089	0.9500	0.0

Table 19. (Continued)

Point	$|_{3,1}\rangle$	$|_{3,2}\rangle$	$|_{3,3}\rangle$	$|a\rangle$	$|b\rangle$	$|T\rangle$
1	-0.0101	0.0048	-0.0031	0.9771	0.0185	0.0169
2	-0.0459	0.0284	0.0180	0.9566	0.0387	0.0288
3	-0.0895	0.0583	-0.1497	0.9029	0.0788	-0.0516
4	-0.0827	0.0527	-0.2005	0.8786	0.0914	-0.0642
5	-0.0715	0.0429	-0.2289	0.8493	0.1008	-0.0797
6	-0.0530	0.0290	0.2530	0.7962	0.1104	0.1040
7	-0.0177	0.0009	0.1441	-0.2016	-0.0820	0.1738
8	-0.0126	0.0004	0.1213	-0.1531	-0.0785	0.1652
9	-0.0053	-0.0008	0.1099	-0.1166	-0.0924	0.1777
10	-0.0008	-0.0001	-0.1049	-0.1043	-0.1019	-0.1785
∞	0.0	0.0	-0.1089	-0.1089	-0.1089	-0.1886

result, our CCRS is a very reasonable approximation to the true one; and along the C_{2V} dissociation path, we can accept the MCSCF dissociation curve as an essentially final result.

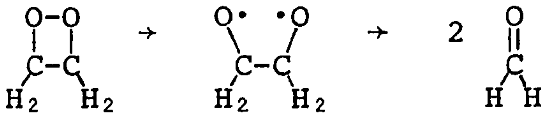
General Conclusions and Criticisms

The MCSCF function predicts a dissociation energy of 70.9 kcal/mole, only slightly greater than the value from Part IV, so our use of a limited optimization for the SPIP functions was adequate. The activation energy is predicted to be 27.5 kcal/mole, and this is essentially the expected experimental value (Kopecky and Mumford, 1969; O'Neal and Richardson, 1970, 1971; Richardson *et al*., 1972; Wilson and Schaap, 1971; Turro and Lechtken, 1973).

Other authors (Dewar and Kirschner, 1974) using a semi-empirical approach, two configuration MINDO/3 (Bingham *et al*., 1975a,b,c,d; Bingham and Dewar, 1972) calculated an activation energy of 45.0 kcal/mole along a reaction path unconstrained as to symmetry or planarity and involving a puckered ring with a dihedral angle of 31.5°. In contrast to the semi-empirical results the quantitative results of our twelve configuration *ab initio* MCSCF calculation are in gratifying agreement with the experimental values. It therefore seems questionable whether a distortion of the ring would substantially lower the activation energy, although these paths deserve further investigation.

Using our dissociation energy of 0.113 a.u. and the formaldehyde triplet $n \rightarrow \pi^*$ excitation energy of 0.115 a.u. (Herzberg, 1966) the energy difference between the barrier maximum and the reaction products is adequate to create an excited formaldehyde molecule. But we have seen that the energy of ground state 1,2-dioxetane is strongly dependent on the carbon-oxygen bond length, and this parameter is a feature of the triplet state surfaces too. On these excited surfaces, however, we must take care to let the two halves of the molecule dissociate to different geometries because the ground and excited states of formaldehyde do have different structures, and these structures do differ greatly in the carbon-oxygen bond length (Herzberg, 1966).

As a final note, this reaction is an example of a symmetry forbidden reaction (Woodward and Hoffmann, 1970), which means the reaction must pass through the avoided crossing we have discussed. An attempt to avoid the crossing by distorting the molecule from its C_{2v} symmetry to the lower C_2 symmetry is futile; even for the reaction with C_2 symmetry, the HF molecule must still discontinuously cross over from a wavefunction with two doubly occupied A-type RMO's to a wavefunction with one doubly occupied A-type and one doubly occupied B-type RMO. This process still presents a crossing, and avoiding the crossing still creates a barrier. Further reduction of symmetry cannot really avoid the crossing; the distortion must be great enough to invert the energy order of the |a> and |2,2> HF functions, and at the molecular equilibrium, these functions are 176 kcal/mole apart. Clearly, no symmetry allowed path is possible, and the conventional expectation is that the reaction proceeds through an intermediate biradicaloid (Dewar et al., 1974)



(119)

An intermediate like the one above can be represented by the one- or two-geminal SPIP functions $\hat{\Phi}$ or Φ where the expansion coefficients of the first geminal are almost equal and opposite in sign:

$$\Phi \approx 1/\sqrt{2}\ A\{F(a_1^2 - b_2^2)\, a_2^2\ \Theta_{--}\} . \tag{120}$$

The transformation in equation 9-1,3 then leads to the expression

$$\Phi \approx A\{F(\ell_o r_o + r_o \ell_o)\, a_2^2\ \Theta_{--}\}, \tag{121-1}$$

with

$$\langle \ell_o | r_o \rangle = 0, \tag{121-2}$$

which is the biradical intermediate above. From the discussion of orbital crossing shown in Table 15 it is apparent that the biradical structure occurs at a carbon-carbon bond length about 0.1 a.u. longer than that of the barrier maximum. At the position of the maximum itself the occupation numbers in Table 16 and 17 show that the molecular HF configuration $|a\rangle$ still dominates in both SPIP functions. At this point the one-geminal SPIP function can be cast in the form of equation 121-1 if, in contrast to equation 121-2, the orbitals ℓ_0 and r_0 are permitted to be the nonorthogonal GVB orbitals (Hay et al., 1972a,b,c) defined by

$$\begin{pmatrix} \ell_o \\ r_o \end{pmatrix} \approx \begin{pmatrix} u \\ \nu \end{pmatrix} = \begin{pmatrix} 0.8331 & 0.5532 \\ 0.8331 & -0.5532 \end{pmatrix} \begin{pmatrix} a_1 \\ b_2 \end{pmatrix} ,$$

$$\langle u|\nu\rangle = 0.3881.$$

The overlap between u and ν indicates that the oxygen-oxygen bond has been substantially weakened. The orbital, u, is shown in the contour plot of Figure 25; there we see that the oxygen-oxygen bond is almost broken, but the electron density does cover both atoms, so the system is not a biradical, although it is well on its way toward becoming one.

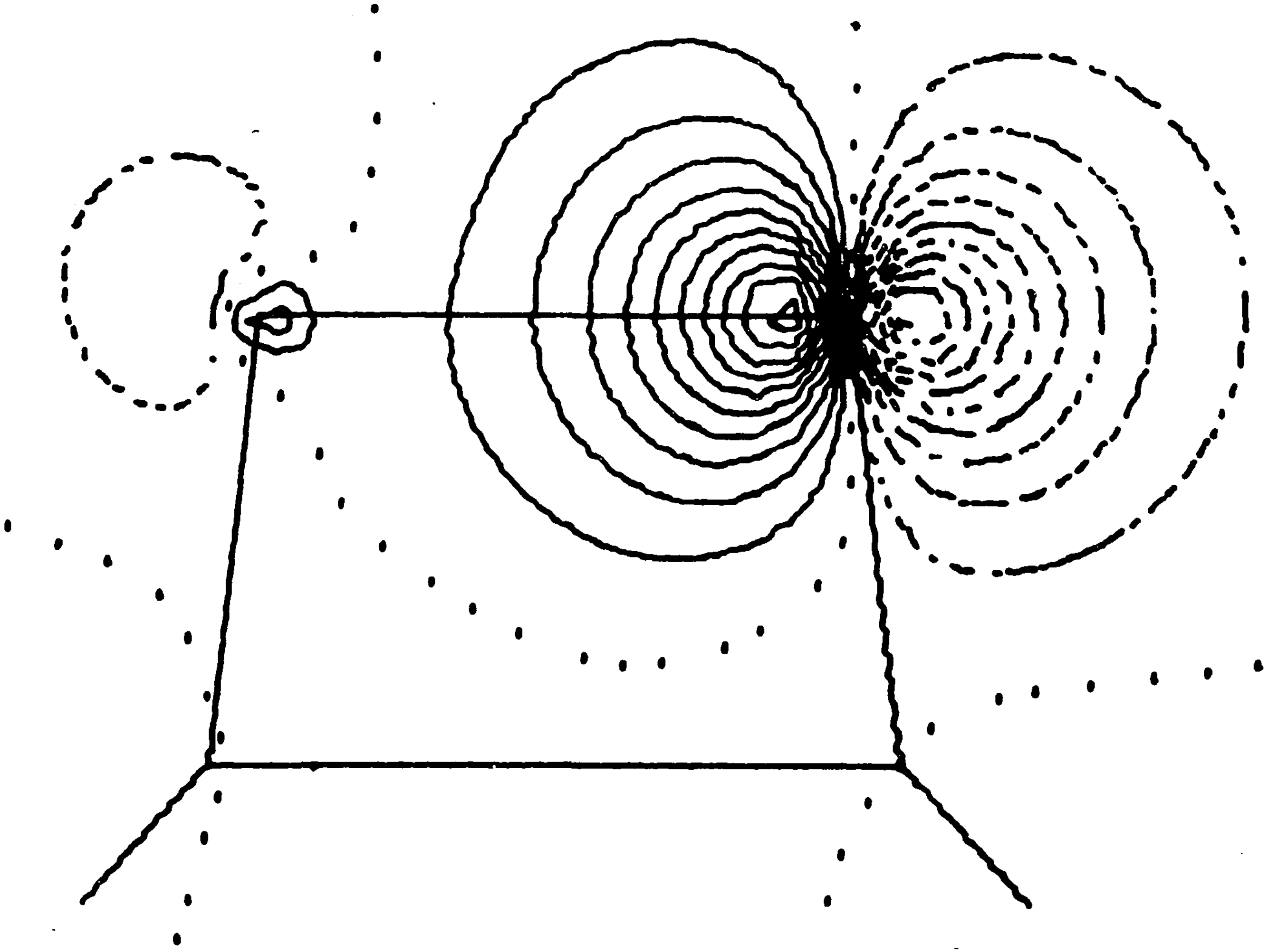


Figure 25. GVB orbital for the one-geminal SPIP function $\hat{\Phi}$ at the barrier maximum

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APPENDIX A: BASIS SETS FOR THE GEOMETRY OPTIMIZATION

BASIS SETS FOR THE GEOMETRY OPTIMIZATION

The choice of atomic orbital basis sets is an important step in the execution of any molecular calculation; accordingly, we used several well tested and optimized even-tempered contracted gaussian atomic orbital (ETCGAO) bases (Raffenetti, 1973c; Ruedenberg et al., 1973; Bardo and Ruedenberg, 1974a,b). The general form of these functions is given by

$$\chi(x,y,z) = x^{\ell} y^{m} z^{n} R(r) ,$$

$$R(r) = \sum_{\kappa=1}^{N} C_{\kappa} \exp\{-\alpha\beta^{\kappa} r^{2}\},$$

$$r^{2} = x^{2} + y^{2} + z^{2},$$

$$\alpha > o, \beta > 1.$$

The even-tempered parameters (α,β) are optimized using uncontracted Hartree-Fock calculations to minimize the energy of an appropriate molecule; these parameters and the molecule used to optimize them are shown in Tables 20 to 29 . The contraction coefficients (C_{κ}) in Tables 20 to 25 are unpublished data from Lap M. Cheung, for H_2CO, and Mary G. Dombeck, for HNO, using a modification (Cheung, 1975) of the Bardo and Ruedenberg (1974a) contraction method. The parameters and expansions in Tables 26 to 28 are from Bardo and Ruedenberg (1974b). The ozone basis in Table 29 is an unpublished calculation by Lap M. Cheung.

Table 20. ETCGAO basis for hydrogen in formaldehyde

	$\alpha(s)=0.0299867$	$\beta(s)4.5997410$
primitive	s	s'
1	0.6789260	0.7340750
2	0.7213810	-0.6634220
3	0.1331470	-0.1415190
4	0.0306930	-0.0312770

Table 21. ETCGAO basis for carbon in formaldehyde

	$\alpha(s)=0.1075284$	$\beta(s)=4.1288545$	
primitive	s	s'	s"
1	0.5475800	0.8340390	0.0482220
2	-0.3012810	0.1308840	0.9095570
3	-0.7202730	0.4781380	-0.3943320
4	-0.2948490	0.2371270	0.1215780
5	-0.0587260	0.0475310	0.0078740
6	-0.0144200	0.0119690	0.0062930

	$\alpha(p)=0.0390466$	$\beta(p)=3.8845222$
primitive	p	p'
1	0.4094760	0.9122590
2	0.8685250	-0.3933400
3	0.2729360	-0.1115800
4	0.0591570	-0.0248240

Table 22. ETCGAO basis for oxygen in formaldehyde

	$\alpha(s)=0.1679649$	$\beta(s)=4.1371204$	
primitive	s	s'	s"
1	0.8111110	0.5824290	-0.0506600
2	-0.1103360	0.2104570	0.8285180
3	-0.5278950	0.6911300	-0.4121000
4	-0.2218300	0.3648890	0.3692490
5	-0.0439200	0.0730870	0.0659010
6	-0.0107280	0.0183820	0.0218420

	$\alpha(p)=0.0599647$	$\beta(p)=4.0108372$
primitive	p	p'
1	0.5995470	0.7965440
2	0.7383900	-0.5878460
3	0.3025730	-0.1361320
4	0.0614270	-0.0377080

Table 23. ETCGAO basis for hydrogen in nitrosyl hydride

	$\alpha(s)=0.0407336$	$\beta(s)=4.2276422$
primitive	s	s'
1	0.4267770	-1.8382290
2	0.5125120	1.3920570
3	0.0868630	0.3800230
4	0.0244300	0.0855920

Table 24. ETCGAO basis for nitrogen in nitrosyl hydride

	$\alpha(s)=0.0438420$	$\beta(s)=3.8300788$	
primitive	s	s'	s"
1	0.2059580	-0.5137160	-2.4928880
2	0.2442040	-0.7861930	3.1111090
3	0.1140320	0.2291580	-0.3586680
4	0.3508160	0.6257830	-0.4379740
5	0.1870370	0.2759150	-0.1145250
6	0.0411870	0.0601480	-0.0215390
7	0.0119970	0.0170750	-0.0056920

	$\alpha(p)=0.055881$	$\beta(p)=3.7693262$
primitive	p	p'
1	0.3533540	1.3246520
2	0.5498460	-0.9337550
3	0.1992790	-0.2243110
4	0.0457080	-0.0595210

Table 25. ETCGAO basis for oxygen in nitrosyl hydride

	$\alpha(s)=0.1109396$	$\beta(s)=4.1552987$	
primitive	s	s'	s"
1	0.3165290	-1.0336990	-2.4141910
2	0.1129470	-0.2599030	4.0645910
3	0.3419410	0.6732800	-1.8057270
4	0.2856780	0.4024100	-0.0665220
5	0.0646890	0.0874620	-0.0272530
6	0.0165950	0.0218640	0.0034260

	$\alpha(p)=0.0663290$	$\beta(p)=3.9550482$
primitive	p	p'
1	0.4282910	1.3032600
2	0.4973540	-1.0026360
3	0.1956070	-0.1792170
4	0.0394200	-0.0590200

Table 26. ETCGAO basis for hydrogen in formaldehyde

	$\alpha(s)=0.0299909$	$\beta(s)=4.6010943$
primitive	s	s'
1	0.5859375	0.7987733
2	0.7968974	-0.5376933
3	0.1431862	-0.2671444
4	0.0336078	-0.0384845

Table 27. ETCGAO basis for carbon in carbon monoxide

	$\alpha(s)=0.0543828$	$\beta(s)=4.3195748$	
primitive	s	s'	s"
1	0.8662280	0.4529010	-0.2101710
2	0.1663410	0.1166960	0.9559890
3	-0.4105110	0.6963390	-0.1401550
4	-0.2260000	0.5313010	0.1462500
5	-0.0475840	0.1155050	0.0284490
6	-0.0110000	0.0274370	0.0084800

	$\alpha(p)=0.0550266$	$\beta(p)=3.2337097$
primitive	p	p'
1	0.6206510	0.7837900
2	0.7532790	-0.5886280
3	0.2135540	-0.1954240
4	0.0419360	-0.0316140

Table 28. ETCGAO basis for oxygen in carbon monoxide

	$\alpha(s)=0.0725275$	$\beta(s)=3.2337097$	
primitive	s	s'	s"
1	0.4521470	0.3491610	0.8145230
2	0.6830450	0.4412730	-0.5764880
3	0.0171610	0.1419560	0.0459140
4	-0.4601460	0.5743340	-0.0257760
5	-0.3231320	0.5417950	-0.0335440
6	-0.1077980	0.1914300	-0.0172070
7	-0.0301020	0.0550010	-0.0044330
8	-0.0060170	0.0109640	-0.0010460
9	-0.0024360	0.0044800	-0.0003810

	$\alpha(p)=0.0784011$	$\beta(p)=3.2225504$
primitive	p	p'
1	0.4770330	0.8778440
2	0.7608550	-0.4368230
3	0.4220640	-0.1885180
4	0.1206710	-0.0532240
5	0.0289700	-0.0142500

Table 29. ETCGAO basis for oxygen in ozone

	$\alpha(s)=0.1594857$	$\beta(s)=4.2541016$	
primitive	s	s'	s"
1	0.8618460	0.5048050	-0.0388990
2	-0.0963350	0.2254870	0.9475750
3	-0.4627540	0.7447290	-0.3045840
4	-0.1804570	0.3667310	0.0881110
5	-0.0342370	0.0702540	0.0059670
6	-0.0078860	0.0166980	0.0042510

	$\alpha(p)=0.0643795$	$\beta(p)=3.9815829$
primitive	p	p'
1	0.5187570	0.8503720
2	0.7992440	-0.5187550
3	0.2972350	-0.0833670
4	0.0612470	-0.0284880

APPENDIX B: BASIS SETS FOR THE FINAL CALCULATIONS

BASIS SETS FOR THE FINAL CALCULATIONS

The basis sets used to perform the final calculations are an extended version of the basis sets used to optimize the molecular geometries. They are all even-tempered contracted gaussian atomic orbital bases, and a discussion of the meaning of their parameters and coefficients is contained in Appendix A. All of the optimizations and contractions in the following tables are unpulbished results by Lap M. Cheung using his contraction method (Cheung, 1975).

Table 30. ETCGAO basis for carbon in formaldehyde

	$\alpha(s)=0.0242195$	$\beta(s)=3.2063925$	
primitive	s	s'	s"
1	0.0137150	-0.0629870	-1.8029280
2	0.1088610	-0.8917030	0.4542790
3	0.0358780	-0.4706850	2.1151470
4	0.2346590	0.3971780	-0.7930900
5	0.4232030	0.4442640	-0.2474450
6	0.2039680	0.1924340	-0.0885440
7	0.0644190	0.0583470	-0.0136200
8	0.0137500	0.0124280	-0.0433720
9	0.0056360	0.0050410	-0.0113790

	$\alpha(p)=0.0268053$	$\beta(p)=2.9919340$
primitive	p	p'
1	0.0567650	-0.8538230
2	0.4117370	-0.3165590
3	0.4551000	0.6802190
4	0.1599700	0.1895550
5	0.0445040	0.0594730
6	0.0116540	0.0138630

Table 31. ETCGAO basis for oxygen in formaldehyde

	$\alpha(s)=0.0731968$	$\beta(s)=3.2282784$	
primitive	s	s'	s"
1	0.4392040	0.3355600	0.8272630
2	0.6693410	0.4812820	-0.5594070
3	0.0167120	0.1439360	0.0470140
4	-0.4794780	0.5591720	-0.0061970
5	-0.3391210	0.5327290	-0.0174100
6	-0.1133720	0.1884420	-0.0118110
7	-0.0316450	0.0541300	-0.0028680
8	-0.0063280	0.0107890	-0.0007430
9	-0.0025580	0.0044030	-0.0002530

	$\alpha(p)=0.0535923$	$\beta(p)=3.1166450$
primitive	p	p'
1	0.3412510	0.8989150
2	0.7239350	-0.0703100
3	0.5560660	-0.4212830
4	0.2185960	-0.0904760
5	0.0484450	-0.0362580
6	0.0112040	-0.0053350

Table 32. ETCGAO basis for hydrogen in ethylene

	$\alpha(s)=0.0390622$	$\beta(s)=4.3199940$
primitive	s	s'
1	0.4178300	-1.7319180
2	0.5043660	1.1741740
3	0.1075540	0.5039230
4	0.0246300	0.0818230

Table 33. ETCGAO basis for carbon in methane

	$\alpha(s)=0.0243209$	$\beta(s)=3.2033715$	
primitive	s	s'	s"
1	0.0068870	-0.0749460	2.3602130
2	0.1388180	-0.9229470	-1.7568120
3	0.0444630	-0.4027730	-1.0288460
4	0.2250360	0.3868860	5.2700320
5	0.4124420	0.4466200	0.2066050
6	0.1998360	0.1935270	0.0709750
7	0.0632650	0.0590250	0.0140780
8	0.0135180	0.0125420	0.0036720
9	0.0055550	0.0051150	0.0011460

	$\alpha(p)=0.0263207$	$\beta(p)=2.9985940$
primitive	p	p'
1	0.0979820	-0.4563680
2	0.4205740	-0.8567460
3	0.4256950	0.9267840
4	0.1525060	0.2211000
5	0.0429550	0.0887280
6	0.0107020	0.0197940

Table 34. ETCGAO basis for oxygen in hydrogen peroxide

	$\alpha(s)=0.0733730$	$\beta(s)=3.2270940$	
primitive	s	s'	s"
1	0.4676040	0.3271170	0.8130580
2	0.6711700	0.4571110	-0.5782460
3	0.0211140	0.1435800	0.0648080
4	-0.4620280	0.5739050	-0.0008770
5	-0.3230880	0.5423740	-0.0147600
6	-0.1078430	0.1916310	-0.0118700
7	-0.0300700	0.0550450	-0.0028210
8	-0.0060170	0.0109730	-0.0007610
9	-0.0024320	0.0044810	-0.0002580

	$\alpha(p)=0.0586350$	$\beta(p)=3.068709$
primitive	p	p'
1	0.3853470	0.9203380
2	0.7276870	-0.3458710
3	0.5257570	-0.1754550
4	0.2081410	-0.0474840
5	0.0459540	-0.0173230
6	0.0111230	-0.0033650

Table 35. ETCGAO basis for hydrogen in nitrosyl hydride

primitive	$\alpha(s)=0.0500366$ s	$\beta(s)=4.1661819$ s'
1	0.5188660	-1.8293740
2	0.4358940	1.4253440
3	0.0730970	0.3865590
4	0.0206670	0.0872400

Table 36. ETCGAO basis for nitrogen in nitrosyl hydride

primitive	$\alpha(s)=0.033651$ s	$\beta(s)=3.2142257$ s'	s"
1	0.0770050	-0.1906600	2.2333020
2	0.2974990	-0.7565320	-1.5296660
3	0.1210840	-0.3539770	-1.2501790
4	0.1481040	0.3992680	0.5606030
5	0.3028230	0.5285130	0.2425950
6	0.1485370	0.2297940	0.0913100
7	0.0464450	0.0700390	0.0186980
8	0.0099150	0.0147460	0.0048830
9	0.0040260	0.0059900	0.0015760

primitive	$\alpha(p)=0.0289206$ p	$\beta(p)=3.0952397$ p'
1	0.0591830	-0.5281820
2	0.3869920	-0.7924210
3	0.4538760	0.8786590
4	0.1913060	0.1796480
5	0.0510060	0.0774770
6	0.0124760	0.0152180

Table 37. ETCGAO basis for oxygen in nitrosyl hydride

	$\alpha(s)=0.0733254$	$\beta(s)=3.2273069$	
primitive	s	s'	s"
1	0.2066350	-0.4766670	-2.8047140
2	0.2931850	-0.6966010	3.2875840
3	0.0720650	-0.0074890	-0.0801760
4	0.2350160	0.5703730	-0.4729610
5	0.2333000	0.4144480	-0.2008850
6	0.0830640	0.1394900	-0.0419520
7	0.0239460	0.0390720	-0.0118240
8	0.0047720	0.0078120	-0.0018970
9	0.0019510	0.0031630	-0.0008630

	$\alpha(p)=0.0592139$	$\beta(p)=3.0634773$
primitive	p	p'
1	0.2249900	-1.1202020
2	0.4472430	0.2230740
3	0.3310850	0.5895570
4	0.1286790	0.1249650
5	0.0288170	0.0516300
6	0.0069130	0.0078610

Table 38. ETCGAO basis for hydrogen in ammonia

	$\alpha(s)=0.0376519$	$\beta(s)=4.6017842$
primitive	s	s'
1	0.3928510	1.6595630
2	0.5306940	-1.0940650
3	0.1128660	-0.5158390
4	0.0213100	-0.0653530

Table 39. ETCGAO basis for nitrogen in ammonia

	$\alpha(s)=0.0339598$	$\beta(s)=3.2088370$	
primitive	s	s'	s"
1	0.0071930	-0.0695780	2.4243490
2	0.1919810	-0.9106650	-1.9537570
3	0.0721350	-0.4049810	-0.7134660
4	0.2074860	0.3911200	0.2643340
5	0.3845690	0.4807060	0.2729130
6	0.1847940	0.2039870	0.0857680
7	0.0577870	0.0619560	0.0269720
8	0.0123130	0.0130190	0.0050240
9	0.0050350	0.0053200	0.0022010

	$\alpha(p)=0.0368008$	$\beta(p)=3.0087726$
primitive	p	p'
1	0.1932010	-1.7314670
2	0.4272230	0.2004870
3	0.3526290	0.5635610
4	0.1486160	0.1368180
5	0.0384560	0.0562590
6	0.0101800	0.0111430

Table 40. ETCGAO basis for oxygen in ozone

	$\alpha(s)=0.0731993$	$\beta(s)=3.2281750$	
primitive	s	s'	s"
1	0.4361870	0.2820060	0.8488880
2	0.7168680	0.4501760	-0.5257340
3	0.0231180	0.1384850	0.0519210
4	-0.4385050	0.5918240	-0.0004860
5	-0.3034350	0.5539230	-0.0133700
6	-0.1006190	0.1956010	-0.0105570
7	-0.0280570	0.0560840	-0.0025280
8	-0.0055990	0.0111890	-0.0006730
9	-0.0022650	0.0045620	-0.0002260

	$\alpha(p)=0.0592139$	$\beta(p)=3.0634773$
primitive	p	p'
1	0.2433170	0.9693970
2	0.7827070	-0.2140310
3	0.5294690	-0.1156670
4	0.2134040	-0.0306150
5	0.0464530	-0.0117930
6	0.0114320	-0.0020380

APPENDIX C: MOLECULAR ORBITALS FOR THE RADICAL-DIMER SYSTEMS

MOLECULAR ORBITALS FOR THE RADICAL-DIMER SYSTEMS

In Part IV of this work we calculated wavefunctions for the dimers and monomers shown in equations 83-1,3. In the following tables we present their MO's and occupation numbers calculated using the Hartree-Fock method and the SPIP procedure outlined in Parts I to III of this work. The basis sets were taken from the even-tempered contracted bases (ETCGAO) in Appendices A and B, and the specific basis for each wavefunction is specified in Table 5 of Part IV.

Table 41. Hartree-Fock orbitals for formyl radical

		(1a)	(2a)	(3a)	(4a)	(5a)	(6a)	(7a)	(1b)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.000000	2.000000
C	S	0.000018	-0.000902	0.000210	-0.326245	0.219747	-0.191566	0.359949	0.0
	S'	0.000058	-0.000547	0.015279	0.043762	-0.014169	-0.016067	0.028145	0.0
	S''	0.000639	-0.323816	-0.283617	-0.620307	-0.113962	-0.179581	-0.485763	0.0
	X	0.000482	0.943933	-0.009276	-0.192495	-0.015627	-0.058696	-0.208817	0.0
	X'	-0.000082	0.012329	-0.060678	-0.018376	-0.030551	0.000353	0.026989	0.0
	Y	0.000260	0.003196	-0.189287	0.123582	-0.368748	0.241283	0.360752	0.0
	Y'	0.000213	0.000390	0.043481	-0.020304	0.015862	-0.013363	0.064872	0.0
	Z	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.446536
	Z'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.039277
O	S	-0.000038	0.001414	-0.023252	-0.253068	0.238458	0.252468	0.714293	0.0
	S'	-0.000025	0.000069	-0.008014	-0.015278	0.007921	0.021528	0.106991	0.0
	S''	-0.431764	-0.000931	-0.705657	0.413972	0.378322	-0.057296	0.026979	0.0
	X	0.903814	-0.002210	-0.288999	0.244410	0.238244	-0.040139	-0.009622	0.0
	X'	-0.013140	-0.002810	0.088074	0.071220	0.102973	-0.029963	-0.059597	0.0
	Y	-0.001206	0.000744	0.202572	0.212190	0.610231	-0.234680	-0.110430	0.0
	Y'	0.001275	0.002189	-0.050563	-0.048911	-0.038019	0.003775	0.016194	0.0
	Z	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.764947
	Z'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.049500
H	S	0.000032	-0.000337	-0.004028	-0.087873	0.258344	0.781946	-0.571397	0.0
	S'	-0.000000	-0.000206	0.003206	0.018280	0.002084	0.047397	-0.110303	0.0

Table 42. SPIP MO's and occupation numbers for trans-glyoxal

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.983770	2.000000	2.000000
H1	S	-0.000092	-0.000376	-0.022742	0.231823	-0.151008	0.193771	-0.146731	0.000011	-0.000392
	S'	0.000015	-0.000368	0.008448	-0.032192	0.018087	0.017571	-0.010436	0.000025	-0.000182
H2	S	-0.000092	-0.000376	-0.022742	0.231823	-0.151008	0.193771	-0.146731	-0.000011	0.000392
	S'	0.000015	-0.000368	0.008448	-0.032192	0.018087	0.017571	-0.010436	-0.000025	0.000182
C1	S	0.000214	-0.228323	-0.190451	0.379049	0.036864	-0.067228	0.378726	0.000374	-0.225967
	S'	0.000158	0.667689	-0.007206	0.107912	0.001123	-0.062191	0.123272	0.000256	0.669830
	S''	0.000002	0.008703	-0.038066	0.016009	0.016977	0.022623	0.002205	0.000012	0.007538
	X	-0.000092	0.002339	-0.117368	-0.169438	0.374524	-0.122236	0.111477	0.000212	0.001728
	X'	-0.000088	0.000884	0.013947	-0.009988	0.027031	-0.022938	0.064326	0.000165	0.000477
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Z	-0.000029	-0.001317	0.108236	-0.190351	-0.019496	0.055678	0.473214	-0.000226	0.001345
	Z'	0.000000	-0.000763	-0.006807	-0.024857	0.006418	0.001741	-0.015793	-0.000186	0.001182
C2	S	0.000214	-0.228323	-0.190451	0.379049	0.036864	-0.067229	0.378726	-0.000374	0.225967
	S'	0.000158	0.667689	-0.007206	0.107912	0.001123	-0.062191	0.123272	-0.000256	-0.669830
	S''	0.000002	0.008703	-0.038066	0.016009	0.016977	0.022623	0.002205	-0.000012	-0.007538
	X	0.000092	-0.002339	0.117368	0.169438	-0.374524	0.122236	-0.111477	0.000212	0.001728
	X'	0.000088	-0.000884	-0.013947	0.009988	-0.027031	0.022938	-0.064326	0.000165	0.000477
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Z	0.000029	0.001317	-0.108236	0.190351	0.019496	-0.055678	-0.473214	-0.000226	0.001345
	Z'	-0.000000	0.000763	0.006807	0.024857	-0.006418	-0.001741	0.015793	-0.000186	0.001182
O1	S	-0.305162	-0.001133	-0.494839	-0.313005	-0.244057	0.060780	-0.090879	-0.305359	-0.000823
	S'	0.639266	-0.001927	-0.200127	-0.179347	-0.164187	0.053659	-0.070126	0.639042	-0.001569
	S''	-0.009094	-0.002275	0.066223	-0.046208	-0.086349	0.044984	-0.043066	-0.009344	-0.001870
	X	-0.000798	0.000779	0.113214	-0.182045	-0.269588	0.412803	0.023519	-0.000666	0.000453
	X'	0.000655	0.001547	-0.033991	0.034495	0.027405	0.005247	0.008530	0.000793	0.001103
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Z	0.000506	-0.000390	-0.080035	0.058872	0.389347	0.512201	-0.211808	0.000427	-0.000719
	Z'	-0.000407	-0.000768	0.014407	0.002155	-0.014313	0.057768	-0.069224	-0.000475	-0.001123
O2	S	-0.305162	-0.001133	-0.494839	-0.313005	-0.244057	0.060780	-0.090879	0.305359	0.000823
	S'	0.639266	-0.001927	-0.200127	-0.179347	-0.164187	0.053659	-0.070126	-0.639042	0.001569
	S''	-0.009094	-0.002275	0.066223	-0.046208	-0.086949	0.044984	-0.043066	0.009344	0.001870
	X	0.000798	-0.000779	-0.113214	0.182045	0.269588	-0.412803	-0.023519	-0.000666	0.000453
	X'	-0.000655	-0.001547	0.033991	-0.034495	-0.027405	-0.005247	-0.008530	0.000793	0.001103
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Z	-0.000506	0.000390	0.080035	-0.058872	-0.389347	-0.512201	0.211808	0.000427	-0.000719
	Z'	0.000407	0.000768	-0.014407	-0.002155	0.014313	-0.057768	0.069224	-0.000475	-0.001123

Table 42. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(1a2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	0.016230	2.000000	2.000000
H1	S	0.006068	-0.220429	-0.059354	0.212802	-0.118582	0.0	0.0
	S'	-0.005774	0.039766	0.013878	0.004794	0.001589	0.0	0.0
H2	S	-0.006068	0.220429	0.059354	-0.212802	0.118582	0.0	0.0
	S'	0.005774	-0.039766	-0.013878	-0.004794	-0.001589	0.0	0.0
C1	S	0.218460	-0.388295	0.218548	0.236857	0.643277	0.0	0.0
	S'	0.035022	-0.124206	0.085541	0.121721	0.183125	0.0	0.0
	S''	0.025858	-0.008181	0.001147	-0.031247	0.154340	0.0	0.0
	X	0.121459	0.227444	0.299112	-0.106282	0.059817	0.0	0.0
	X'	-0.023377	0.003134	0.011196	0.018959	0.016349	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.383627	0.344354
	Y'	0.0	0.0	0.0	0.0	0.0	0.037839	0.049421
	Z	-0.053628	0.154494	-0.007458	0.147446	0.778786	0.0	0.0
	Z'	0.034485	0.003785	0.030211	0.047280	-0.107357	0.0	0.0
C2	S	-0.218460	0.388295	-0.218548	-0.236857	-0.643277	0.0	0.0
	S'	-0.035022	0.124206	-0.085541	-0.121721	-0.183125	0.0	0.0
	S''	-0.025858	0.008181	-0.001147	0.031247	-0.154340	0.0	0.0
	X	0.121459	0.227444	0.299112	-0.106282	0.059817	0.0	0.0
	X'	-0.023377	0.003134	0.011196	0.018959	0.016349	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.383627	-0.344354
	Y'	0.0	0.0	0.0	0.0	0.0	0.037839	-0.049421
	Z	-0.053628	0.154494	-0.007458	0.147446	0.778786	0.0	0.0
	Z'	0.034485	0.003785	0.030211	0.047280	-0.107357	0.0	0.0
O1	S	0.504592	0.188169	-0.347448	0.008314	-0.061764	0.0	0.0
	S'	0.208842	0.110177	-0.219671	0.005363	-0.042977	0.0	0.0
	S''	-0.057757	0.031260	-0.092843	0.007046	-0.013066	0.0	0.0
	X	-0.118730	0.169156	-0.302181	0.424258	-0.024673	0.0	0.0
	X'	0.025996	-0.024328	0.031757	0.028177	-0.009035	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.452622	0.549407
	Y'	0.0	0.0	0.0	0.0	0.0	0.024662	0.042232
	Z	0.068531	0.086269	0.344180	0.482559	-0.211128	0.0	0.0
	Z'	-0.019898	0.004834	-0.026945	0.030530	-0.040824	0.0	0.0
O2	S	-0.504592	-0.188169	0.347448	-0.008314	0.061764	0.0	0.0
	S'	-0.208842	-0.110177	0.219671	-0.005363	0.042977	0.0	0.0
	S''	0.057757	-0.031260	0.092843	-0.007046	0.013066	0.0	0.0
	X	-0.118730	0.169156	-0.302181	0.424258	-0.024673	0.0	0.0
	X'	0.025996	-0.024328	0.031757	0.028177	-0.009035	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.452622	-0.549407
	Y'	0.0	0.0	0.0	0.0	0.0	0.024662	-0.042232
	Z	0.068531	0.086269	0.344180	0.482559	-0.211128	0.0	0.0
	Z'	-0.019898	0.004834	-0.026945	0.030530	-0.040824	0.0	0.0

Table 43. SPIP MO's and occupation numbers for cis-glyoxal

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.983350	2.000000	2.000000
H1	S	0.000059	-0.000817	0.013847	-0.246017	-0.067916	-0.214394	-0.168722	-0.000117	0.000250
	S'	0.000050	-0.000426	-0.009018	0.033760	0.012215	-0.019077	-0.016291	-0.000006	-0.000010
H2	S	0.000059	-0.000817	0.013847	-0.246017	-0.067916	-0.214394	-0.168722	0.000117	-0.000250
	S'	0.000050	-0.000426	-0.009018	0.033760	0.012215	-0.019077	-0.016291	0.000006	0.000010
C1	S	0.000385	-0.228776	0.182710	-0.344548	0.133890	0.037595	0.362521	0.000184	-0.225332
	S'	0.000295	0.667328	0.002855	-0.093327	0.033880	0.041994	0.110703	0.000105	0.670336
	S''	-0.000050	0.008853	0.039445	-0.015805	0.017614	-0.016162	0.006224	0.000069	0.007336
	X	0.000181	0.001226	0.109222	0.230832	0.300108	0.097349	0.064827	-0.000037	0.003181
	X'	0.000149	0.000142	-0.026164	0.004480	0.007518	-0.007122	0.026087	-0.000048	0.001633
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Z	-0.000095	-0.001194	-0.106465	0.173706	-0.070055	-0.046571	0.477998	-0.000182	0.000972
	Z'	-0.000037	-0.000659	0.008857	0.020845	-0.003298	0.006054	-0.009098	-0.000160	0.000967
C2	S	0.000385	-0.228776	0.182710	-0.344548	0.133890	0.037595	0.362521	-0.000184	0.225332
	S'	0.000295	0.667328	0.002855	-0.093327	0.033880	0.041994	0.110703	-0.000105	-0.670336
	S''	-0.000050	0.008853	0.039445	-0.015805	0.017614	-0.016162	0.006224	-0.000069	-0.007336
	X	0.000181	0.001226	0.109222	0.230832	0.300108	0.097349	0.064827	0.000037	-0.003181
	X'	0.000149	0.000142	-0.026164	0.004480	0.007518	-0.007122	0.026087	0.000048	-0.001633
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Z	0.000095	0.001194	0.106465	-0.173706	0.070055	0.046571	-0.477998	-0.000182	0.000972
	Z'	0.000037	0.000659	-0.008857	-0.020845	0.003298	-0.006054	0.009098	-0.000160	0.000967
O1	S	-0.305328	-0.000661	0.496262	0.220575	-0.335406	-0.046057	-0.068131	-0.305222	-0.001500
	S'	0.639092	-0.001444	0.203538	0.123779	-0.212594	-0.036559	-0.046389	0.639201	-0.002319
	S''	-0.009263	-0.001846	-0.061902	0.026750	-0.092123	-0.028225	-0.022561	-0.009165	-0.002619
	X	-0.000714	0.000505	-0.114681	0.136992	-0.265727	-0.444429	0.004083	-0.000753	0.000798
	X'	0.000739	0.001290	0.030358	-0.027405	0.035479	-0.017316	-0.004501	0.000707	0.001424
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Z	0.000440	-0.000229	0.084741	0.009007	0.384002	-0.480730	-0.206593	0.000519	-0.001014
	Z'	-0.000473	-0.000693	-0.015088	-0.007818	-0.017486	-0.052827	-0.064914	-0.000413	-0.001420
O2	S	-0.305328	-0.000661	0.496262	0.220575	-0.335406	-0.046057	-0.068131	0.305222	0.001500
	S'	0.639092	-0.001444	0.203538	0.123779	-0.212594	-0.036559	-0.046389	-0.639201	0.002319
	S''	-0.009263	-0.001846	-0.061902	0.026750	-0.092123	-0.028225	-0.022561	0.009165	0.002619
	X	-0.000714	0.000505	-0.114681	0.136992	-0.265727	-0.444429	0.004083	0.000753	-0.000798
	X'	0.000739	0.001290	0.030358	-0.027405	0.035479	-0.017316	-0.004501	-0.000707	-0.001424
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Z	-0.000440	0.000229	-0.084741	-0.009007	-0.384002	0.480730	0.206593	0.000519	-0.001014
	Z'	0.000473	0.000693	0.015088	0.007818	0.017486	0.052827	0.064914	-0.000413	-0.001420

Table 43. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(1a2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	0.016650	2.000000	2.000000
H1	S	-0.015120	0.218507	-0.143019	0.221257	0.116810	0.0	0.0
	S'	0.005925	-0.034623	0.018938	0.012824	-0.001010	0.0	0.0
H2	S	0.015120	-0.218507	0.143019	-0.221257	-0.116810	0.0	0.0
	S'	-0.005925	0.034623	-0.018938	-0.012824	0.001010	0.0	0.0
C1	S	-0.232372	0.426286	0.120791	0.217963	-0.651287	0.0	0.0
	S'	-0.041491	0.141435	0.052038	0.111263	-0.189629	0.0	0.0
	S''	-0.024872	0.006768	0.000978	-0.029299	-0.149819	0.0	0.0
	X	-0.127084	-0.167712	0.376100	-0.121279	-0.090872	0.0	0.0
	X'	0.009409	-0.009069	0.034318	-0.004506	-0.033857	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.357477	0.328123
	Y'	0.0	0.0	0.0	0.0	0.0	0.054215	0.592204
	Z	0.065492	-0.155873	0.025856	0.188753	-0.758543	0.0	0.0
	Z'	-0.030946	-0.001872	0.029652	0.070686	0.114300	0.0	0.0
C2	S	0.232372	-0.426286	-0.120791	-0.217963	0.651287	0.0	0.0
	S'	0.041491	-0.141436	-0.052038	-0.111263	0.189629	0.0	0.0
	S''	0.024872	-0.006768	-0.000978	0.029299	0.149819	0.0	0.0
	X	0.127084	0.167712	-0.376100	0.121279	0.090872	0.0	0.0
	X'	-0.009409	0.009069	-0.034318	0.004506	0.033857	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	-0.357477	0.328123
	Y'	0.0	0.0	0.0	0.0	0.0	-0.054215	0.592204
	Z	0.065492	-0.155873	0.025856	0.188753	-0.758543	0.0	0.0
	Z'	-0.030946	-0.001872	0.029652	0.070686	0.114300	0.0	0.0
O1	S	-0.499974	-0.297914	-0.260222	0.034323	0.074093	0.0	0.0
	S'	-0.201585	-0.174031	-0.175276	0.027998	0.054883	0.0	0.0
	S''	0.067416	-0.048466	-0.091156	0.022692	0.022367	0.0	0.0
	X	0.115683	-0.220501	-0.253378	0.431847	0.025323	0.0	0.0
	X'	-0.030520	0.032218	0.028956	0.013330	0.003121	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.542612	-0.433771
	Y'	0.0	0.0	0.0	0.0	0.0	0.035886	-0.378375
	Z	-0.062771	-0.001298	0.393324	0.469730	0.218623	0.0	0.0
	Z'	0.023398	-0.010421	-0.023646	0.028498	0.042012	0.0	0.0
O2	S	0.499974	0.297914	0.260222	-0.034323	-0.074093	0.0	0.0
	S'	0.201585	0.174031	0.175276	-0.027998	-0.054883	0.0	0.0
	S''	-0.067416	0.048466	0.091156	-0.022692	-0.022367	0.0	0.0
	X	-0.115683	0.220501	0.253378	-0.431847	-0.025323	0.0	0.0
	X'	0.030520	-0.032218	-0.028956	-0.013330	-0.003121	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	-0.542612	-0.433771
	Y'	0.0	0.0	0.0	0.0	0.0	-0.035886	-0.378375
	Z	-0.062771	-0.001298	0.393324	0.469730	0.218623	0.0	0.0
	Z'	0.023398	-0.010421	-0.023646	0.028498	0.042012	0.0	0.0

Table 44. Hartree-Fock orbitals for nitric oxide

		(1a)	(2a)	(3a)	(4a)	(5a)	(1x)	(2x)	(1y)	(2y)
ETCSAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	0.500000	2.000000	0.500000
N	S	0.000466	0.851585	0.177971	0.397564	0.335424	0.0	0.0	0.0	0.0
	S'	-0.000385	0.506627	-0.345543	-0.629257	-0.493150	0.0	0.0	0.0	0.0
	S''	0.000241	-0.004867	-0.059144	-0.030107	0.094191	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.466448	-0.957615	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	-0.003220	0.086918	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.456448	-0.957515
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.003220	0.085913
	Z	-0.000021	0.003577	0.209765	-0.049895	-0.572434	0.0	0.0	0.0	0.0
	Z'	-0.000043	0.000192	0.061329	0.007521	-0.061591	0.0	0.0	0.0	0.0
O	S	0.837800	-0.002524	0.326148	-0.425888	0.102326	0.0	0.0	0.0	0.0
	S'	0.558411	0.002262	-0.538830	0.600076	-0.142983	0.0	0.0	0.0	0.0
	S''	0.002448	0.001755	0.067398	0.036420	-0.033518	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.771037	0.725341	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	-0.000329	-0.072823	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.771087	0.725341
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.000329	-0.072823
	Z	-0.001250	0.001941	-0.194976	-0.360397	0.553453	0.0	0.0	0.0	0.0
	Z'	-0.001289	-0.002097	-0.071870	-0.051238	0.049768	0.0	0.0	0.0	0.0

Table 45. SPIP MO's and occupation numbers for trans-NO dimer

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.946250	2.000000	2.000000
O1	S	0.592547	-0.001475	-0.221867	-0.302047	0.109574	-0.029293	0.012058	0.592442	-0.001553
	S'	0.394725	0.001322	0.364481	0.432149	-0.149784	0.044710	-0.016313	0.394830	0.001391
	S''	0.001635	0.001016	-0.042245	0.015666	-0.027366	0.003544	-0.001955	0.001662	0.001013
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000283	-0.000234	-0.070044	0.122111	0.262510	0.610003	0.252215	0.000383	-0.000560
	Y'	0.000447	0.000171	-0.011116	0.000824	-0.018995	0.004735	-0.045953	0.000305	0.000525
	Z	-0.000868	0.001256	0.121078	-0.116411	0.480970	-0.061201	0.015656	-0.000791	0.001074
	Z'	-0.000791	-0.001371	0.042331	-0.024486	0.031971	-0.012809	-0.012876	-0.000846	-0.001080
N1	S	0.000203	0.602081	-0.143330	0.282002	0.087219	-0.134384	0.015867	0.000032	0.601940
	S'	-0.000134	0.358259	0.274506	-0.449004	-0.127997	0.193643	-0.000683	0.000096	0.358523
	S''	0.000088	-0.003444	0.048104	-0.009716	0.055771	-0.036535	0.057424	-0.000110	-0.003944
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000105	-0.000387	0.064963	-0.047366	0.060103	0.041206	-0.635301	-0.000212	0.000544
	Y'	-0.000120	0.000924	0.004170	0.025233	0.037432	0.000095	-0.008863	0.000223	0.000362
	Z	-0.000221	0.002251	-0.108023	-0.133925	-0.325587	0.253863	-0.213701	-0.000008	0.002312
	Z'	0.000208	0.000306	-0.042496	-0.002193	-0.019564	0.044207	0.036295	-0.000004	0.000152
N2	S	0.000203	0.602081	-0.143330	0.282002	0.087219	-0.134384	0.015867	-0.000032	-0.601940
	S'	-0.000134	0.358259	0.274506	-0.449004	-0.127997	0.193643	-0.000683	-0.000096	-0.358523
	S''	0.000088	-0.003444	0.048104	-0.009716	0.055771	-0.036535	0.057424	0.000110	0.003944
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000105	0.000387	-0.064963	0.047366	-0.060103	-0.041206	0.635301	-0.000212	0.000544
	Y'	0.000120	-0.000924	-0.004170	-0.025233	-0.037432	-0.000095	0.008863	0.000223	0.000362
	Z	0.000221	-0.002251	0.108023	0.133925	0.325587	-0.253863	0.213701	-0.000008	0.002312
	Z'	-0.000208	-0.000306	0.042496	0.002193	0.019564	-0.044207	-0.036295	-0.000004	0.000152
O2	S	0.592547	-0.001475	-0.221867	-0.302047	0.109574	-0.029293	0.012058	-0.592442	0.001553
	S'	0.394725	0.001322	0.364481	0.432149	-0.149764	0.044710	-0.016313	-0.394830	-0.001391
	S''	0.001635	0.001016	-0.042245	0.015666	-0.027368	0.003544	-0.001955	-0.001662	-0.001013
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000283	0.000234	0.070044	-0.122111	-0.262510	-0.610003	-0.252215	0.000383	-0.000560
	Y'	-0.000447	-0.000171	0.011116	-0.000824	0.018995	-0.004735	0.045953	0.000305	0.000525
	Z	0.000868	-0.001256	-0.121078	0.116411	-0.480970	0.061201	-0.015656	-0.000791	0.001074
	Z'	0.000791	0.001371	-0.042331	0.024486	-0.031971	0.012809	0.012876	-0.000846	-0.001080

Table 45. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(1a2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	0.053750	2.000000	2.000000
O1	S	-0.243335	-0.268657	-0.149857	0.012981	0.011639	0.0	0.0
	S'	0.397808	0.379005	0.200991	-0.018501	-0.015547	0.0	0.0
	S''	-0.044284	0.023716	0.036096	-0.007234	0.002467	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.423168	0.535114
	X'	0.0	0.0	0.0	0.0	0.0	0.002614	-0.015396
	Y	-0.049134	-0.004211	0.445419	0.464578	0.240272	0.0	0.0
	Y'	-0.016445	0.006624	0.020625	-0.011783	-0.019771	0.0	0.0
	Z	0.127942	-0.298143	-0.128004	0.368805	0.011771	0.0	0.0
	Z'	0.041474	-0.037219	-0.025367	0.009125	-0.005472	0.0	0.0
N1	S	-0.133535	0.287480	-0.043455	0.325724	-0.256762	0.0	0.0
	S'	0.244695	-0.449091	0.075860	-0.462891	0.349881	0.0	0.0
	S''	0.032591	-0.016690	0.018001	0.109332	0.013210	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.427488	0.385752
	X'	0.0	0.0	0.0	0.0	0.0	-0.014113	-0.023264
	Y	0.038013	-0.099332	0.130850	0.104052	-0.835010	0.0	0.0
	Y'	0.028160	-0.017019	-0.023633	-0.025808	-0.097698	0.0	0.0
	Z	-0.154708	-0.044482	0.361734	-0.295925	-0.094971	0.0	0.0
	Z'	-0.038958	0.015800	0.003712	-0.011708	-0.029326	0.0	0.0
N2	S	0.133535	-0.287480	0.043455	-0.325724	0.256762	0.0	0.0
	S'	-0.244695	0.449091	-0.075860	0.462891	-0.349881	0.0	0.0
	S''	-0.032591	0.016690	-0.018001	-0.109332	-0.013210	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.427488	-0.385752
	X'	0.0	0.0	0.0	0.0	0.0	-0.014113	0.023264
	Y	0.038013	-0.099332	0.130850	0.104052	-0.835010	0.0	0.0
	Y'	0.028160	-0.017019	-0.023633	-0.025808	-0.097698	0.0	0.0
	Z	-0.154708	-0.044482	0.361734	-0.295925	-0.094971	0.0	0.0
	Z'	-0.038958	0.015800	0.008712	-0.011708	-0.029326	0.0	0.0
O2	S	0.243335	0.268657	0.149857	-0.012981	-0.011639	0.0	0.0
	S'	-0.397808	-0.379005	-0.200991	0.018501	0.015547	0.0	0.0
	S''	0.044284	-0.023716	-0.036096	0.007234	-0.002467	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.423168	-0.535114
	X'	0.0	0.0	0.0	0.0	0.0	0.002614	0.015396
	Y	-0.049134	-0.004211	0.445419	0.464578	0.240272	0.0	0.0
	Y'	-0.016445	0.006624	0.020625	-0.011783	-0.019771	0.0	0.0
	Z	0.127942	-0.298143	-0.128004	0.368805	0.011771	0.0	0.0
	Z'	0.041474	-0.037219	-0.025367	0.009125	-0.005472	0.0	0.0

Table 46. SPIP MO's and occupation numbers for cis-NO dimer

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.916780	2.000000	2.000000
O1	S	0.592402	-0.001235	-0.222813	-0.282044	-0.134058	0.073536	0.030201	0.592561	-0.001703
	S'	0.394872	0.001020	0.367151	0.402686	0.183701	-0.101497	-0.037639	0.394702	0.001571
	S''	0.001703	0.000790	-0.041144	0.016493	0.023852	-0.019085	-0.011714	0.001626	0.001223
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000387	-0.000214	-0.079336	0.106680	0.448499	0.416394	0.312790	0.000378	-0.000752
	Y'	0.000387	0.000206	-0.012614	0.002766	0.010843	-0.016841	-0.050258	0.000429	0.000760
	Z	0.000809	-0.001107	-0.117820	0.120576	0.178865	-0.439895	-0.031637	0.000832	-0.001132
	Z'	0.000803	0.001253	-0.042473	0.024148	0.025323	-0.025049	0.016599	0.000818	0.001132
N1	S	0.000292	0.601842	-0.135117	0.287947	-0.111420	0.050159	0.000097	0.000081	0.602098
	S'	-0.000242	0.358608	0.260195	-0.458513	0.164660	-0.073259	0.014137	0.000049	0.358309
	S''	0.000156	-0.003590	0.049196	-0.015385	-0.030016	0.041589	0.030560	-0.000092	-0.003668
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000018	-0.000484	0.059124	-0.023678	0.009505	0.111173	-0.624156	-0.000066	0.000293
	Y'	-0.000018	0.000726	0.006971	0.019954	-0.002063	0.039184	0.009445	0.000100	0.000193
	Z	-0.000019	-0.002089	0.124662	0.134341	-0.351912	0.197676	0.249239	0.000201	-0.002441
	Z'	0.000056	-0.000559	0.039960	0.004324	-0.028160	0.019116	-0.045064	-0.000190	-0.000230
N2	S	0.000292	0.601842	-0.135117	0.287947	-0.111420	0.050159	0.000097	-0.000081	-0.602098
	S'	-0.000242	0.358608	0.260195	-0.458513	0.164660	-0.073259	0.014137	-0.000049	-0.358309
	S''	0.000156	-0.003590	0.049196	-0.015385	-0.030016	0.041589	0.030560	0.000092	0.003668
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000018	0.000484	-0.059124	0.023678	-0.009505	-0.111173	0.624156	-0.000066	0.000293
	Y'	0.000018	-0.000726	-0.006971	-0.019954	0.002063	-0.039184	-0.009445	0.000100	0.000193
	Z	-0.000019	-0.002089	0.124662	0.134341	-0.351912	0.197676	0.249239	-0.000201	0.002441
	Z'	0.000056	-0.000559	0.039960	0.004324	-0.028160	0.019116	-0.045064	0.000190	0.000230
O2	S	0.592402	-0.001235	-0.222813	-0.282044	-0.134058	0.073536	0.030201	-0.592561	0.001703
	S'	0.394872	0.001020	0.367151	0.402686	0.183701	-0.101497	-0.037639	-0.394702	-0.001571
	S''	0.001703	0.000790	-0.041144	0.016493	0.023852	-0.019085	-0.011714	-0.001626	-0.001223
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000387	0.000214	0.079336	-0.106680	-0.448499	-0.416394	-0.312790	0.000378	-0.000752
	Y'	-0.000387	-0.000206	0.012614	-0.002766	-0.010843	0.016841	0.050258	0.000429	0.000760
	Z	0.000809	-0.001107	-0.117820	0.120576	0.178865	-0.439895	-0.031637	-0.000832	0.001132
	Z'	0.000803	0.001253	-0.042473	0.024148	0.025323	-0.025049	0.016599	-0.000818	-0.001132

Table 46. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(1a2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	0.083220	2.000000	2.000000
O1	S	-0.244106	0.304860	0.038793	0.017922	0.038179	0.0	0.0
	S'	0.398112	-0.428193	-0.054196	-0.025697	-0.047533	0.0	0.0
	S''	-0.044790	-0.030525	-0.013371	-0.012431	-0.003019	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.452797	0.530922
	X'	0.0	0.0	0.0	0.0	0.0	-0.003923	-0.009595
	Y	-0.047982	-0.070797	-0.545443	0.330232	0.314114	0.0	0.0
	Y'	-0.020483	-0.011545	-0.019730	-0.015220	-0.023011	0.0	0.0
	Z	-0.131368	-0.294194	-0.031606	-0.425016	-0.027410	0.0	0.0
	Z'	-0.040541	-0.040980	-0.011884	-0.014501	0.008769	0.0	0.0
N1	S	-0.133674	-0.281503	0.085043	0.340745	-0.250118	0.0	0.0
	S'	0.249881	0.438811	-0.130347	-0.487906	0.343185	0.0	0.0
	S''	0.039333	0.015079	0.003882	0.112196	-0.024257	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.402873	0.386193
	X'	0.0	0.0	0.0	0.0	0.0	-0.011113	-0.021959
	Y	0.043108	0.072273	-0.183908	0.126306	-0.808207	0.0	0.0
	Y'	0.028845	0.012879	0.036160	-0.015804	-0.060213	0.0	0.0
	Z	0.139435	-0.005757	0.308631	0.338557	0.157609	0.0	0.0
	Z'	0.042843	0.013056	0.027215	0.015442	0.013364	0.0	0.0
N2	S	0.133674	0.281503	-0.085043	-0.340745	0.250118	0.0	0.0
	S'	-0.249681	-0.438811	0.130347	0.487906	-0.343185	0.0	0.0
	S''	-0.039333	-0.015079	-0.003882	-0.112196	0.024257	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.402873	-0.386193
	X'	0.0	0.0	0.0	0.0	0.0	-0.011113	0.021959
	Y	0.043109	0.072273	-0.183908	0.126306	-0.808207	0.0	0.0
	Y'	0.028845	0.012879	0.036160	-0.015804	-0.060213	0.0	0.0
	Z	-0.139435	0.005757	-0.308631	-0.338557	-0.157609	0.0	0.0
	Z'	-0.042843	-0.013056	-0.027215	-0.015442	-0.013364	0.0	0.0
O2	S	0.244106	-0.304860	-0.038793	-0.017922	-0.038179	0.0	0.0
	S'	-0.398112	0.428193	0.054196	0.025697	0.047533	0.0	0.0
	S''	0.044790	0.030525	0.013371	0.012431	0.003019	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.452797	-0.530922
	X'	0.0	0.0	0.0	0.0	0.0	-0.003923	0.009595
	Y	-0.047982	-0.070797	-0.545443	0.330232	0.314114	0.0	0.0
	Y'	-0.020483	-0.011545	-0.019730	-0.015220	-0.023011	0.0	0.0
	Z	0.131368	0.294194	0.031606	0.425016	0.027410	0.0	0.0
	Z'	0.040541	0.040980	0.011884	0.014501	-0.008769	0.0	0.0

Table 47. Hartree-Fock orbitals for oxygen molecule ion (+)

		(1a)	(2a)	(3a)	(1a*)	(2a*)	(1x)	(1x*)	(1y)	(1y*)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	0.500000	2.000000	0.500000
O	S	-0.286627	0.544246	-0.297983	-0.286322	0.713371	0.0	0.0	0.0	0.0
	S'	0.654398	0.195310	-0.146182	0.654776	0.319491	0.0	0.0	0.0	0.0
	S''	-0.001292	-0.080104	-0.040538	-0.000832	0.003391	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.650431	0.803749	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	-0.021645	0.002639	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.650431	0.803749
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.021645	0.002639
	Z	0.001359	0.237572	0.607701	0.001950	-0.186303	0.0	0.0	0.0	0.0
	Z'	-0.000844	-0.061428	-0.074574	-0.000309	0.040595	0.0	0.0	0.0	0.0
O	S	-0.286627	0.544246	-0.297983	0.286322	-0.713371	0.0	0.0	0.0	0.0
	S'	0.654398	0.195310	-0.146182	-0.654776	-0.319491	0.0	0.0	0.0	0.0
	S''	-0.001292	-0.080104	-0.040538	0.000832	-0.003391	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.650431	-0.803749	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	-0.021645	-0.002639	0.0	0.0
	Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.650431	-0.803749
	Y'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.021645	-0.002639
	Z	-0.001359	-0.237572	-0.607701	0.001950	-0.186303	0.0	0.0	0.0	0.0
	Z'	0.000844	0.061428	0.074574	-0.000309	0.040595	0.0	0.0	0.0	0.0

Table 48. SPIP MO's and occupation numbers for trans-O_2^+ dimer

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.803010	2.000000	2.000000
O1	S	-0.283441	0.042192	0.348014	0.504625	-0.273476	-0.105511	-0.005370	-0.283633	0.041120
	S'	0.647472	-0.096251	0.126799	0.220300	-0.132715	-0.043747	0.002340	0.647777	-0.094040
	S''	-0.000939	0.000116	-0.051612	-0.008763	-0.031766	0.012297	0.020898	-0.000915	0.000015
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000667	-0.000205	0.074983	-0.058684	-0.178844	0.606554	0.276071	0.000761	-0.000146
	Y'	-0.000385	0.000019	-0.019874	0.004880	-0.015576	-0.035978	0.014890	-0.000106	0.000034
	Z	-0.001382	0.000310	-0.131363	-0.011897	-0.432273	-0.000472	0.095303	-0.001387	0.000339
	Z'	0.000432	0.000044	0.031187	-0.017020	0.056584	0.001860	-0.001841	0.000491	0.000161
O2	S	-0.042261	-0.283348	0.432341	-0.450567	0.002234	-0.122906	0.064182	-0.041426	-0.283545
	S'	0.096073	0.647418	0.159242	-0.202639	-0.000712	-0.064795	0.031525	0.093628	0.647763
	S''	-0.000527	-0.001323	-0.056256	-0.016043	-0.014808	-0.033844	-0.002416	-0.000933	-0.001148
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000180	0.000224	-0.030055	-0.093415	-0.189249	0.056567	-0.608257	-0.000050	0.000044
	Y'	0.000212	-0.000173	0.015129	0.030179	0.024584	0.018219	0.037216	-0.000324	-0.000153
	Z	-0.000100	0.001407	0.123509	0.185790	0.293493	0.280746	-0.284155	-0.000032	0.001428
	Z'	-0.000644	-0.000777	-0.038244	-0.044341	-0.022674	-0.065476	-0.019624	-0.000415	-0.000556
O3	S	-0.042261	-0.283348	0.432341	-0.450567	0.002234	-0.122906	0.054182	0.041426	0.283545
	S'	0.096073	0.647418	0.159242	-0.202639	-0.000712	-0.064795	0.031525	-0.093628	-0.647763
	S''	-0.000527	-0.001323	-0.056256	-0.016043	-0.014303	-0.033844	-0.002416	0.000933	0.001148
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000180	-0.000224	0.030055	0.098415	0.189249	-0.056567	0.608257	-0.000050	0.000044
	Y'	-0.000212	0.000173	-0.015129	-0.030179	-0.024584	-0.018219	-0.037216	-0.000324	-0.000153
	Z	0.000100	-0.001407	-0.123509	-0.185790	-0.293493	-0.280746	0.284156	-0.000032	0.001428
	Z'	0.000644	0.000777	0.038244	0.044341	0.022674	0.065476	0.019624	-0.000415	-0.000556
O4	S	-0.283441	0.042192	0.348014	0.504625	-0.273476	-0.105511	-0.005370	0.283633	-0.041120
	S'	0.647472	-0.096251	0.126799	0.220300	-0.132715	-0.043747	0.002340	-0.647777	0.094040
	S''	-0.000939	0.000116	-0.051612	-0.008763	-0.031766	0.012297	0.020898	0.000915	-0.000015
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000667	0.000205	-0.074983	0.058684	0.178344	-0.606554	-0.276071	0.000761	-0.000146
	Y'	0.000385	-0.000019	0.019874	-0.004880	0.015676	0.035978	-0.014890	-0.000106	0.000034
	Z	0.001382	-0.000310	0.131363	0.011897	0.482273	0.000472	-0.095303	-0.001387	0.000339
	Z'	-0.000432	-0.000044	-0.031187	0.017020	-0.056584	-0.001860	0.001841	0.000491	0.000161

Table 48. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(1a2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	0.196390	2.000000	2.000000
O1	S	0.405923	0.476204	-0.262671	0.063373	0.006446	0.0	0.0
	S'	0.152506	0.211442	-0.129243	0.028837	0.004695	0.0	0.0
	S''	-0.043590	-0.003222	-0.025420	0.002457	0.008354	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.296727	0.365963
	X'	0.0	0.0	0.0	0.0	0.0	-0.015255	-0.007161
	Y	0.069655	0.007554	0.420587	0.426569	0.303709	0.0	0.0
	Y'	-0.010571	0.012378	-0.031369	-0.020527	0.003133	0.0	0.0
	Z	-0.150882	0.143683	-0.160739	0.440214	0.051110	0.0	0.0
	Z'	0.029409	-0.030077	0.035661	-0.027293	-0.005482	0.0	0.0
O2	S	0.382144	-0.541143	-0.093060	0.246014	-0.195781	0.0	0.0
	S'	0.142652	-0.244754	-0.041125	0.127414	-0.106069	0.0	0.0
	S''	-0.047032	-0.005089	0.004656	0.053546	-0.052782	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.565762	0.567313
	X'	0.0	0.0	0.0	0.0	0.0	-0.001597	0.002390
	Y	-0.061291	0.023648	0.060037	0.222578	-0.785467	0.0	0.0
	Y'	0.032149	-0.010832	-0.000426	0.007241	0.058987	0.0	0.0
	Z	0.160861	0.138568	0.411097	-0.211963	-0.188214	0.0	0.0
	Z'	-0.043129	-0.016561	-0.014139	0.034584	0.026674	0.0	0.0
O3	S	-0.382144	0.541143	0.093060	-0.246014	0.196781	0.0	0.0
	S'	-0.142652	0.244754	0.041125	-0.127414	0.106069	0.0	0.0
	S''	0.047032	0.005089	-0.004656	-0.053546	0.052782	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.565762	-0.567313
	X'	0.0	0.0	0.0	0.0	0.0	-0.001597	-0.002390
	Y	-0.061291	0.023648	0.060037	0.222578	-0.785467	0.0	0.0
	Y'	0.032149	-0.010832	-0.000426	0.007241	0.058987	0.0	0.0
	Z	0.160861	0.138568	0.411097	-0.211963	-0.188214	0.0	0.0
	Z'	-0.043129	-0.016561	-0.014139	0.034584	0.026674	0.0	0.0
O4	S	-0.405923	-0.476204	0.262671	-0.063373	-0.006446	0.0	0.0
	S'	-0.152506	-0.211442	0.129243	-0.028837	-0.004695	0.0	0.0
	S''	0.043590	0.003222	0.025420	-0.002457	-0.008354	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.296727	-0.365963
	X'	0.0	0.0	0.0	0.0	0.0	-0.015255	0.007161
	Y	0.069655	0.007554	0.420587	0.426569	0.303709	0.0	0.0
	Y'	-0.010571	0.012378	-0.031369	-0.020527	0.003133	0.0	0.0
	Z	-0.150882	0.143683	-0.160739	0.440214	0.051110	0.0	0.0
	Z'	0.029409	-0.030077	0.035661	-0.027293	-0.005482	0.0	0.0

Table 49. SPIP MO's and occupation numbers for cis-o_2^+ dimer

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.748230	2.000000	2.000000
O1	S	-0.037443	-0.284235	0.353533	-0.469678	-0.308902	0.133397	0.006498	-0.041006	-0.283416
	S'	0.085299	0.648888	0.127260	-0.204821	-0.147921	0.062480	0.009962	0.093819	0.648000
	S''	-0.000219	-0.001054	-0.054168	0.004646	-0.026542	-0.002653	0.024894	-0.000166	-0.000635
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000007	0.001011	0.106678	0.043427	-0.001443	-0.551211	0.309435	0.000071	0.001113
	Y'	-0.000049	-0.000384	-0.023907	-0.011585	-0.029907	0.021358	0.015375	-0.000134	-0.000251
	Z	0.000043	0.001165	0.112914	-0.019173	0.479634	0.195073	-0.176231	0.000058	0.001280
	Z'	-0.000245	-0.000385	-0.029606	-0.012826	-0.049416	-0.001042	-0.002237	-0.000194	-0.000244
O2	S	-0.284086	0.037275	0.422155	0.461753	0.003338	0.088611	0.044806	-0.283649	0.040815
	S'	0.648900	-0.085511	0.155203	0.206594	-0.000311	0.042876	0.018773	0.647707	-0.094106
	S''	-0.001265	-0.000004	-0.053853	0.010685	-0.014166	0.005517	-0.017904	-0.001301	-0.000495
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000148	0.000157	-0.063291	0.147489	-0.260689	-0.055516	-0.514698	-0.000281	0.000245
	Y'	-0.000018	0.000157	0.019810	-0.036651	0.033644	-0.003607	0.035974	0.000169	0.000250
	Z	-0.001462	0.000354	-0.124125	0.172100	-0.253238	0.282793	0.400173	-0.001300	0.000558
	Z'	0.000669	0.000037	0.025112	-0.034930	0.022725	-0.019719	0.017611	0.000941	0.000617
O3	S	-0.284086	0.037275	0.422155	0.461753	0.003338	0.088611	0.044806	0.283649	-0.040815
	S'	0.648900	-0.085511	0.155203	0.206594	-0.000811	0.042876	0.018773	-0.647707	0.094106
	S''	-0.001265	-0.000004	-0.053853	0.010685	-0.014166	0.005517	-0.017904	0.001301	0.000495
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000148	-0.000157	0.063291	-0.147489	0.260689	0.055516	0.514698	-0.000281	0.000245
	Y'	0.000018	-0.000157	-0.019810	0.036651	-0.033644	0.003607	-0.035974	0.000169	0.000250
	Z	-0.001462	0.000354	-0.124125	0.172100	-0.253238	0.282793	0.400173	0.001300	-0.000558
	Z'	0.000669	0.000037	0.025112	-0.034930	0.022725	-0.019719	0.017611	-0.000941	-0.000617
O4	S	-0.037443	-0.284235	0.353533	-0.469678	-0.308902	0.133397	0.006498	0.041006	0.283416
	S'	0.085299	0.648888	0.127260	-0.204821	-0.147921	0.062480	0.009962	-0.093819	-0.648000
	S''	-0.000219	-0.001054	-0.054168	0.004646	-0.026542	-0.002653	0.024894	0.000166	0.000635
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000007	-0.001011	-0.106678	-0.043427	0.001443	0.551211	-0.309435	0.000071	0.001113
	Y'	0.000049	0.000384	0.023907	0.011585	0.029907	-0.021358	-0.015375	-0.000134	-0.000251
	Z	0.000043	0.001165	0.112914	-0.019173	0.479634	0.195073	-0.176231	-0.000058	-0.001280
	Z'	-0.000245	-0.000385	-0.029606	-0.012826	-0.049416	-0.001042	-0.002237	0.000194	0.000244

Table 49. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(1a2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	0.251770	2.000000	2.000000
01	S	0.410349	-0.523264	0.120946	-0.090334	0.021790	0.0	0.0
	S'	0.158333	-0.235342	0.050817	-0.043307	0.013352	0.0	0.0
	S''	-0.031839	-0.002959	-0.016658	-0.015121	0.008905	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.317775	0.378027
	X'	0.0	0.0	0.0	0.0	0.0	-0.009751	-0.011507
	Y	0.102875	0.056615	-0.537613	-0.107802	0.337689	0.0	0.0
	Y'	-0.020507	-0.023006	0.038850	-0.005658	0.000452	0.0	0.0
	Z	0.134383	0.152219	0.107861	0.521416	-0.123646	0.0	0.0
	Z'	-0.018571	-0.030852	-0.008615	-0.036462	0.004908	0.0	0.0
02	S	0.387632	0.526109	0.084792	-0.313260	-0.187865	0.0	0.0
	S'	0.144293	0.239479	0.037023	-0.158931	-0.101898	0.0	0.0
	S''	-0.048292	0.007909	-0.011864	-0.056739	-0.050141	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.554509	0.553291
	X'	0.0	0.0	0.0	0.0	0.0	-0.006190	0.006719
	Y	-0.084148	0.003307	-0.109592	-0.271722	-0.683884	0.0	0.0
	Y'	0.062421	0.000687	-0.064013	0.009512	0.048717	0.0	0.0
	Z	-0.134187	0.089013	0.347938	-0.284322	0.358546	0.0	0.0
	Z'	0.055287	-0.020290	-0.051994	0.045113	-0.027333	0.0	0.0
03	S	-0.387632	-0.526109	-0.084792	0.313260	0.187865	0.0	0.0
	S'	-0.144293	-0.239479	-0.037023	0.158931	0.101898	0.0	0.0
	S''	0.048292	-0.007909	0.011864	0.056739	0.050141	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.554509	-0.553291
	X'	0.0	0.0	0.0	0.0	0.0	-0.006190	-0.006719
	Y	-0.084148	0.003307	-0.109592	-0.271722	-0.683884	0.0	0.0
	Y'	0.062421	0.000687	-0.064013	0.009512	0.048717	0.0	0.0
	Z	0.134187	-0.089013	-0.347938	0.284322	-0.358546	0.0	0.0
	Z'	-0.055287	0.020290	0.051994	-0.045113	0.027333	0.0	0.0
04	S	-0.410349	0.523264	-0.120946	0.090334	-0.021790	0.0	0.0
	S'	-0.158333	0.235342	-0.050817	0.043307	-0.013352	0.0	0.0
	S''	0.031839	0.002959	0.016658	0.015121	-0.008905	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.317775	-0.378027
	X'	0.0	0.0	0.0	0.0	0.0	-0.009751	0.011507
	Y	0.102875	0.056615	-0.537613	-0.107802	0.337689	0.0	0.0
	Y'	-0.020507	-0.023006	0.038850	-0.005658	0.000452	0.0	0.0
	Z	-0.134383	-0.152219	-0.107861	-0.521416	0.123646	0.0	0.0
	Z'	0.018571	0.030852	0.008615	0.036462	-0.004908	0.0	0.0

APPENDIX D: MOLECULAR ORBITALS FOR THE CYCLIC DIMER SYSTEMS

MOLECULAR ORBITALS FOR THE CYCLIC DIMER SYSTEMS

In Part IV of this work we calculated wavefunctions for the cyclic dimers and monomers shown in equations 84-1,2. In the following tables we present their MO's and occupation numbers calculated using the Hartree-Fock method and the SPIP procedure outlined in Parts I to III of this work. The basis sets are taken from the even-tempered contracted orbital (ETCGAO) basis in Appendices A and B, and the specific basis for each wavefunction is specified in Table 5 of Part IV.

Table 50. Hartree-Fock orbitals for formaldehyde

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(1b2)	(2b2)	(1b1)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000
C	S	0.000258	0.954489	-0.097919	0.221301	0.040839	0.0	0.0	0.0
	S'	-0.000402	0.155874	0.346905	-0.633614	-0.103320	0.0	0.0	0.0
	S''	-0.000130	0.006563	-0.013157	0.001241	0.016493	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.494798
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.043944
	Y	0.0	0.0	0.0	0.0	0.0	-0.557100	0.217931	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.008632	0.051089	0.0
	Z	-0.000062	0.001167	-0.175700	-0.241491	0.429513	0.0	0.0	0.0
	Z'	-0.000046	0.000642	-0.052180	-0.007461	0.058893	0.0	0.0	0.0
O	S	-0.450252	-0.000252	-0.689208	-0.363806	-0.378975	0.0	0.0	0.0
	S'	0.885562	-0.001206	-0.324752	-0.208667	-0.242674	0.0	0.0	0.0
	S''	-0.004621	-0.002183	0.058580	-0.021967	-0.088334	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.731976
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.021304
	Y	0.0	0.0	0.0	0.0	0.0	-0.455381	-0.868425	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.033858	-0.050134	0.0
	Z	-0.001305	0.000120	0.171572	-0.149244	-0.674356	0.0	0.0	0.0
	Z'	0.001124	0.001983	-0.057676	0.018889	0.066317	0.0	0.0	0.0
H1	S	-0.000001	-0.001642	-0.009670	0.228591	-0.157525	0.243793	-0.433090	0.0
	S'	0.000026	-0.001278	0.017548	-0.050359	0.002358	-0.042305	-0.032301	0.0
H2	S	-0.000001	-0.001542	-0.009670	0.228591	-0.157625	-0.243793	0.433090	0.0
	S'	0.000026	-0.001278	0.017548	-0.050359	0.002358	0.042305	0.032301	0.0

Table 51. SPIP MO's and occupation numbers for formaldehyde

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(1b2)	(2b2)	(1b1)	(2b1)
ETCSAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.900142	0.099858
C	S	0.000258	0.954489	-0.093553	0.221326	0.027925	0.0	0.0	0.0	0.0
	S'	-0.000402	0.155974	0.336360	-0.635272	-0.071271	0.0	0.0	0.0	0.0
	S''	-0.000130	0.006563	-0.013034	0.000167	0.016492	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.537219	0.837052
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.046415	-0.087022
	Y	0.0	0.0	0.0	0.0	0.0	-0.542022	0.250570	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.012255	0.039912	0.0	0.0
	Z	-0.000062	0.001167	-0.172567	-0.218208	0.427303	0.0	0.0	0.0	0.0
	Z'	-0.000046	0.000642	-0.052091	-0.005102	0.059586	0.0	0.0	0.0	0.0
O	S	-0.450252	-0.000252	-0.697259	-0.379923	-0.354529	0.0	0.0	0.0	0.0
	S'	0.885562	-0.001206	-0.329688	-0.216500	-0.227569	0.0	0.0	0.0	0.0
	S''	-0.004621	-0.002183	0.068506	-0.025285	-0.085007	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.705174	-0.766075
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.002774	0.133418
	Y	0.0	0.0	0.0	0.0	0.0	-0.492024	-0.852868	0.0	0.0
	Y'	0.0	0.0	0.0	0.0	0.0	0.032216	-0.052411	0.0	0.0
	Z	-0.001305	0.000120	0.179991	-0.177046	-0.678777	0.0	0.0	0.0	0.0
	Z'	0.001124	0.001983	-0.067069	0.021726	0.063932	0.0	0.0	0.0	0.0
H1	S	-0.000001	-0.001642	-0.008821	0.226448	-0.168494	0.231681	-0.432214	0.0	0.0
	S'	0.000026	-0.001278	0.017027	-0.048637	0.003305	-0.041353	-0.027720	0.0	0.0
H2	S	-0.000001	-0.001642	-0.008821	0.226448	-0.168494	-0.231681	0.432214	0.0	0.0
	S'	0.000026	-0.001278	0.017027	-0.048637	0.003305	0.041353	0.027720	0.0	0.0

Table 52. Hartree-Fock orbitals for 1,2-dioxetane

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000
C1	S	0.000071	-0.666568	-0.045356	0.179776	0.019862	-0.005706	0.042278	-0.000221	0.667745
	S'	-0.000149	-0.135316	0.160039	-0.508759	-0.050601	0.026580	-0.092490	0.000223	0.134002
	S''	0.000050	-0.000283	0.000766	0.000533	0.001752	0.000505	0.000202	0.000109	0.000137
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000035	-0.000021	0.023934	-0.070590	0.265266	0.257296	-0.435135	0.000211	-0.000743
	Y'	0.000022	0.000329	0.011332	-0.016899	0.018179	0.005988	-0.000227	-0.000107	0.000210
	Z	0.000040	-0.001050	-0.064791	-0.033324	-0.232628	0.226866	-0.022136	-0.000353	0.001220
	Z'	0.000025	0.000024	-0.021802	-0.012905	-0.021654	0.014629	-0.008536	0.000232	-0.000110
C2	S	0.000071	-0.666568	-0.045356	0.179776	0.019862	-0.005706	0.042278	0.000221	-0.667745
	S'	-0.000149	-0.135316	0.160039	-0.508759	-0.050601	0.026580	-0.092490	-0.000223	-0.134002
	S''	0.000050	-0.000283	0.000766	0.000533	0.001752	0.000505	0.000202	-0.000109	-0.000137
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000035	0.000021	-0.023934	0.070590	-0.265266	-0.257296	0.435135	0.000211	-0.000743
	Y'	-0.000022	-0.000329	-0.011332	0.016899	-0.018179	-0.005988	0.000227	-0.000107	0.000210
	Z	0.000040	-0.001050	-0.064791	-0.033324	-0.232628	0.226866	-0.022136	0.000353	-0.001220
	Z'	0.000025	0.000024	-0.021802	-0.012905	-0.021654	0.014629	-0.008536	-0.000232	0.000110
O1	S	-0.306353	0.000319	-0.504158	-0.251062	0.182487	0.075791	0.118741	-0.306168	-0.000827
	S'	0.640041	0.000472	-0.216749	-0.131895	0.101658	0.038920	0.067292	0.640305	-0.000985
	S''	-0.001398	0.000711	0.043428	-0.025940	0.025502	0.000243	0.017468	-0.000694	-0.001301
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000601	-0.000032	0.114720	0.078399	0.145693	0.430485	0.452423	-0.000831	0.000192
	Y'	0.000454	-0.000012	-0.021649	-0.016163	-0.005385	-0.030247	0.014833	0.000065	0.000253
	Z	-0.000647	-0.000545	0.087916	-0.127949	0.352281	-0.252992	0.247513	-0.000841	0.000695
	Z'	0.000471	-0.000935	-0.015852	0.035291	-0.019169	0.025451	0.018082	0.000285	0.001303
O2	S	-0.306353	0.000319	-0.504158	-0.251062	0.182487	0.075791	0.118741	0.306168	0.000827
	S'	0.640041	0.000472	-0.216749	-0.131895	0.101658	0.038920	0.067292	-0.640305	0.000985
	S''	-0.001398	0.000711	0.043428	-0.025940	0.025502	0.000243	0.017468	0.000694	0.001301
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000601	0.000032	-0.114720	-0.078399	-0.145693	-0.430485	-0.452423	-0.000831	0.000192
	Y'	-0.000454	0.000012	0.021649	0.016163	0.005385	0.030247	-0.014833	0.000065	0.000253
	Z	-0.000647	-0.000545	0.087916	-0.127949	0.352281	-0.252992	0.247513	0.000841	-0.000695
	Z'	0.000471	-0.000935	-0.015852	0.035291	-0.019169	0.025451	0.018082	-0.000285	-0.001303
H1	S	0.000004	-0.000024	0.003825	0.089850	0.157163	-0.006222	-0.122806	-0.000129	-0.000241
	S'	-0.000003	-0.000106	-0.011213	0.018866	-0.003631	-0.000309	0.004259	0.000094	0.000172
H2	S	0.000004	-0.000024	0.003825	0.089850	0.157163	-0.006222	-0.122806	-0.000129	-0.000241
	S'	-0.000003	-0.000106	-0.011213	0.018866	-0.003631	-0.000309	0.004259	0.000094	0.000172
H3	S	0.000004	-0.000024	0.003825	0.089850	0.157163	-0.006222	-0.122806	0.000129	0.000241
	S'	-0.000003	-0.000106	-0.011213	0.018866	-0.003631	-0.000309	0.004259	-0 000094	-0.000172
H4	S	0.000004	-0.000024	0.003825	0.089850	0.157163	-0.006222	-0.122806	0.000129	0.000241
	S'	-0.000003	-0.000106	-0.011213	0.018866	-0.003631	-0.000309	0.004259	-0.000094	-0.000172

Table 52. (Continued)

		(3b2)	(4b2)	(5b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000
C1	S	0.081224	0.168157	0.042149	0.0	0.0	0.0	0.0
	S'	-0.230923	-0.451503	-0.092665	0.0	0.0	0.0	0.0
	S''	-0.000407	0.002508	0.000305	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.356200	0.263870	0.455576	-0.152732
	X'	0.0	0.0	0.0	0.001296	0.017259	-0.031108	-0.031111
	Y	0.021757	0.154304	-0.082395	0.0	0.0	0.0	0.0
	Y'	0.013541	0.016981	0.008494	0.0	0.0	0.0	0.0
	Z	0.100899	-0.110891	0.326666	0.0	0.0	0.0	0.0
	Z'	0.018276	-0.007630	0.008408	0.0	0.0	0.0	0.0
C2	S	-0.081224	-0.168157	-0.042149	0.0	0.0	0.0	0.0
	S'	0.230923	0.451503	0.092665	0.0	0.0	0.0	0.0
	S''	0.000407	-0.002508	-0.000305	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.356200	0.263870	-0.455576	0.152732
	X'	0.0	0.0	0.0	0.001296	0.017259	0.031108	0.031111
	Y	0.021757	0.154304	-0.082395	0.0	0.0	0.0	0.0
	Y'	0.013541	0.016981	0.008494	0.0	0.0	0.0	0.0
	Z	-0.100899	0.110891	-0.326666	0.0	0.0	0.0	0.0
	Z'	-0.018276	0.007630	-0.008408	0.0	0.0	0.0	0.0
O1	S	0.580929	-0.285187	-0.172316	0.0	0.0	0.0	0.0
	S'	0.276004	-0.149724	-0.092751	0.0	0.0	0.0	0.0
	S''	-0.006967	-0.017622	-0.010417	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.377603	-0.542674	0.303608	0.705469
	X'	0.0	0.0	0.0	-0.026525	-0.014060	-0.016080	0.044686
	Y	0.064253	-0.049111	-0.136090	0.0	0.0	0.0	0.0
	Y'	-0.028299	-0.005385	-0.030750	0.0	0.0	0.0	0.0
	Z	-0.111673	-0.092460	-0.564955	0.0	0.0	0.0	0.0
	Z'	0.028447	0.016177	0.012649	0.0	0.0	0.0	0.0
O2	S	-0.580929	0.285187	0.172316	0.0	0.0	0.0	0.0
	S'	-0.276004	0.149724	0.092751	0.0	0.0	0.0	0.0
	S''	0.006967	0.017622	0.010417	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.377603	-0.542674	-0.303608	-0.705469
	X'	0.0	0.0	0.0	-0.026525	-0.014060	0.016080	-0.044686
	Y	0.064253	-0.049111	-0.136090	0.0	0.0	0.0	0.0
	Y'	-0.028299	-0.005385	-0.030750	0.0	0.0	0.0	0.0
	Z	0.111673	0.092460	0.564955	0.0	0.0	0.0	0.0
	Z'	-0.028447	-0.016177	-0.012649	0.0	0.0	0.0	0.0
H1	S	0.025659	0.182111	-0.102308	0.132400	0.214970	0.221771	-0.237020
	S'	0.005843	0.012430	0.004539	0.015785	-0.015268	0.004602	0.033768
H2	S	0.025659	0.182111	-0.102308	-0.132400	-0.214970	-0.221771	0.237020
	S'	0.005843	0.012430	0.004539	-0.015785	0.015268	-0.004602	-0.033768
H3	S	-0.025659	-0.182111	0.102308	0.132400	0.214970	-0.221771	0.237020
	S'	-0.005843	-0.012430	-0.004539	0.015785	-0.015268	-0.004602	-0.033768
H4	S	-0.025659	-0.182111	0.102308	-0.132400	-0.214970	0.221771	-0.237020
	S'	-0.005843	-0.012430	-0.004539	-0.015785	0.015268	0.004602	0.033768

Table 53. MO's and occupation numbers for 1(st) SPIP model of 1,2-dioxetane

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.924389	2.000000	2.000000
C1	S	0.000071	-0.666568	-0.062997	0.170964	0.018734	-0.027800	0.042250	-0.000221	0.667745
	S'	-0.000149	-0.135316	0.204205	-0.486892	-0.050703	0.067225	-0.091762	0.000223	0.134002
	S''	0.000050	-0.000283	0.000565	0.000377	0.001652	0.000384	0.000894	0.000109	0.000137
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000035	-0.000021	0.032123	-0.074675	0.235611	0.514468	-0.067127	0.000211	-0.000743
	Y'	0.000022	0.000329	0.010701	-0.017810	0.016900	0.004932	0.005411	-0.000107	0.000210
	Z	0.000040	-0.001050	-0.085185	-0.058683	-0.269513	0.147915	0.076801	-0.000353	0.001220
	Z'	0.000025	0.000024	-0.020934	-0.014249	-0.023638	0.012946	-0.003486	0.000232	-0.000110
C2	S	0.000071	-0.666568	-0.062997	0.170964	0.018734	-0.027800	0.042250	0.000221	-0.667745
	S'	-0.000149	-0.135316	0.204205	-0.486892	-0.050703	0.067225	-0.091762	-0.000223	-0.134002
	S''	0.000050	-0.000283	0.000565	0.000377	0.001652	0.000384	0.000894	-0.000109	-0.000137
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000035	0.000021	-0.032123	0.074675	-0.235611	-0.514468	0.067127	0.000211	-0.000743
	Y'	-0.000022	-0.000329	-0.010701	0.017810	-0.016900	-0.004932	-0.005411	-0.000107	0.000210
	Z	0.000040	-0.001050	-0.085185	-0.058683	-0.269513	0.147915	0.076801	0.000353	-0.001220
	Z'	0.000025	0.000024	-0.020934	-0.014249	-0.023638	0.012946	-0.003486	-0.000232	0.000110
O1	S	-0.306353	0.000319	-0.506145	-0.295991	0.157833	-0.041501	0.003077	-0.306168	-0.000827
	S'	0.640041	0.000472	-0.219748	-0.154266	0.088802	-0.024835	0.016045	0.640305	-0.000985
	S''	-0.001398	0.000711	0.040521	-0.026781	0.024372	-0.011208	0.025935	-0.000694	-0.001301
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000601	-0.000032	-0.028736	-0.035434	0.044418	-0.033913	0.653695	-0.000831	0.000192
	Y'	0.000454	-0.000012	-0.015138	-0.012810	0.000067	-0.032131	-0.033227	0.000065	0.000253
	Z	-0.000647	-0.000545	0.091655	-0.120192	0.377753	-0.322526	0.031239	-0.000841	0.000695
	Z'	0.000471	-0.000935	-0.023674	0.028774	-0.023322	0.002265	0.026453	0.000285	0.001303
O2	S	-0.306353	0.000319	-0.506145	-0.295991	0.157833	-0.041501	0.003077	0.306168	0.000827
	S'	0.640041	0.000472	-0.219748	-0.154266	0.088802	-0.024835	0.016045	-0.640305	0.000985
	S''	-0.001398	0.000711	0.040521	-0.026781	0.024372	-0.011208	0.025935	0.000694	0.001301
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000601	0.000032	0.028736	0.035434	-0.044418	0.033913	-0.653695	-0.000831	0.000192
	Y'	-0.000454	0.000012	0.015138	0.012810	-0.000367	0.032131	0.033227	0.000065	0.000253
	Z	-0.000647	-0.000545	0.091655	-0.120192	0.377753	-0.322526	0.031239	0.000841	-0.000695
	Z'	0.000471	-0.000935	-0.023674	0.028774	-0.023322	0.002265	0.026453	-0.000285	-0.001303
H1	S	0.000004	-0.000024	0.007151	0.095577	0.162148	0.102886	-0.041948	-0.000129	-0.000241
	S'	-0.000003	-0.000106	-0.012674	0.017864	-0.003764	-0.003275	0.002750	0.000094	0.000172
H2	S	0.000004	-0.000024	0.007151	0.095577	0.162148	0.102886	-0.041948	-0.000129	-0.000241
	S'	-0.000003	-0.000106	-0.012674	0.017864	-0.003764	-0.003275	0.002750	0.000094	0.000172
H3	S	0.000004	-0.000024	0.007151	0.095577	0.162148	0.102886	-0.041948	0.000129	0.000241
	S'	-0.000003	-0.000106	-0.012674	0.017864	-0.003764	-0.003275	0.002750	-0.000094	-0.000172
H4	S	0.000004	-0.000024	0.007151	0.095577	0.162148	0.102886	-0.041948	0.000129	0.000241
	S'	-0.000003	-0.000106	-0.012674	0.017864	-0.003764	-0.003275	0.002750	-0.000094	-0.000172

Table 53. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.075611	2.000000	2.000000	2.000000	2.000000
C1	S	0.081491	0.167881	0.042856	0.006974	0.0	0.0	0.0	0.0
	S'	-0.231656	-0.450850	-0.094397	-0.006364	0.0	0.0	0.0	0.0
	S''	-0.000419	0.002495	0.000279	-0.000031	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.359165	0.259355	0.456782	-0.148239
	X'	0.0	0.0	0.0	0.0	0.001378	0.017448	-0.030986	-0.031740
	Y	0.021735	0.154924	-0.080144	0.003299	0.0	0.0	0.0	0.0
	Y'	0.013540	0.016733	0.008217	0.003827	0.0	0.0	0.0	0.0
	Z	0.100977	-0.111040	0.329954	0.044373	0.0	0.0	0.0	0.0
	Z'	0.018145	-0.007798	0.007693	-0.006057	0.0	0.0	0.0	0.0
C2	S	-0.081491	-0.167881	-0.042856	-0.006974	0.0	0.0	0.0	0.0
	S'	0.231656	0.450850	0.094397	0.006364	0.0	0.0	0.0	0.0
	S''	0.000419	-0.002495	-0.000279	0.000031	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.359165	0.259355	-0.456782	0.148239
	X'	0.0	0.0	0.0	0.0	0.001378	0.017448	0.030986	0.031740
	Y	0.021735	0.154924	-0.080144	0.003299	0.0	0.0	0.0	0.0
	Y'	0.013540	0.016733	0.008217	0.003827	0.0	0.0	0.0	0.0
	Z	-0.100977	0.111040	-0.329954	-0.044373	0.0	0.0	0.0	0.0
	Z'	-0.018145	0.007798	-0.007693	0.006057	0.0	0.0	0.0	0.0
O1	S	0.583148	-0.287491	-0.180475	-0.313106	0.0	0.0	0.0	0.0
	S'	0.277537	-0.151179	-0.097947	-0.185785	0.0	0.0	0.0	0.0
	S''	-0.005905	-0.018346	-0.012479	-0.040808	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.371201	-0.546315	0.297965	0.708050
	X'	0.0	0.0	0.0	0.0	-0.025862	-0.014969	-0.015424	0.046946
	Y	0.057445	-0.044459	-0.121845	0.868263	0.0	0.0	0.0	0.0
	Y'	-0.028671	-0.005133	-0.030127	-0.098424	0.0	0.0	0.0	0.0
	Z	-0.111027	-0.091060	-0.564599	-0.058575	0.0	0.0	0.0	0.0
	Z'	0.028594	0.015708	0.010570	-0.008859	0.0	0.0	0.0	0.0
O2	S	-0.583148	0.287491	0.180475	0.313106	0.0	0.0	0.0	0.0
	S'	-0.277537	0.151179	0.097947	0.185785	0.0	0.0	0.0	0.0
	S''	0.005905	0.018346	0.012479	0.040808	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.371201	-0.546315	-0.297965	-0.708050
	X'	0.0	0.0	0.0	0.0	-0.025862	-0.014969	0.015424	-0.046946
	Y	0.057445	-0.044459	-0.121845	0.868263	0.0	0.0	0.0	0.0
	Y'	-0.028671	-0.005133	-0.030127	-0.098424	0.0	0.0	0.0	0.0
	Z	0.111027	0.091060	0.564599	0.058575	0.0	0.0	0.0	0.0
	Z'	-0.028594	-0.015708	-0.010570	0.008859	0.0	0.0	0.0	0.0
H1	S	0.026173	0.182114	-0.103126	-0.019110	0.134497	0.214345	0.223524	-0.236266
	S'	0.005763	0.012444	0.004940	0.001223	0.015675	-0.015742	0.004348	0.034212
H2	S	0.026173	0.182114	-0.103126	-0.019110	-0.134497	-0.214345	-0.223524	0.236266
	S'	0.005763	0.012444	0.004940	0.001223	-0.015675	0.015742	-0.004348	-0.034212
H3	S	-0.026173	-0.182114	0.103126	0.019110	0.134497	0.214345	-0.223524	0.236266
	S'	-0.005763	-0.012444	-0.004940	-0.001223	0.015675	-0.015742	-0.004348	-0.034212
H4	S	-0.026173	-0.182114	0.103126	0.019110	-0.134497	-0.214345	0.223524	-0.236266
	S'	-0.005763	-0.012444	-0.004940	-0.001223	-0.015675	0.015742	0.004348	0.034212

Table 54. MO's and occupation numbers for 2(nd) SPIP model of 1,2-dioxetane

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	1.980813	1.925455	2.000000	2.000000
C1	S	0.000071	-0.666568	-0.043585	0.145379	0.016046	-0.106566	0.040107	-0.000221	0.667745
	S'	-0.000149	-0.135316	0.149962	-0.420323	-0.039732	0.295397	-0.085784	0.000223	0.134002
	S''	0.000050	-0.000283	0.000553	0.000648	0.001482	-0.000486	0.000916	0.000109	0.000137
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000035	-0.000021	-0.030129	0.187948	0.099093	0.529586	-0.052373	0.000211	-0.000743
	Y'	0.000022	0.000329	0.007685	-0.010711	0.015792	0.023455	0.005412	-0.000107	0.000210
	Z	0.000040	-0.001050	-0.096925	-0.029645	-0.294609	0.087238	0.079877	-0.000353	0.001220
	Z'	0.000025	0.000024	-0.022719	-0.009958	-0.025359	0.011232	-0.003233	0.000232	-0.000110
C2	S	0.000071	-0.666568	-0.043585	0.145379	0.016046	-0.106566	0.040107	0.000221	-0.667745
	S'	-0.000149	-0.135316	0.149962	-0.420323	-0.039732	0.295397	-0.085784	-0.000223	-0.134002
	S''	0.000050	-0.000283	0.000553	0.000648	0.001482	-0.000486	0.000916	-0.000109	-0.000137
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000035	0.000021	0.030129	-0.187948	-0.099093	-0.529586	0.052373	0.000211	-0.000743
	Y'	-0.000022	-0.000329	-0.007685	0.010711	-0.015792	-0.023455	-0.005412	-0.000107	0.000210
	Z	0.000040	-0.001050	-0.096925	-0.029645	-0.294609	0.087238	0.079877	0.000353	-0.001220
	Z'	0.000025	0.000024	-0.022719	-0.009958	-0.025359	0.011232	-0.003233	-0.000232	0.000110
O1	S	-0.306353	0.000319	-0.529903	-0.234639	0.175701	0.060112	0.004010	-0.306168	-0.000827
	S'	0.640041	0.000472	-0.232404	-0.124467	0.099004	0.035351	0.016560	0.640305	-0.000985
	S''	-0.001398	0.000711	0.037964	-0.026323	0.028097	0.012443	0.025951	-0.000694	-0.001301
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000601	-0.000032	-0.028994	-0.040004	0.055812	-0.024853	0.652886	-0.000831	0.000192
	Y'	0.000454	-0.000012	-0.013234	-0.024262	0.008821	-0.022676	-0.033916	0.000065	0.000253
	Z	-0.000647	-0.000545	0.100280	-0.186339	0.454679	-0.135468	0.024534	-0.000841	0.000695
	Z'	0.000471	-0.000935	-0.020246	0.023652	-0.024600	-0.019530	0.026212	0.000285	0.001303
O2	S	-0.306353	0.000319	-0.529903	-0.234639	0.175701	0.060112	0.004010	0.306168	0.000827
	S'	0.640041	0.000472	-0.232404	-0.124467	0.099004	0.035351	0.016560	-0.640305	0.000985
	S''	-0.001398	0.000711	0.037964	-0.026323	0.028097	0.012443	0.025951	0.000694	0.001301
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000601	0.000032	0.028994	0.040004	-0.055812	0.024853	-0.652886	-0.000831	0.000192
	Y'	-0.000454	0.000012	0.013234	0.024262	-0.008821	0.022676	0.033916	0.000065	0.000253
	Z	-0.000647	-0.000545	0.100280	-0.186339	0.454679	-0.135468	0.024534	0.000841	-0.000695
	Z'	0.000471	-0.000935	-0.020246	0.023652	-0.024600	-0.019530	0.026212	-0.000285	-0.001303
H1	S	0.000004	-0.000024	0.002167	0.155336	0.125033	0.083249	-0.039757	-0.000129	-0.000241
	S'	-0.000003	-0.000106	-0.010382	0.014205	-0.003851	-0.014042	0.002557	0.000094	0.000172
H2	S	0.000004	-0.000024	0.002167	0.155336	0.125033	0.083249	-0.039757	-0.000129	-0.000241
	S'	-0.000003	-0.000106	-0.010382	0.014205	-0.003851	-0.014042	0.002557	0.000094	0.000172
H3	S	0.000004	-0.000024	0.002167	0.155336	0.125033	0.083249	-0.039757	0.000129	0.000241
	S'	-0.000003	-0.000106	-0.010382	0.014205	-0.003851	-0.014042	0.002557	-0.000094	-0.000172
H4	S	0.000004	-0.000024	0.002167	0.155336	0.125033	0.083249	-0.039757	0.000129	0.000241
	S'	-0.000003	-0.000106	-0.010382	0.014205	-0.003851	-0.014042	0.002557	-0.000094	-0.000172

Table 54. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.074545	0.019187	2.000000	2.000000	2.000000	2.000000
C1	S	0.081279	0.167550	0.042760	0.013358	0.343965	0.0	0.0	0.0	0.0
	S'	-0.231114	-0.450151	-0.094126	-0.019387	-0.743318	0.0	0.0	0.0	0.0
	S''	-0.000460	0.002406	0.000265	0.000438	0.041944	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.358101	0.259662	0.456270	-0.148533
	X'	0.0	0.0	0.0	0.0	0.0	0.001146	0.017306	-0.031411	-0.031548
	Y	0.021594	0.155055	-0.080217	-0.015473	-0.835372	0.0	0.0	0.0	0.0
	Y'	0.013569	0.016721	0.008291	0.004255	-0.139617	0.0	0.0	0.0	0.0
	Z	0.100919	-0.110603	0.329486	0.037317	-0.140485	0.0	0.0	0.0	0.0
	Z'	0.018101	-0.007633	0.007503	-0.005695	-0.058284	0.0	0.0	0.0	0.0
C2	S	-0.081279	-0.167550	-0.042760	-0.013358	-0.343965	0.0	0.0	0.0	0.0
	S'	0.231114	0.450151	0.094126	0.019387	0.743318	0.0	0.0	0.0	0.0
	S''	0.000460	-0.002406	-0.000265	-0.000438	-0.041944	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.358101	0.259662	-0.456270	0.148533
	X'	0.0	0.0	0.0	0.0	0.0	0.001146	0.017306	0.031411	0.031548
	Y	0.021594	0.155055	-0.080217	-0.015473	-0.835372	0.0	0.0	0.0	0.0
	Y'	0.013569	0.016721	0.008291	0.004255	-0.139617	0.0	0.0	0.0	0.0
	Z	-0.100919	0.110603	-0.329486	-0.037317	0.140485	0.0	0.0	0.0	0.0
	Z'	-0.018101	0.007633	-0.007503	0.005695	0.058284	0.0	0.0	0.0	0.0
O1	S	0.583467	-0.287121	-0.179673	-0.312489	-0.069625	0.0	0.0	0.0	0.0
	S'	0.277725	-0.150974	-0.097461	-0.185474	-0.058193	0.0	0.0	0.0	0.0
	S''	-0.005825	-0.018276	-0.012311	-0.040905	-0.055372	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.372420	-0.545458	0.298827	0.707677
	X'	0.0	0.0	0.0	0.0	0.0	-0.025815	-0.015048	-0.015397	0.047003
	Y	0.057346	-0.044656	-0.122576	0.870488	0.071383	0.0	0.0	0.0	0.0
	Y'	-0.028674	-0.005180	-0.030285	-0.097588	0.020008	0.0	0.0	0.0	0.0
	Z	-0.111012	-0.091483	-0.564892	-0.060888	0.064877	0.0	0.0	0.0	0.0
	Z'	0.028560	0.015661	0.010561	-0.007838	0.032693	0.0	0.0	0.0	0.0
O2	S	-0.583467	0.287121	0.179673	0.312489	0.069625	0.0	0.0	0.0	0.0
	S'	-0.277725	0.150974	0.097461	0.185474	0.058193	0.0	0.0	0.0	0.0
	S''	0.005825	0.018276	0.012311	0.040905	0.055372	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.372420	-0.545458	-0.298827	-0.707677
	X'	0.0	0.0	0.0	0.0	0.0	-0.025815	-0.015048	0.015397	-0.047003
	Y	0.057346	-0.044656	-0.122576	0.870488	0.071383	0.0	0.0	0.0	0.0
	Y'	-0.028674	-0.005180	-0.030285	-0.097588	0.020008	0.0	0.0	0.0	0.0
	Z	0.111012	0.091483	0.564892	0.060888	-0.064877	0.0	0.0	0.0	0.0
	Z'	-0.028560	-0.015661	-0.010561	0.007838	-0.032693	0.0	0.0	0.0	0.0
H1	S	0.026201	0.182455	-0.103285	-0.019444	-0.076574	0.134424	0.215036	0.223522	-0.236753
	S'	0.005712	0.012319	0.004967	0.001056	0.012010	0.015589	-0.015851	0.004281	0.034302
H2	S	0.026201	0.182455	-0.103285	-0.019444	-0.076574	-0.134424	-0.215036	-0.223522	0.236753
	S'	0.005712	0.012319	0.004967	0.001056	0.012010	-0.015589	0.015851	-0.004281	-0.034302
H3	S	-0.026201	-0.182455	0.103285	0.019444	0.076574	0.134424	0.215036	-0.223522	0.236753
	S'	-0.005712	-0.012319	-0.004967	-0.001056	-0.012010	0.015589	-0.015851	-0.004281	-0.034302
H4	S	-0.026201	-0.182455	0.103285	0.019444	0.076574	-0.134424	-0.215036	0.223522	-0.236753
	S'	-0.005712	-0.012319	-0.004967	-0.001056	-0.012010	-0.015589	0.015851	0.004281	0.034302

Table 55. Hartree-Fock orbitals for nitrosyl hydride

		(1a)	(2a)	(3a)	(4a)	(5a)	(6a)	(7a)	(1b)
ETOGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000
N	S	0.000411	0.851313	-0.198918	-0.357363	0.098596	0.167691	-0.251444	0.0
	S'	-0.000354	0.506841	0.374027	0.574711	-0.158465	-0.250126	0.371610	0.0
	S''	0.000190	-0.005103	0.061655	0.025906	-0.037800	0.045749	-0.088730	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.560993
	S'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.035694
	Y	-0.000022	0.001185	-0.051367	-0.210889	-0.437342	-0.254636	0.560954	0.0
	Y'	0.000026	0.000815	0.001252	-0.020408	-0.011706	0.009279	-0.019880	0.0
	Z	0.000040	0.002889	-0.135409	0.159549	0.201192	-0.469918	0.264834	0.0
	Z'	-0.000055	-0.000052	-0.050769	0.027985	0.052428	-0.029020	-0.035792	0.0
O	S	0.837767	-0.002116	-0.328718	0.364276	-0.198475	0.151246	-0.005935	0.0
	S'	0.558461	0.001970	0.537104	-0.521761	0.279484	-0.205410	0.002915	0.0
	S''	0.002403	0.001479	-0.057100	-0.020383	0.026288	-0.035343	0.017756	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.693316
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.018924
	Y	0.000093	-0.000027	-0.013034	-0.056407	-0.434480	-0.501222	-0.777373	0.0
	Y'	0.000072	-0.000067	-0.002048	-0.011270	-0.017577	-0.004111	0.049443	0.0
	Z	-0.001125	0.001795	0.181638	0.131168	-0.427605	0.472055	-0.076123	0.0
	Z'	-0.001232	-0.001813	0.056933	0.024968	-0.034079	0.032342	-0.016157	0.0
H	S	0.000052	-0.000167	-0.035000	-0.258321	-0.228591	0.092155	0.394535	0.0
	S'	-0.000028	-0.000245	-0.016264	-0.035891	-0.015195	-0.000320	-0.037977	0.0

Table 56. SPIP MO's and occupation numbers for nitrosyl hydride

		(1a)	(2a)	(3a)	(4a)	(5a)	(6a)	(7a)	(1b)	(2b)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.863647	0.136353
N	S	0.000411	0.851313	-0.192577	-0.358841	0.083180	0.174705	-0.273400	0.0	0.0
	S'	-0.000354	0.506841	0.364740	0.578031	-0.135723	-0.260321	0.388763	0.0	0.0
	S''	0.000190	-0.005103	0.061431	0.023635	-0.038598	0.048080	-0.093522	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.592257	0.817042
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.025290	-0.020475
	Y	-0.000022	0.001185	-0.049329	-0.205357	-0.423806	-0.235667	0.576956	0.0	0.0
	Y'	0.000026	0.000816	0.001030	-0.018903	-0.010763	0.010478	-0.025879	0.0	0.0
	Z	0.000040	0.002889	-0.133202	0.141981	0.208129	-0.452663	0.270187	0.0	0.0
	Z'	-0.000055	-0.000052	-0.050956	0.026150	0.053045	-0.029483	-0.037457	0.0	0.0
O	S	0.837767	-0.002116	-0.334659	0.369722	-0.188935	0.135888	-0.003033	0.0	0.0
	S'	0.558461	0.001970	0.545163	-0.528020	0.266187	-0.185073	-0.000638	0.0	0.0
	S''	0.002403	0.001479	-0.056546	-0.023205	0.025907	-0.032040	0.016955	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.672350	-0.767781
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.004316	-0.083202
	Y	0.000093	-0.000027	-0.013227	-0.057478	-0.446252	-0.523347	-0.754089	0.0	0.0
	Y'	0.000072	-0.000067	-0.001844	-0.010890	-0.015843	-0.001734	0.051527	0.0	0.0
	Z	-0.001125	0.001795	0.182560	0.149249	-0.437479	0.471610	-0.086184	0.0	0.0
	Z'	-0.001232	-0.001813	0.056357	0.026459	-0.032399	0.028394	-0.015244	0.0	0.0
H	S	0.000052	-0.000167	-0.034742	-0.254712	-0.231515	0.105000	0.397751	0.0	0.0
	S'	-0.000028	-0.000245	-0.015462	-0.036139	-0.015027	-0.000418	-0.038917	0.0	0.0

Table 57. Hartree-Fock orbitals for HNO dimer

		(1a)	(2a)	(3a)	(4a)	(5a)	(6a)	(7a)	(8a)	(9a)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000
N1	S	0.000090	0.649643	0.090497	-0.193905	0.043610	-0.006468	0.085108	-0.007267	-0.111199
	S'	-0.000103	0.195300	-0.252130	0.470116	-0.092269	0.018446	-0.166125	0.021992	0.218794
	S''	-0.000000	0.001672	-0.022612	-0.002007	0.017930	0.003851	0.049986	0.011315	-0.046866
	X	0.000034	-0.000348	-0.019330	0.060147	-0.199717	0.006118	0.311624	-0.120997	-0.452154
	X'	-0.000015	-0.000974	-0.003033	0.023184	-0.041977	0.017703	0.032443	0.020963	-0.014979
	Y	-0.000030	-0.000381	-0.063008	0.125344	0.365965	0.265051	-0.073706	-0.300585	-0.268340
	Y'	0.000066	-0.000599	-0.021791	0.037292	0.067910	0.042262	-0.018052	-0.033576	0.004456
	Z	0.000081	0.000955	0.079307	0.029898	-0.163825	0.323489	-0.098762	0.130798	0.222327
	Z'	-0.000025	0.000470	0.030479	0.015540	-0.036839	0.044760	-0.016346	-0.011026	-0.035984
N2	S	0.000090	0.649643	0.090497	-0.193905	0.043610	-0.006468	0.085108	-0.007267	-0.111199
	S'	-0.000103	0.195300	-0.252130	0.470116	-0.092269	0.018446	-0.166125	0.021992	0.218794
	S''	-0.000000	0.001672	-0.022612	-0.002007	0.017930	0.003851	0.049986	0.011315	-0.046866
	X	-0.000034	0.000348	0.019330	-0.060147	0.199717	-0.006118	-0.311624	0.120997	0.452154
	X'	0.000015	0.000974	0.003033	-0.023184	0.041977	-0.017703	-0.032443	-0.020963	0.014979
	Y	0.000030	0.000381	0.063008	-0.125344	-0.365965	-0.265051	0.073706	0.300585	0.268340
	Y'	-0.000066	0.000599	0.021791	-0.037292	-0.067910	-0.042262	0.018052	0.033576	-0.004456
	Z	0.000081	0.000955	0.079307	0.029898	-0.163825	0.323489	-0.098762	0.130798	0.222327
	Z'	-0.000025	0.000470	0.030479	0.015540	-0.036839	0.044760	-0.016346	-0.011026	-0.035984
O1	S	-0.306532	0.000059	0.444825	0.367597	0.129745	-0.054731	0.157829	0.035798	0.022989
	S'	0.639957	0.000013	0.195543	0.176904	0.066824	-0.031855	0.084096	0.015133	0.004920
	S''	-0.001360	-0.000062	-0.025901	0.001624	-0.000709	-0.009742	0.003516	-0.011781	-0.022440
	X	-0.000261	0.000097	-0.033582	-0.017662	-0.053617	-0.006158	0.329714	-0.498804	0.463925
	X'	0.000212	0.000115	0.007008	0.001272	0.000076	-0.001810	-0.003974	-0.012956	0.025434
	Y	-0.000541	0.000010	-0.090321	-0.076452	0.205076	0.230030	0.397354	0.403089	0.102673
	Y'	0.000416	0.000046	0.016221	0.015004	-0.005928	-0.015016	-0.009503	0.004584	-0.003478
	Z	-0.000562	0.000487	-0.086213	0.060329	0.211496	-0.391640	0.102137	0.143167	0.053449
	Z'	0.000451	0.000417	0.012198	-0.018455	-0.003844	0.025802	0.015055	0.014143	0.017031
O2	S	-0.306532	0.000059	0.444825	0.367597	0.129745	-0.054731	0.157829	0.035798	0.022989
	S'	0.639957	0.000013	0.195543	0.176904	0.066824	-0.031855	0.084096	0.015133	0.004920
	S''	-0.001360	-0.000062	-0.025901	0.001624	-0.000709	-0.009742	0.003516	-0.011781	-0.022440
	X	0.000261	-0.000097	0.033582	0.017662	0.053617	0.006158	-0.329714	0.498804	-0.463925
	X'	-0.000212	-0.000115	-0.007008	-0.001272	-0.000076	0.001810	0.003974	0.012956	-0.025434
	Y	0.000541	-0.000010	0.090321	0.076452	-0.205076	-0.230030	-0.397354	-0.403089	-0.102673
	Y'	-0.000416	-0.000046	-0.016221	-0.015004	0.005928	0.015016	0.009503	-0.004584	0.003478
	Z	-0.000562	0.000487	-0.086213	0.060329	0.211496	-0.391640	0.102137	0.143167	0.053449
	Z'	0.000451	0.000417	0.012198	-0.018455	-0.003844	0.025802	0.015055	0.014143	0.017031
H1	S	0.000089	0.000598	0.031263	-0.091821	0.240998	-0.013040	-0.171159	-0.098864	0.198805
	S'	0.000068	0.000576	-0.005011	0.008886	0.009168	-0.006864	-0.014006	-0.022001	0.026100
H2	S	0.000089	0.000598	0.031263	-0.091821	0.240998	-0.013040	-0.171159	-0.098864	0.198805
	S'	0.000068	0.000576	-0.005011	0.008886	0.009168	-0.006864	-0.014006	-0.022001	0.026100

Table 57. (Continued)

		(1b)	(2b)	(3b)	(4b)	(5b)	(6b)	(7b)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000
N1	S	-0.000748	0.645841	0.137882	0.194631	0.048001	-0.045572	0.020361
	S'	0.001344	0.202208	-0.322726	-0.441088	-0.140962	0.093242	-0.069465
	S''	-0.001015	-0.004370	0.023481	0.019066	-0.101406	-0.014217	-0.066514
	X	0.000042	-0.000311	-0.027011	-0.221055	0.338788	-0.262124	0.306302
	X'	-0.000059	-0.000877	-0.005051	-0.053840	0.020874	-0.036709	-0.010184
	Y	0.000294	0.000369	0.037307	0.097210	0.108535	-0.002796	0.194968
	Y'	-0.000370	-0.002871	0.020942	0.031265	-0.038276	0.011087	-0.047951
	Z	-0.000178	0.000659	0.108187	-0.045202	-0.041129	-0.173693	-0.410084
	Z'	0.000214	0.000976	0.027221	-0.013773	0.032085	-0.027716	-0.009286
N2	S	0.000748	-0.645841	-0.137882	-0.194631	-0.048001	0.045572	-0.020361
	S'	-0.001344	-0.202208	0.322726	0.441088	0.140962	-0.093242	0.069465
	S''	0.001015	0.004370	-0.023481	-0.019066	0.101406	0.014217	0.066514
	X	0.000042	-0.000311	-0.027011	-0.221055	0.338788	-0.262124	0.306302
	X'	-0.000059	-0.000877	-0.005051	-0.053840	0.020874	-0.036709	-0.010184
	Y	0.000294	0.000369	0.037307	0.097210	0.108535	-0.002796	0.194968
	Y'	-0.000370	-0.002871	0.020942	0.031265	-0.038276	0.011087	-0.047951
	Z	0.000178	-0.000659	-0.108187	0.045202	0.041129	0.173693	0.410084
	Z'	-0.000214	-0.000976	-0.027221	0.013773	-0.032085	0.027716	0.009286
O1	S	-0.306452	-0.000233	0.542723	-0.349572	-0.150868	0.134155	0.031743
	S'	0.640124	-0.000260	0.257496	-0.176869	-0.073955	0.069083	0.017492
	S''	-0.000777	-0.000241	-0.006351	-0.007675	0.008959	-0.003683	0.001654
	X	-0.000319	0.000068	-0.013822	-0.094543	0.359435	0.496909	-0.179848
	X'	0.000063	-0.000039	-0.002641	0.005791	-0.017473	0.004287	-0.009011
	Y	-0.000598	0.000466	0.044972	-0.027239	-0.145439	-0.058236	0.185877
	Y'	0.000168	0.000658	-0.024342	0.003043	0.006294	0.016353	0.024883
	Z	-0.000691	0.000386	-0.102660	-0.060061	-0.214081	0.262078	0.414494
	Z'	0.000312	0.000235	0.023969	0.005714	0.003802	-0.009646	-0.007298
O2	S	0.306452	0.000233	-0.542723	0.349572	0.150868	-0.134155	-0.031743
	S'	-0.640124	0.000260	-0.257496	0.176869	0.073955	-0.069083	-0.017492
	S''	0.000777	0.000241	0.006351	0.007675	-0.008959	0.003683	-0.001654
	X	-0.000319	0.000068	-0.013822	-0.094543	0.359435	0.496909	-0.179848
	X'	0.000063	-0.000039	-0.002641	0.005791	-0.017473	0.004287	-0.009011
	Y	-0.000598	0.000466	0.044972	-0.027239	-0.145439	-0.058236	0.185877
	Y'	0.000168	0.000658	-0.024342	0.003043	0.006294	0.016353	0.024883
	Z	0.000691	-0.000386	0.102660	0.060061	0.214081	-0.262078	-0.414494
	Z'	-0.000312	-0.000235	-0.023969	-0.005714	-0.003802	0.009646	0.007298
H1	S	0.000158	0.000899	0.048276	0.217780	-0.026031	0.179406	0.020049
	S'	0.000085	0.000809	-0.009827	-0.003926	0.015233	0.016197	0.015926
H2	S	-0.000158	-0.000899	-0.048276	-0.217780	0.026031	-0.179406	-0.020049
	S'	-0.000085	-0.000809	0.009827	0.003926	-0.015233	-0.016197	-0.015926

Table 58. MO's and occupation numbers for (1st) SPIP model of HNO dimer

		(1a)	(2a)	(3a)	(4a)	(5a)	(6a)	(7a)	(8a)	(9a)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.894562
N1	S	0.000090	0.649643	0.107345	-0.181366	0.035073	-0.031658	0.068756	-0.122465	0.029324
	S'	-0.000103	0.195300	-0.290164	0.441275	-0.077029	0.064781	-0.141312	0.237933	-0.056838
	S''	-0.000000	0.001672	-0.017661	0.002160	0.010274	-0.016221	0.023022	-0.060264	0.024978
	X	0.000034	-0.000348	-0.025285	0.057852	-0.223416	-0.121598	0.320718	-0.433154	-0.044003
	X'	-0.000015	-0.000974	-0.001161	0.026547	-0.049592	-0.004968	-0.002018	-0.027242	0.017597
	Y	-0.000030	-0.000381	-0.073991	0.121628	0.334003	0.341848	0.333652	-0.161351	-0.077732
	Y'	0.000066	-0.000599	-0.022062	0.038684	0.061253	0.053646	0.028498	0.013595	0.005419
	Z	0.000081	0.000955	0.096310	0.056007	-0.219397	0.290480	-0.165807	0.152903	0.122819
	Z'	-0.000025	0.000470	0.026974	0.014698	-0.040808	0.046024	0.012614	-0.026417	-0.021367
N2	S	0.000090	0.649643	0.107345	-0.181366	0.035073	-0.031658	0.068756	-0.122465	0.029324
	S'	-0.000103	0.195300	-0.290164	0.441275	-0.077029	0.064781	-0.141312	0.237933	-0.056838
	S''	-0.000000	0.001672	-0.017661	0.002160	0.010274	-0.016221	0.023022	-0.060264	0.024978
	X	-0.000034	0.000348	0.025285	-0.057852	0.223416	0.121598	-0.320718	0.433154	0.044003
	X'	0.000015	0.000974	0.001161	-0.026547	0.049592	0.004968	0.002018	0.027242	-0.017597
	Y	0.000030	0.000381	0.073991	-0.121628	-0.334003	-0.341848	-0.333652	0.161351	0.077732
	Y'	-0.000066	0.000599	0.022062	-0.038684	-0.061253	-0.053646	-0.028498	-0.013595	-0.005419
	Z	0.000081	0.000955	0.096310	0.056007	-0.219397	0.290480	-0.165807	0.152903	0.122819
	Z'	-0.000025	0.000470	0.026974	0.014698	-0.040808	0.046024	0.012614	-0.026417	-0.021367
O1	S	-0.306532	0.000059	0.432870	0.406571	0.105157	-0.121664	0.024448	-0.022150	0.016601
	S'	0.639957	0.000013	0.190300	0.195117	0.055039	-0.066258	0.017807	-0.017060	0.013292
	S''	-0.001360	-0.000062	-0.027097	-0.001395	0.001740	-0.007866	0.014608	-0.015693	-0.002254
	X	-0.000261	0.000097	-0.001417	0.014413	-0.094754	-0.148236	0.481923	0.510823	0.229234
	X'	0.000212	0.000115	0.006522	0.001435	0.000744	-0.000977	0.006248	0.030555	-0.004876
	Y	-0.000541	0.000010	0.002509	0.018151	0.072766	-0.003205	-0.155367	-0.178305	0.618190
	Y'	0.000416	0.000046	0.011651	0.012399	-0.000579	-0.010274	-0.010155	-0.001537	-0.034086
	Z	-0.000562	0.000487	-0.088021	0.054699	0.256574	-0.382248	-0.128087	0.000368	0.019153
	Z'	0.000451	0.000417	0.017628	-0.012297	-0.011214	0.012058	-0.005836	0.003875	0.030063
O2	S	-0.306532	0.000059	0.432870	0.406571	0.105157	-0.121664	0.024448	-0.022150	0.016601
	S'	0.639957	0.000013	0.190300	0.195117	0.055039	-0.066258	0.017807	-0.017060	0.013292
	S''	-0.001360	-0.000062	-0.027097	-0.001395	0.001740	-0.007866	0.014608	-0.015693	-0.002254
	X	0.000261	-0.000097	0.001417	-0.014413	0.094754	0.148236	-0.481923	-0.510823	-0.229234
	X'	-0.000212	-0.000115	-0.006522	-0.001435	-0.000744	0.000977	-0.006248	-0.030555	0.004876
	Y	0.000541	-0.000010	-0.002509	-0.018151	-0.072766	0.003205	0.155367	0.178305	-0.618190
	Y'	-0.000416	-0.000046	-0.011651	-0.012399	0.000579	0.010274	0.010155	0.001537	0.034086
	Z	-0.000562	0.000487	-0.088021	0.054699	0.256574	-0.382248	-0.128087	0.000368	0.019153
	Z'	0.000451	0.000417	0.017628	-0.012297	-0.011214	0.012058	-0.005836	0.003875	0.030063
H1	S	0.000089	0.000598	0.032412	-0.094463	0.261011	0.088628	-0.015883	0.245065	-0.018745
	S'	0.000068	0.000576	-0.007087	0.006818	0.012641	0.001654	0.007708	0.034974	-0.007897
H2	S	0.000089	0.000598	0.032412	-0.094463	0.261011	0.088628	-0.015883	0.245065	-0.018745
	S'	0.000068	0.000576	-0.007087	0.006818	0.012641	0.001654	0.007708	0.034974	-0.007897

Table 58. (Continued)

		(1b)	(2b)	(3b)	(4b)	(5b)	(6b)	(7b)	(8b)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	0.105438
N1	S	-0.000748	0.645841	0.138686	0.194254	0.048770	-0.045267	0.019730	-0.001515
	S'	0.001344	0.202208	-0.324370	-0.440346	-0.142641	0.092516	-0.067734	-0.003533
	S''	-0.001015	-0.004370	0.024175	0.018864	-0.101335	-0.014620	-0.065695	-0.009657
	X	0.000042	-0.000311	-0.026984	-0.221137	0.343694	-0.259235	0.303153	0.027300
	X'	-0.000059	-0.000877	-0.005145	-0.053690	0.021196	-0.036567	-0.011177	-0.003333
	Y	0.000294	0.000369	0.037310	0.097504	0.109728	-0.004340	0.193081	0.007575
	Y'	-0.000370	-0.002871	0.020977	0.031153	-0.038572	0.011122	-0.048235	-0.011331
	Z	-0.000178	0.000659	0.107999	-0.045152	-0.041049	-0.174746	-0.415034	-0.062253
	Z'	0.000214	0.000976	0.027049	-0.013816	0.032352	-0.026806	-0.008860	0.005253
N2	S	0.000748	-0.645841	-0.138686	-0.194254	-0.048770	0.045267	-0.019730	0.001515
	S'	-0.001344	-0.202208	0.324370	0.440346	0.142641	-0.092516	0.067734	0.003533
	S''	0.001015	0.004370	-0.024175	-0.018864	0.101335	0.014620	0.065695	0.009657
	X	0.000042	-0.000311	-0.026984	-0.221137	0.343694	-0.259235	0.303153	0.027300
	X'	-0.000059	-0.000877	-0.005145	-0.053690	0.021196	-0.036567	-0.011177	-0.003333
	Y	0.000294	0.000369	0.037310	0.097504	0.109728	-0.004340	0.193081	0.007575
	Y'	-0.000370	-0.002871	0.020977	0.031153	-0.038572	0.011122	-0.048235	-0.011331
	Z	0.000178	-0.000659	-0.107999	0.045152	0.041049	0.174746	0.415034	0.062253
	Z'	-0.000214	-0.000976	-0.027049	0.013816	-0.032352	0.026806	0.008860	-0.005253
O1	S	-0.306452	-0.000233	0.544732	-0.353021	-0.153401	0.139212	0.041341	0.259898
	S'	0.640124	-0.000260	0.258910	-0.179000	-0.075428	0.072462	0.023221	0.153979
	S''	-0.000777	-0.000241	-0.005259	-0.008628	0.008552	-0.002053	0.003144	0.039889
	X	-0.000319	0.000068	-0.015845	-0.091032	0.353245	0.497367	-0.183876	-0.244881
	X'	0.000063	-0.000039	-0.002712	0.005590	-0.016656	0.005398	-0.009638	0.034019
	Y	-0.000598	0.000466	0.037651	-0.019617	-0.140214	-0.075275	0.170455	-0.812353
	Y'	0.000168	0.000658	-0.024800	0.003388	0.005957	0.015402	0.024421	0.084690
	Z	-0.000691	0.000386	-0.101665	-0.059694	-0.213974	0.257108	0.418169	0.089505
	Z'	0.000312	0.000235	0.024118	0.005112	0.003068	-0.008123	-0.005059	0.007828
O2	S	0.306452	0.000233	-0.544732	0.353021	0.153401	-0.139212	-0.041341	-0.259898
	S'	-0.640124	0.000260	-0.258910	0.179000	0.075428	-0.072462	-0.023221	-0.153979
	S''	0.000777	0.000241	0.005259	0.008628	-0.008552	0.002053	-0.003144	-0.039889
	X	-0.000319	0.000068	-0.015845	-0.091032	0.353245	0.497367	-0.183876	-0.244881
	X'	0.000063	-0.000039	-0.002712	0.005590	-0.016656	0.005398	-0.009638	0.034019
	Y	-0.000598	0.000466	0.037651	-0.019617	-0.140214	-0.075275	0.170455	-0.812353
	Y'	0.000168	0.000658	-0.024800	0.003388	0.005957	0.015402	0.024421	0.084690
	Z	0.000691	-0.000386	0.101665	0.059694	0.213974	-0.257108	-0.418169	-0.089505
	Z'	-0.000312	-0.000235	-0.024118	-0.005112	-0.003068	0.008123	0.005059	-0.007828
H1	S	0.000158	0.000899	0.048559	0.217964	-0.028100	0.179933	0.021946	0.010444
	S'	0.000085	0.000809	-0.009834	-0.003889	0.015137	0.016802	0.016233	0.003500
H2	S	-0.000158	-0.000899	-0.048559	-0.217964	0.028100	-0.179933	-0.021946	-0.010444
	S'	-0.000085	-0.000809	0.009834	0.003889	-0.015137	-0.016802	-0.016233	-0.003500

Table 59. MO's and occupation numbers for 2(nd) SPIP model of HNO dimer

		(1a)	(2a)	(3a)	(4a)	(5a)	(6a)	(7a)	(8a)	(9a)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	1.972014	1.896004
N1	S	0.000090	0.649643	0.074651	-0.190708	0.030322	0.086809	0.115409	-0.050883	0.028708
	S'	-0.000103	0.195300	-0.207489	0.462024	-0.063504	-0.180576	-0.224695	0.146458	-0.054765
	S''	-0.000000	0.001672	-0.014601	-0.000770	0.014241	0.029868	0.057145	0.022205	0.025195
	X	0.000034	-0.000348	-0.015783	0.077550	-0.153865	0.408000	0.399632	0.051826	-0.041071
	X'	-0.000015	-0.000974	-0.000275	0.037503	-0.037502	0.010724	0.028599	-0.009675	0.017345
	Y	-0.000030	-0.000381	0.044228	-0.134272	0.051897	0.071071	0.070971	0.596508	-0.059574
	Y'	0.000066	-0.000599	-0.000274	-0.000267	0.018976	-0.014927	-0.024470	0.098983	0.007500
	Z	0.000081	0.000955	0.102488	0.043373	-0.321345	-0.243633	-0.139958	-0.015213	0.122327
	Z'	-0.000025	0.000470	0.031747	0.003762	-0.060673	0.000292	0.022772	0.018153	-0.020545
N2	S	0.000090	0.649643	0.074651	-0.190708	0.030322	0.086809	0.115409	-0.050883	0.028708
	S'	-0.000103	0.195300	-0.207489	0.462024	-0.063504	-0.180576	-0.224695	0.146458	-0.054765
	S''	-0.000000	0.001672	-0.014601	-0.000770	0.014241	0.029868	0.057145	0.022205	0.025195
	X	-0.000034	0.000348	0.015783	-0.077550	0.153865	-0.408000	-0.399632	-0.051826	0.041071
	X'	0.000015	0.000974	0.000275	-0.037503	0.037502	-0.010724	-0.028599	0.009675	-0.017345
	Y	0.000030	0.000381	-0.044228	0.134272	-0.051897	-0.071071	-0.070971	-0.596508	0.059574
	Y'	-0.000066	0.000599	0.000274	0.000267	-0.018976	0.014927	0.024470	-0.098983	-0.007500
	Z	0.000081	0.000955	0.102488	0.043373	-0.321345	-0.243633	-0.139958	-0.015213	0.122327
	Z'	-0.000025	0.000470	0.031747	0.003762	-0.060673	0.000292	0.022772	0.018153	-0.020545
O1	S	-0.306532	0.000059	0.496880	0.319477	0.160489	0.044810	0.019587	0.047658	0.017735
	S'	0.639957	0.000013	0.221580	0.155345	0.084668	0.029524	0.015168	0.026450	0.014001
	S''	-0.001360	-0.000062	-0.025994	0.000893	0.004299	0.016567	0.013795	0.008009	-0.001898
	X	-0.000261	0.000097	-0.000458	0.026440	-0.030790	0.460558	-0.556597	0.009921	0.230777
	X'	0.000212	0.000115	0.006373	0.001027	0.001154	0.003282	-0.031053	-0.002441	-0.004874
	Y	-0.000541	0.000010	0.003483	0.018287	0.076332	-0.135637	0.194466	-0.024299	0.617000
	Y'	0.000416	0.000046	0.011986	0.014468	0.006449	-0.004211	0.003604	-0.007307	-0.034280
	Z	-0.000562	0.000487	-0.102382	0.126793	0.440490	0.008233	0.034130	-0.130107	0.011973
	Z'	0.000451	0.000417	0.014495	-0.012598	-0.015728	-0.007643	-0.003107	-0.009631	0.029861
O2	S	-0.306532	0.000059	0.496880	0.319477	0.160489	0.044810	0.019587	0.047658	0.017735
	S'	0.639957	0.000013	0.221580	0.155345	0.084668	0.029524	0.015168	0.026450	0.014001
	S''	-0.001360	-0.000062	-0.025994	0.000893	0.004299	0.016567	0.013795	0.008009	-0.001898
	X	0.000261	-0.000097	0.000458	-0.026440	0.030790	-0.460558	0.556597	-0.009921	-0.230777
	X'	-0.000212	-0.000115	-0.006373	-0.001027	-0.001154	-0.003282	0.031053	0.002441	0.004874
	Y	0.000541	-0.000010	-0.003483	-0.018287	-0.076332	0.135637	-0.194466	0.024299	-0.617000
	Y'	-0.000416	-0.000046	-0.011986	-0.014468	-0.006449	0.004211	-0.003604	0.007307	0.034280
	Z	-0.000562	0.000487	-0.102382	0.126793	0.440490	0.008233	0.034130	-0.130107	0.011973
	Z'	0.000451	0.000417	0.014495	-0.012598	-0.015728	-0.007643	-0.003107	-0.009631	0.029861
H1	S	0.000089	0.000598	0.039061	-0.169375	0.168804	-0.121381	-0.256103	0.082132	-0.016046
	S'	0.000068	0.000576	-0.004505	0.003501	0.009907	0.000034	-0.036525	0.007241	-0.007573
H2	S	0.000089	0.000598	0.039061	-0.169375	0.168804	-0.121381	-0.256103	0.082132	-0.016046
	S'	0.000068	0.000576	-0.004505	0.003501	0.009907	0.000034	-0.036525	0.007241	-0.007573

Table 59. (Continued)

		(1b)	(2b)	(3b)	(4b)	(5b)	(6b)	(7b)	(8b)	(9b)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	2.000000	0.103996	0.027986
N1	S	-0.000748	0.645841	0.138830	0.194855	0.049345	-0.045434	0.021829	-0.005275	0.066968
	S'	0.001344	0.202208	-0.324551	-0.441504	-0.143568	0.092866	-0.071700	0.003379	-0.146675
	S''	-0.001015	-0.004370	0.024575	0.019385	-0.100746	-0.014612	-0.065403	-0.008896	-0.309539
	X	0.000042	-0.000311	-0.026866	-0.220555	0.342146	-0.259716	0.303942	0.027309	0.002188
	X'	-0.000059	-0.000877	-0.005134	-0.053616	0.020821	-0.036518	-0.011688	-0.003036	-0.017390
	Y	0.000294	0.000369	0.036828	0.096676	0.107892	-0.004386	0.188956	0.021286	-0.806544
	Y'	-0.000370	-0.002871	0.021137	0.031377	-0.038456	0.011194	-0.048439	-0.008653	-0.356167
	Z	-0.000178	0.000659	0.107926	-0.044807	-0.040874	-0.174411	-0.414956	-0.058066	-0.072680
	Z'	0.000214	0.000976	0.026977	-0.013732	0.032539	-0.026843	-0.007850	0.004852	0.005929
N2	S	0.000748	-0.645841	-0.138830	-0.194855	-0.049345	0.045434	-0.021829	0.005275	-0.066968
	S'	-0.001344	-0.202208	0.324551	0.441504	0.143568	-0.092866	0.071700	-0.003379	0.146675
	S''	0.001015	0.004370	-0.024575	-0.019385	0.100746	0.014612	0.065403	0.008896	0.309539
	X	0.000042	-0.000311	-0.026866	-0.220555	0.342146	-0.259716	0.303942	0.027309	0.002188
	X'	-0.000059	-0.000877	-0.005134	-0.053616	0.020821	-0.036518	-0.011688	-0.003036	-0.017390
	Y	0.000294	0.000369	0.036828	0.096676	0.107892	-0.004386	0.188956	0.021286	-0.806544
	Y'	-0.000370	-0.002871	0.021137	0.031377	-0.038456	0.011194	-0.048439	-0.008653	-0.356167
	Z	0.000178	-0.000659	-0.107926	0.044807	0.040874	0.174411	0.414956	0.058066	0.072680
	Z'	-0.000214	-0.000976	-0.026977	0.013732	-0.032539	0.026843	0.007850	-0.004852	-0.005929
O1	S	-0.306452	-0.000233	0.545085	-0.352826	-0.152700	0.139099	0.040362	0.259281	-0.033462
	S'	0.640124	-0.000260	0.259104	-0.178918	-0.075041	0.072356	0.022677	0.153617	-0.020256
	S''	-0.000777	-0.000241	-0.005191	-0.008631	0.008637	-0.002179	0.003129	0.039999	-0.003160
	X	-0.000319	0.000068	-0.015918	-0.091275	0.354744	0.496407	-0.183316	-0.244818	0.000747
	X'	0.000063	-0.000039	-0.002723	0.005547	-0.016653	0.005505	-0.009752	0.034607	-0.001970
	Y	-0.000598	0.000466	0.037487	-0.019741	-0.141213	-0.074524	0.171000	-0.813434	0.061646
	Y'	0.000168	0.000659	-0.024840	0.003345	0.005928	0.015485	0.024822	0.084554	0.014135
	Z	-0.000691	0.000386	-0.101680	-0.059930	-0.214133	0.258206	0.418390	0.090995	0.073199
	Z'	0.000312	0.000235	0.024115	0.005140	0.003030	-0.008076	-0.004995	0.006557	-0.005217
O2	S	0.306452	0.000233	-0.545085	0.352826	0.152700	-0.139099	-0.040362	-0.259281	0.033462
	S'	-0.640124	0.000260	-0.259104	0.178918	0.075041	-0.072356	-0.022677	-0.153617	0.020256
	S''	0.000777	0.000241	0.005191	0.008631	-0.008637	0.002179	-0.003129	-0.039999	0.003160
	X	-0.000319	0.000068	-0.015918	-0.091275	0.354744	0.496407	-0.183316	-0.244818	0.000747
	X'	0.000063	-0.000039	-0.002723	0.005547	-0.016653	0.005505	-0.009752	0.034607	-0.001970
	Y	-0.000598	0.000466	0.037487	-0.019741	-0.141213	-0.074524	0.171000	-0.813434	0.061646
	Y'	0.000168	0.000659	-0.024840	0.003345	0.005928	0.015485	0.024822	0.084554	0.014135
	Z	0.000691	-0.000386	0.101680	0.059930	0.214133	-0.258206	-0.418390	-0.090995	-0.073199
	Z'	-0.000312	-0.000235	-0.024115	-0.005140	-0.003030	0.008076	0.004995	-0.006557	0.005217
H1	S	0.000158	0.000899	0.048509	0.218316	-0.028138	0.180709	0.021616	0.010979	-0.023457
	S'	0.000085	0.000809	-0.009812	-0.003780	0.015072	0.016929	0.016300	0.003510	0.009192
H2	S	-0.000158	-0.000899	-0.048509	-0.218316	0.028138	-0.180709	-0.021616	-0.010979	0.023457
	S'	-0.000085	-0.000809	0.009812	0.003780	-0.015072	-0.016929	-0.016300	-0.003510	-0.009192

APPENDIX E: NATURAL REACTION ORBITALS FOR THE THERMOLYSIS OF 1,2-DIOXETANE

NATURAL REACTION ORBITALS FOR THE THERMOLYSIS OF 1,2-DIOXETANE

In Part V of this work we calculated several wavefunctions for 1,2-dioxetane along an optimized reaction path. We developed the concept of reaction molecular orbitals and natural reaction orbitals (NRO's) in Part V, and in the following tables we display the core molecular orbitals, the NRO's, and their occupation numbers for 1,2-dioxetane as determined with a multiconfiguration self-consistent field wavefunction for each point on the reaction path.

Table 60. CMO's and NBO's for 1,2-dioxetane at R_{CC} = 2.8754 a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	1.927700	1.981000	2.000000	2.000000
C1	S	0.000345	-0.670785	-0.041439	0.064949	-0.145708	0.046576	-0.082546	-0.000123	0.674110
	S'	-0.000326	-0.121888	0.148308	-0.185336	0.396878	-0.105970	0.237958	0.000677	0.115408
	S''	0.000021	-0.004152	-0.009796	0.004626	0.004748	-0.013766	0.006939	0.000503	0.001090
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000050	0.002207	0.031737	-0.022704	-0.171216	-0.078200	0.539663	0.000492	-0.005546
	Y'	0.000185	0.000521	0.014305	-0.018411	0.006550	0.020307	-0.007151	-0.000049	0.001051
	Z	-0.000167	-0.002132	-0.170197	0.164615	0.179822	0.090954	0.107972	-0.001005	0.002577
	Z'	-0.000444	-0.000178	-0.025626	0.006246	0.011353	-0.013679	0.007351	-0.000303	-0.000362
C2	S	0.000345	-0.670785	-0.041439	0.064949	-0.145708	0.046576	-0.082546	0.000123	-0.674110
	S'	-0.000326	-0.121888	0.148308	-0.185336	0.396878	-0.105970	0.237958	-0.000677	-0.115408
	S''	0.000021	-0.004152	-0.009796	0.004626	0.004748	-0.013766	0.006939	-0.000503	-0.001090
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000050	-0.002207	-0.031737	0.022704	0.171216	0.078200	-0.539663	0.000492	-0.005546
	Y'	-0.000185	-0.000521	-0.014305	0.018411	-0.006550	-0.020307	0.007151	-0.000049	0.001051
	Z	-0.000167	-0.002132	-0.170197	0.164615	0.179822	0.090954	0.107972	0.001005	-0.002577
	Z'	-0.000444	-0.000178	-0.025626	0.006246	0.011353	-0.013679	0.007351	0.000303	0.000362
O1	S	-0.332834	0.000549	-0.420334	-0.411822	0.015531	0.019844	0.051351	-0.335127	-0.001395
	S'	0.618591	0.000373	-0.213161	-0.240338	0.012931	0.023633	0.031053	0.616858	-0.001260
	S''	-0.003107	0.000529	0.031074	-0.019294	0.012188	0.015966	0.006588	-0.003642	-0.001527
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.001445	-0.000219	0.012939	-0.068323	-0.011494	0.654086	-0.012377	-0.002818	0.000393
	Y'	0.000190	0.000009	-0.010716	-0.017952	0.007563	-0.010011	-0.021810	0.001009	0.000191
	Z	-0.002863	-0.003609	0.242719	-0.408301	-0.102966	0.024705	-0.179494	-0.003099	0.004734
	Z'	0.000609	-0.000333	-0.020754	0.019954	-0.007881	0.030093	-0.015577	0.000366	0.001081
O2	S	-0.332834	0.000549	-0.420334	-0.411822	0.015531	0.019844	0.051351	0.335127	0.001395
	S'	0.618591	0.000373	-0.213161	-0.240338	0.012931	0.023633	0.031053	-0.616858	0.001260
	S''	-0.003107	0.000529	0.031074	-0.019294	0.012188	0.015966	0.006588	0.003642	0.001527
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.001445	0.000219	-0.012939	0.068323	0.011494	-0.654086	0.012377	-0.002818	0.000393
	Y'	-0.000190	-0.000009	0.010716	0.017952	-0.007563	0.010011	0.021810	0.001009	0.000191
	Z	-0.002863	-0.003609	0.242719	-0.408301	-0.102966	0.024705	-0.179494	0.003099	-0.004734
	Z'	0.000609	-0.000333	-0.020754	0.019954	-0.007881	0.030093	-0.015577	-0.000366	-0.001081
H1	S	0.000559	0.005254	0.032371	-0.009959	-0.189513	-0.048819	0.087687	0.000664	-0.005851
	S'	0.000077	0.000174	0.007699	-0.009606	0.032612	0.000422	0.000728	0.000000	0.000015
H2	S	0.000559	0.005254	0.032371	-0.009959	-0.189513	-0.048819	0.087687	0.000664	-0.005851
	S'	0.000077	0.000174	0.007699	-0.009606	0.032612	0.000422	0.000728	0.000000	0.000015
H3	S	0.000559	0.005254	0.032371	-0.009959	-0.189513	-0.048819	0.087687	-0.000664	0.005851
	S'	0.000077	0.000174	0.007699	-0.009606	0.032612	0.000422	0.000728	-0.000000	-0.000015
H4	S	0.000559	0.005254	0.032371	-0.009959	-0.189513	-0.048819	0.087687	-0.000664	0.005851
	S'	0.000077	0.000174	0.007699	-0.009606	0.032612	0.000422	0.000728	-0.000000	-0.000015

Table 60. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.018800	0.072500	2.000000	2.000000	2.000000	2.000000
C1	S	0.074458	0.081761	0.158067	0.194998	-0.034327	0.0	0.0	0.0	0.0
	S'	-0.206797	-0.196515	-0.414729	-0.407114	0.082448	0.0	0.0	0.0	0.0
	S''	-0.005338	-0.004038	-0.006947	0.008772	0.008456	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.054355	0.434273	0.112364	0.464925
	X'	0.0	0.0	0.0	0.0	0.0	0.013401	-0.006001	-0.068225	-0.035928
	Y	-0.023493	-0.006868	0.177199	-0.912583	0.052583	0.0	0.0	0.0	0.0
	Y'	0.015574	0.016213	0.002979	-0.015619	0.012629	0.0	0.0	0.0	0.0
	Z	0.223055	0.174132	-0.197136	-0.335487	-0.031238	0.0	0.0	0.0	0.0
	Z'	0.021295	-0.005965	0.003493	-0.038152	0.031463	0.0	0.0	0.0	0.0
C2	S	-0.074458	-0.081761	-0.158067	-0.194998	0.034327	0.0	0.0	0.0	0.0
	S'	0.206797	0.196515	0.414729	0.407114	-0.082448	0.0	0.0	0.0	0.0
	S''	0.005338	0.004038	0.006947	-0.008772	-0.008456	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.054355	0.434273	-0.112364	-0.464925
	X'	0.0	0.0	0.0	0.0	0.0	0.013401	-0.006001	0.068225	0.035928
	Y	-0.023493	-0.006868	0.177199	-0.912583	0.052583	0.0	0.0	0.0	0.0
	Y'	0.015574	0.016213	0.002979	-0.015619	0.012629	0.0	0.0	0.0	0.0
	Z	-0.223055	-0.174132	0.197136	0.335487	0.031238	0.0	0.0	0.0	0.0
	Z'	-0.021295	0.005965	-0.003493	0.038152	-0.031463	0.0	0.0	0.0	0.0
O1	S	0.465927	-0.464417	-0.037098	0.038468	-0.278347	0.0	0.0	0.0	0.0
	S'	0.259300	-0.275173	-0.027079	0.023242	-0.199367	0.0	0.0	0.0	0.0
	S''	0.008749	-0.020205	-0.010286	0.006402	-0.121365	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.652515	-0.105790	0.762222	-0.101280
	X'	0.0	0.0	0.0	0.0	0.0	0.000076	-0.025792	0.034549	-0.032222
	Y	-0.004121	-0.136741	0.021229	0.126484	0.901154	0.0	0.0	0.0	0.0
	Y'	-0.037153	-0.010723	-0.001016	0.023419	-0.036873	0.0	0.0	0.0	0.0
	Z	-0.340248	-0.472099	0.109085	-0.159668	-0.118587	0.0	0.0	0.0	0.0
	Z'	0.010903	-0.003596	0.015644	-0.034062	-0.016013	0.0	0.0	0.0	0.0
O2	S	-0.465927	0.464417	0.037098	-0.038468	0.278347	0.0	0.0	0.0	0.0
	S'	-0.259300	0.275173	0.027079	-0.023242	0.199367	0.0	0.0	0.0	0.0
	S''	-0.008749	0.020205	0.010286	-0.006402	0.121365	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.652515	-0.105790	-0.762222	0.101280
	X'	0.0	0.0	0.0	0.0	0.0	0.000076	-0.025792	-0.034549	0.032222
	Y	-0.004121	-0.136741	0.021229	0.126484	0.901154	0.0	0.0	0.0	0.0
	Y'	-0.037153	-0.010723	-0.001016	0.023419	-0.036873	0.0	0.0	0.0	0.0
	Z	0.340248	0.472099	-0.109085	0.159668	0.118587	0.0	0.0	0.0	0.0
	Z'	-0.010903	0.003596	-0.015644	0.034062	0.016013	0.0	0.0	0.0	0.0
H1	S	-0.036284	-0.009525	0.206539	0.050734	-0.019087	0.068131	0.247321	-0.109500	0.315334
	S'	-0.005123	-0.006738	-0.034299	0.021915	-0.002918	0.019382	-0.024798	-0.034087	-0.018751
H2	S	-0.036284	-0.009525	0.206539	0.050734	-0.019087	-0.068131	-0.247321	0.109500	-0.315334
	S'	-0.005123	-0.006738	-0.034299	0.021915	-0.002918	-0.019382	0.024798	0.034087	0.018751
H3	S	0.036284	0.009525	-0.206539	-0.050734	0.019087	0.068131	0.247321	0.109500	-0.315334
	S'	0.005123	0.006738	0.034299	-0.021915	0.002918	0.019382	-0.024798	0.034087	0.018751
H4	S	0.036284	0.009525	-0.206539	-0.050734	0.019087	-0.068131	-0.247321	-0.109500	0.315334
	S'	0.005123	0.006738	0.034299	-0.021915	0.002918	-0.019382	0.024798	-0.034087	-0.018751

Table 61. CMO's and NBO's for 1,2-dioxetane at $R_{CC} = 3.374$ a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	1.877800	1.949600	2.000000	2.000000
C1	S	0.000416	-0.670404	-0.039458	0.072512	0.154428	0.051552	-0.074651	0.000144	0.672876
	S'	-0.000477	-0.122758	0.137514	-0.197934	-0.413513	-0.117885	0.201446	0.000175	0.117797
	S''	-0.000048	-0.004294	-0.009730	0.002440	-0.005048	-0.015640	0.015472	0.000340	0.001571
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000085	0.001722	0.027269	-0.024803	0.163096	-0.156763	0.554156	0.000310	-0.004370
	Y'	0.000215	0.000443	0.012230	-0.013491	-0.004944	0.041459	-0.058405	0.000017	0.000680
	Z	-0.000206	-0.002053	-0.162151	0.174726	-0.175153	0.058854	0.135425	-0.000769	0.002269
	Z'	-0.000506	-0.000263	-0.026761	0.004954	-0.012337	-0.008151	-0.000419	-0.000434	-0.000114
C2	S	0.000416	-0.670404	-0.039458	0.072512	0.154428	0.051552	-0.074651	-0.000144	-0.672876
	S'	-0.000477	-0.122758	0.137514	-0.197934	-0.413513	-0.117885	0.201446	-0.000175	-0.117797
	S''	-0.000048	-0.004294	-0.009730	0.002440	-0.005048	-0.015640	0.015472	-0.000340	-0.001571
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000085	-0.001722	-0.027269	0.024803	-0.163096	0.156763	-0.554156	0.000310	-0.004370
	Y'	-0.000215	-0.000443	-0.012230	0.013491	0.004944	-0.041459	0.058405	0.000017	0.000680
	Z	-0.000206	-0.002053	-0.162151	0.174726	-0.175153	0.058854	0.135425	0.000769	-0.002269
	Z'	-0.000506	-0.000263	-0.026761	0.004954	-0.012337	-0.008151	-0.000419	0.000434	0.000114
O1	S	-0.333013	0.000372	-0.446581	-0.391773	-0.019883	0.023899	0.051840	-0.335141	-0.001150
	S'	0.618445	0.000240	-0.230572	-0.231053	-0.016207	0.020692	0.033327	0.616948	-0.001010
	S''	-0.003109	0.000402	0.027717	-0.023606	-0.013038	0.004022	0.007840	-0.003434	-0.001279
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000886	0.000006	0.003878	-0.043550	0.008292	0.656860	0.055899	-0.002234	0.000109
	Y'	0.000204	0.000042	-0.005370	-0.014306	-0.006945	0.006678	-0.028599	0.000744	0.000006
	Z	-0.002739	-0.003367	0.234893	-0.431368	0.108421	0.063589	-0.146956	-0.003094	0.004817
	Z'	0.000611	-0.000286	-0.018075	0.019322	0.009132	0.031960	-0.012713	0.000497	0.000953
O2	S	-0.333013	0.000372	-0.446581	-0.391773	-0.019883	0.023899	0.051840	0.335141	0.001150
	S'	0.618445	0.000240	-0.230572	-0.231053	-0.016207	0.020692	0.033327	-0.616948	0.001010
	S''	-0.003109	0.000402	0.027717	-0.023606	-0.013038	0.004022	0.007840	0.003434	0.001279
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000886	-0.000006	-0.003878	0.043550	-0.008292	-0.656860	-0.055899	-0.002234	0.000109
	Y'	-0.000204	-0.000042	0.005370	0.014306	0.006945	-0.006678	0.028599	0.000744	0.000006
	Z	-0.002739	-0.003367	0.234893	-0.431368	0.108421	0.063589	-0.146956	0.003094	-0.004817
	Z'	0.000611	-0.000286	-0.018075	0.019322	0.009132	0.031960	-0.012713	-0.000497	-0.000953
H1	S	0.000496	0.005047	0.033136	-0.016537	0.189208	-0.054845	0.070803	0.000650	-0.005917
	S'	0.000064	0.000152	0.007372	-0.010251	-0.033051	0.001493	-0.001675	0.000038	-0.000160
H2	S	0.000496	0.005047	0.033136	-0.016537	0.189208	-0.054845	0.070803	0.000650	-0.005917
	S'	0.000064	0.000152	0.007372	-0.010251	-0.033051	0.001493	-0.001675	0.000038	-0.000160
H3	S	0.000496	0.005047	0.033136	-0.016537	0.189208	-0.054845	0.070803	-0.000650	0.005917
	S'	0.000064	0.000152	0.007372	-0.010251	-0.033051	0.001493	-0.001675	-0.000038	0.000160
H4	S	0.000496	0.005047	0.033136	-0.016537	0.189208	-0.054845	0.070803	-0.000650	0.005917
	S'	0.000064	0.000152	0.007372	-0.010251	-0.033051	0.001493	-0.001675	-0.000038	0.000160

Table 61. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.049700	0.122900	2.000000	2.000000	2.000000	2.000000
C1	S	0.065196	0.084414	0.160476	0.157847	-0.036066	0.0	0.0	0.0	0.0
	S'	-0.191441	-0.208347	-0.423828	-0.355372	0.086081	0.0	0.0	0.0	0.0
	S''	-0.001716	-0.003486	-0.005911	-0.001106	0.006708	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.057071	0.424947	0.099433	0.442627
	X'	0.0	0.0	0.0	0.0	0.0	0.016478	-0.000492	-0.055687	-0.011089
	Y	-0.033776	-0.024534	0.164856	-0.855696	0.108276	0.0	0.0	0.0	0.0
	Y'	0.008860	0.012379	0.002266	0.049277	0.008977	0.0	0.0	0.0	0.0
	Z	0.202464	0.175861	-0.187223	-0.288174	0.015709	0.0	0.0	0.0	0.0
	Z'	0.029935	-0.000367	-0.006465	-0.007184	0.025840	0.0	0.0	0.0	0.0
C2	S	-0.065196	-0.084414	-0.160476	-0.157847	0.036066	0.0	0.0	0.0	0.0
	S'	0.191441	0.208347	0.423828	0.355372	-0.086081	0.0	0.0	0.0	0.0
	S''	0.001716	0.003486	0.005911	0.001106	-0.006708	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.057071	0.424947	-0.099433	-0.442627
	X'	0.0	0.0	0.0	0.0	0.0	0.016478	-0.000492	0.055687	0.011089
	Y	-0.033776	-0.024534	0.164856	-0.855696	0.108276	0.0	0.0	0.0	0.0
	Y'	0.008860	0.012379	0.002266	0.049277	0.008977	0.0	0.0	0.0	0.0
	Z	-0.202464	-0.175861	0.187223	0.288174	-0.015709	0.0	0.0	0.0	0.0
	Z'	-0.029935	0.000367	0.006465	0.007184	-0.025840	0.0	0.0	0.0	0.0
O1	S	0.468590	-0.453783	-0.034241	-0.017950	-0.222998	0.0	0.0	0.0	0.0
	S'	0.255354	-0.269534	-0.024925	-0.015713	-0.152479	0.0	0.0	0.0	0.0
	S''	-0.004030	-0.021014	-0.009567	-0.013249	-0.082360	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.659489	-0.100268	0.746702	-0.098077
	X'	0.0	0.0	0.0	0.0	0.0	-0.002978	-0.024632	0.025654	-0.028189
	Y	0.008142	-0.106217	0.018286	0.234308	0.845498	0.0	0.0	0.0	0.0
	Y'	-0.027095	-0.012494	-0.003826	0.040371	-0.029950	0.0	0.0	0.0	0.0
	Z	-0.309381	-0.472618	0.108240	-0.063913	-0.077163	0.0	0.0	0.0	0.0
	Z'	0.014683	0.004669	0.014099	-0.024625	-0.017204	0.0	0.0	0.0	0.0
O2	S	-0.468590	0.453783	0.034241	0.017950	0.222998	0.0	0.0	0.0	0.0
	S'	-0.255354	0.269534	0.024925	0.015713	0.152479	0.0	0.0	0.0	0.0
	S''	0.004030	0.021014	0.009567	0.013249	0.082360	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.659489	-0.100268	-0.746702	0.098077
	X'	0.0	0.0	0.0	0.0	0.0	-0.002978	-0.024632	-0.025654	0.028189
	Y	0.008142	-0.106217	0.018286	0.234308	0.845498	0.0	0.0	0.0	0.0
	Y'	-0.027095	-0.012494	-0.003826	0.040371	-0.029950	0.0	0.0	0.0	0.0
	Z	0.309381	0.472618	-0.108240	0.063913	0.077163	0.0	0.0	0.0	0.0
	Z'	-0.014683	-0.004669	-0.014099	0.024625	0.017204	0.0	0.0	0.0	0.0
H1	S	-0.037571	-0.013188	0.200815	0.025682	-0.024746	0.071934	0.268896	-0.102587	0.310626
	S'	-0.006821	-0.007547	-0.034314	0.024415	-0.004668	0.020187	-0.020970	-0.031033	-0.017193
H2	S	-0.037571	-0.013188	0.200815	0.025682	-0.024746	-0.071934	-0.268896	0.102587	-0.310626
	S'	-0.006821	-0.007547	-0.034314	0.024415	-0.004668	-0.020187	0.020970	0.031033	0.017193
H3	S	0.037571	0.013188	-0.200815	-0.025682	0.024746	0.071934	0.268896	0.102587	-0.310626
	S'	0.006821	0.007547	0.034314	-0.024415	0.004668	0.020187	-0.020970	0.031033	0.017193
H4	S	0.037571	0.013188	-0.200815	-0.025682	0.024746	-0.071934	-0.268896	-0.102587	0.310626
	S'	0.006821	0.007547	0.034314	-0.024415	0.004668	-0.020187	0.020970	-0.031033	-0.017193

Table 62. CMO's and NBO's for 1,2-dioxetane at R_{CC} = 3.8754 a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	1.729400	1.888700	2.000000	2.000000
C1	S	0.000464	-0.670077	0.040383	0.081790	0.159574	0.055196	-0.052845	0.000352	0.672064
	S'	-0.000570	-0.123488	-0.136721	-0.216157	-0.423898	-0.127520	0.140386	-0.000247	0.119453
	S''	-0.000098	-0.004525	0.009752	0.000749	-0.004918	-0.018049	0.013885	0.000163	0.001993
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000137	0.001499	-0.030085	-0.037206	0.147898	-0.297852	0.517938	0.000166	-0.003518
	Y'	0.000255	0.000526	-0.010620	-0.007109	-0.002125	0.074372	-0.075858	0.000079	0.000535
	Z	-0.000299	-0.001978	0.158840	0.181122	-0.179463	-0.009242	0.156891	-0.000579	0.002163
	Z'	-0.000524	-0.000311	0.028401	0.005825	-0.013203	0.002576	-0.009107	-0.000524	0.000039
C2	S	0.000464	-0.670077	0.040383	0.081790	0.159574	0.055196	-0.052845	-0.000352	-0.672064
	S'	-0.000570	-0.123488	-0.136721	-0.216157	-0.423898	-0.127520	0.140386	0.000247	-0.119453
	S''	-0.000098	-0.004525	0.009752	0.000749	-0.004918	-0.018049	0.013885	-0.000163	-0.001993
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000137	-0.001499	0.030085	0.037206	-0.147898	0.297852	-0.517938	0.000166	-0.003518
	Y'	-0.000255	-0.000526	0.010620	0.007109	0.002125	-0.074372	0.075858	0.000079	0.000535
	Z	-0.000299	-0.001978	0.158840	0.181122	-0.179463	-0.009242	0.156891	0.000579	-0.002163
	Z'	-0.000524	-0.000311	0.028401	0.005825	-0.013203	0.002576	-0.009107	0.000524	-0.000039
O1	S	-0.333242	0.000255	0.464428	-0.381726	-0.022074	0.024301	0.049646	-0.335105	-0.000924
	S'	0.618275	0.000135	0.242708	-0.227268	-0.017729	0.016736	0.031365	0.617062	-0.000803
	S''	-0.003080	0.000260	-0.026103	-0.027961	-0.012352	-0.001848	0.002944	-0.003232	-0.001103
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000279	0.000283	0.007023	-0.004997	0.005613	0.634299	0.203984	-0.001486	-0.000170
	Y'	0.000231	0.000069	0.000690	-0.008769	-0.005546	0.025281	-0.028009	0.000453	-0.000064
	Z	-0.002614	-0.003387	-0.227905	-0.441366	0.115866	0.113898	-0.099020	-0.003062	0.004711
	Z'	0.000592	-0.000253	0.018014	0.020705	0.009473	0.029562	-0.004164	0.000600	0.000800
O2	S	-0.333242	0.000255	0.464428	-0.381726	-0.022074	0.024301	0.049646	0.335105	0.000924
	S'	0.618275	0.000135	0.242708	-0.227268	-0.017729	0.016736	0.031365	-0.617062	0.000803
	S''	-0.003080	0.000260	-0.026103	-0.027961	-0.012352	-0.001848	0.002944	0.003232	0.001103
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000279	-0.000283	-0.007023	0.004997	-0.005613	-0.634299	-0.203984	-0.001486	-0.000170
	Y'	-0.000231	-0.000069	-0.000690	0.008769	0.005546	-0.025281	0.028009	0.000453	-0.000064
	Z	-0.002614	-0.003387	-0.227905	-0.441366	0.115866	0.113898	-0.099020	0.003062	-0.004711
	Z'	0.000592	-0.000253	0.018014	0.020705	0.009473	0.029562	-0.004164	-0.000600	-0.000800
H1	S	0.000436	0.004858	-0.033908	-0.022450	0.188800	-0.061375	0.046261	0.000602	-0.005834
	S'	0.000051	0.000093	-0.007205	-0.010806	-0.033032	0.003550	-0.004197	0.000056	-0.000237
H2	S	0.000436	0.004858	-0.033908	-0.022450	0.188800	-0.061375	0.046261	0.000602	-0.005834
	S'	0.000051	0.000093	-0.007205	-0.010806	-0.033032	0.003550	-0.004197	0.000056	-0.000237
H3	S	0.000436	0.004858	-0.033908	-0.022450	0.188800	-0.061375	0.046261	-0.000602	0.005834
	S'	0.000051	0.000093	-0.007205	-0.010806	-0.033032	0.003550	-0.004197	-0.000056	0.000237
H4	S	0.000436	0.004858	-0.033908	-0.022450	0.188800	-0.061375	0.046261	-0.000602	0.005834
	S'	0.000051	0.000093	-0.007205	-0.010806	-0.033032	0.003550	-0.004197	-0.000056	0.000237

Table 62. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.110200	0.271700	2.000000	2.000000	2.000000	2.000000
C1	S	0.056341	0.085931	0.162248	-0.122062	-0.049714	0.0	0.0	0.0	0.0
	S'	-0.173074	-0.216289	-0.429603	0.285841	0.118669	0.0	0.0	0.0	0.0
	S''	0.003086	-0.001755	-0.004688	0.007848	0.006393	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.060939	0.418951	0.091388	0.430499
	X'	0.0	0.0	0.0	0.0	0.0	0.019857	0.007029	-0.048370	0.003152
	Y	-0.035598	-0.033021	0.153306	0.781669	0.248649	0.0	0.0	0.0	0.0
	Y'	0.002105	0.007014	0.001692	-0.087692	-0.009522	0.0	0.0	0.0	0.0
	Z	0.185115	0.178647	-0.183982	0.252418	0.081589	0.0	0.0	0.0	0.0
	Z'	0.034756	0.004469	-0.012198	-0.013062	0.016026	0.0	0.0	0.0	0.0
C2	S	-0.056341	-0.085931	-0.162248	0.122062	0.049714	0.0	0.0	0.0	0.0
	S'	0.173074	0.216289	0.429603	-0.285841	-0.118669	0.0	0.0	0.0	0.0
	S''	-0.003086	0.001755	0.004688	-0.007848	-0.006393	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.060939	0.418951	-0.091388	-0.430499
	X'	0.0	0.0	0.0	0.0	0.0	0.019857	0.007029	0.048370	-0.003152
	Y	-0.035598	-0.033021	0.153306	0.781669	0.248649	0.0	0.0	0.0	0.0
	Y'	0.002105	0.007014	0.001692	-0.087692	-0.009522	0.0	0.0	0.0	0.0
	Z	-0.185115	-0.178647	0.183982	-0.252418	-0.081589	0.0	0.0	0.0	0.0
	Z'	-0.034756	-0.004469	0.012198	0.013062	-0.016026	0.0	0.0	0.0	0.0
O1	S	0.474742	-0.439578	-0.031125	0.052203	-0.154665	0.0	0.0	0.0	0.0
	S'	0.254340	-0.261681	-0.022850	0.035440	-0.100421	0.0	0.0	0.0	0.0
	S''	-0.016086	-0.022009	-0.009322	0.015623	-0.043473	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.668413	-0.097354	0.730644	-0.095786
	X'	0.0	0.0	0.0	0.0	0.0	-0.005012	-0.023405	0.016656	-0.025213
	Y	0.019295	-0.061999	0.014431	-0.389912	0.740956	0.0	0.0	0.0	0.0
	Y'	-0.016816	-0.014044	-0.005040	-0.045340	-0.027263	0.0	0.0	0.0	0.0
	Z	-0.280073	-0.473586	0.110986	0.009420	-0.031711	0.0	0.0	0.0	0.0
	Z'	0.017668	0.011944	0.012685	0.015560	-0.013606	0.0	0.0	0.0	0.0
O2	S	-0.474742	0.439578	0.031125	-0.052203	0.154665	0.0	0.0	0.0	0.0
	S'	-0.254340	0.261681	0.022850	-0.035440	0.100421	0.0	0.0	0.0	0.0
	S''	0.016086	0.022009	0.009322	-0.015623	0.043473	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.668413	-0.097354	-0.730644	0.095786
	X'	0.0	0.0	0.0	0.0	0.0	-0.005012	-0.023405	-0.016656	0.025213
	Y	0.019295	-0.061999	0.014431	-0.389912	0.740956	0.0	0.0	0.0	0.0
	Y'	-0.016816	-0.014044	-0.005040	-0.045340	-0.027263	0.0	0.0	0.0	0.0
	Z	0.280073	0.473586	-0.110986	-0.009420	0.031711	0.0	0.0	0.0	0.0
	Z'	-0.017668	-0.011944	-0.012685	-0.015560	0.013606	0.0	0.0	0.0	0.0
H1	S	-0.038334	-0.018191	0.197420	-0.004423	-0.027455	0.075305	0.282637	-0.097554	0.306222
	S'	-0.008157	-0.009202	-0.034107	-0.021054	-0.008099	0.021075	-0.018373	-0.028890	-0.016764
H2	S	-0.038334	-0.018191	0.197420	-0.004423	-0.027455	-0.075305	-0.282637	0.097554	-0.306222
	S'	-0.008157	-0.009202	-0.034107	-0.021054	-0.008099	-0.021075	0.018373	0.028890	0.016764
H3	S	0.038334	0.018191	-0.197420	0.004423	0.027455	0.075305	0.282637	0.097554	-0.306222
	S'	0.008157	0.009202	0.034107	0.021054	0.008099	0.021075	-0.018373	0.028890	0.016764
H4	S	0.038334	0.018191	-0.197420	0.004423	0.027455	-0.075305	-0.282637	-0.097554	0.306222
	S'	0.008157	0.009202	0.034107	0.021054	0.008099	-0.021075	0.018373	-0.028890	-0.016764

Table 63. CMO's and NRO's for 1,2-dioxetane at R_{CC} = 3.9872 a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	1.656500	1.870800	2.000000	2.000000
C1	S	0.000468	-0.670022	0.040607	0.083578	0.160436	0.055097	-0.047673	0.000388	0.671897
	S'	-0.000577	-0.123610	-0.136729	-0.219721	-0.425759	-0.127529	0.126903	-0.000324	0.119797
	S''	-0.000104	-0.004562	0.009770	0.000525	-0.004923	-0.018538	0.012636	0.000127	0.002119
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000152	0.001450	-0.030301	-0.040033	0.143739	-0.335635	0.499034	0.000142	-0.003349
	Y'	0.000265	0.000555	-0.010282	-0.005590	-0.001328	0.082842	-0.074559	0.000091	0.000494
	Z	-0.000332	-0.001973	0.158742	0.182165	-0.181017	-0.029073	0.156132	-0.000541	0.002159
	Z'	-0.000519	-0.000314	0.028689	0.006391	-0.013267	0.005723	-0.010395	-0.000537	0.000061
C2	S	0.000468	-0.670022	0.040607	0.083578	0.160436	0.055097	-0.047673	-0.000388	-0.671897
	S'	-0.000577	-0.123610	-0.136729	-0.219721	-0.425759	-0.127529	0.126903	0.000324	-0.119797
	S''	-0.000104	-0.004562	0.009770	0.000525	-0.004923	-0.018538	0.012636	-0.000127	-0.002119
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000152	-0.001450	0.030301	0.040033	-0.143739	0.335635	-0.499034	0.000142	-0.003349
	Y'	-0.000265	-0.000555	0.010282	0.005590	0.001328	-0.082842	0.074559	0.000091	0.000494
	Z	-0.000332	-0.001973	0.158742	0.182165	-0.181017	-0.029073	0.156132	0.000541	-0.002159
	Z'	-0.000519	-0.000314	0.028689	0.006391	-0.013267	0.005723	-0.010395	0.000537	-0.000061
O1	S	-0.333301	0.000238	0.467990	-0.380061	-0.022411	0.024215	0.049390	-0.335095	-0.000873
	S'	0.618236	0.000119	0.245100	-0.226640	-0.017945	0.016162	0.030901	0.617086	-0.000758
	S''	-0.003062	0.000236	-0.025987	-0.028555	-0.012120	-0.001650	0.001792	-0.003190	-0.001065
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000134	0.000365	0.010081	0.006496	0.005060	0.620664	0.247238	-0.001287	-0.000242
	Y'	0.000236	0.000077	-0.000117	-0.007436	-0.005164	0.029194	-0.026302	0.000395	-0.000070
	Z	-0.002580	-0.003397	-0.226628	-0.442690	0.117628	0.124915	-0.082987	-0.003052	0.004658
	Z'	0.000584	-0.000246	0.018214	0.021117	0.009495	0.028052	-0.002161	0.000616	0.000764
O2	S	-0.333301	0.000238	0.467990	-0.380061	-0.022411	0.024215	0.049390	0.335095	0.000873
	S'	0.618236	0.000119	0.245100	-0.226640	-0.017945	0.016162	0.030901	-0.617086	0.000758
	S''	-0.003062	0.000236	-0.025987	-0.028555	-0.012120	-0.001650	0.001792	0.003190	0.001065
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000134	-0.000365	-0.010081	-0.006496	-0.005060	-0.620664	-0.247238	-0.001287	-0.000242
	Y'	-0.000236	-0.000077	0.000117	0.007436	0.005164	-0.029194	0.026302	0.000395	-0.000070
	Z	-0.002580	-0.003397	-0.226628	-0.442690	0.117628	0.124915	-0.082987	0.003052	-0.004658
	Z'	0.000584	-0.000246	0.018214	0.021117	0.009495	0.028052	-0.002161	-0.000616	-0.000764
H1	S	0.000424	0.004832	-0.033982	-0.023625	0.188741	-0.062456	0.040452	0.000587	-0.005800
	S'	0.000048	0.000083	-0.007167	-0.010943	-0.032993	0.004208	-0.004531	0.000058	-0.000244
H2	S	0.000424	0.004832	-0.033982	-0.023625	0.188741	-0.062456	0.040452	0.000587	-0.005800
	S'	0.000048	0.000083	-0.007167	-0.010943	-0.032993	0.004208	-0.004531	0.000058	-0.000244
H3	S	0.000424	0.004832	-0.033982	-0.023625	0.188741	-0.062456	0.040452	-0.000587	0.005800
	S'	0.000048	0.000083	-0.007167	-0.010943	-0.032993	0.004208	-0.004531	-0.000058	0.000244
H4	S	0.000424	0.004832	-0.033982	-0.023625	0.188741	-0.062456	0.040452	-0.000587	0.005800
	S'	0.000048	0.000083	-0.007167	-0.010943	-0.032993	0.004208	-0.004531	-0.000058	0.000244

Table 63. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.127800	0.344900	2.000000	2.000000	2.000000	2.000000
C1	S	0.054503	-0.086155	0.162650	-0.114275	-0.054331	0.0	0.0	0.0	0.0
	S'	-0.168858	0.217627	-0.430719	0.269025	0.130127	0.0	0.0	0.0	0.0
	S''	0.004040	0.001341	-0.004392	0.008712	0.006700	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.061575	0.418119	0.089820	0.428760
	X'	0.0	0.0	0.0	0.0	0.0	0.020515	0.008577	-0.047172	0.005320
	Y	-0.034995	0.033570	0.150383	0.757900	0.292299	0.0	0.0	0.0	0.0
	Y'	0.000886	-0.005961	0.001575	-0.092479	-0.016582	0.0	0.0	0.0	0.0
	Z	0.181846	-0.179892	-0.184018	0.241812	0.096989	0.0	0.0	0.0	0.0
	Z'	0.035263	-0.005436	-0.013004	-0.015887	0.012971	0.0	0.0	0.0	0.0
C2	S	-0.054503	0.086155	-0.162650	0.114275	0.054331	0.0	0.0	0.0	0.0
	S'	0.168858	-0.217627	0.430719	-0.269025	-0.130127	0.0	0.0	0.0	0.0
	S''	-0.004040	-0.001341	0.004392	-0.008712	-0.006700	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.061575	0.418119	-0.089820	-0.428760
	X'	0.0	0.0	0.0	0.0	0.0	0.020515	0.008577	0.047172	-0.005320
	Y	-0.034995	0.033570	0.150383	0.757900	0.292299	0.0	0.0	0.0	0.0
	Y'	0.000886	-0.005361	0.001575	-0.092479	-0.016582	0.0	0.0	0.0	0.0
	Z	-0.181846	0.179892	0.184018	-0.241812	-0.096989	0.0	0.0	0.0	0.0
	Z'	-0.035263	0.005436	0.013004	0.015887	-0.012971	0.0	0.0	0.0	0.0
O1	S	0.476827	0.435910	-0.030443	0.057331	-0.137540	0.0	0.0	0.0	0.0
	S'	0.254760	0.259672	-0.022420	0.037972	-0.088448	0.0	0.0	0.0	0.0
	S''	-0.018364	0.022346	-0.009316	0.014728	-0.036187	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.670634	-0.096809	0.727376	-0.095275
	X'	0.0	0.0	0.0	0.0	0.0	-0.005208	-0.023121	0.014785	-0.024647
	Y	0.021910	0.048961	0.013066	-0.432065	0.707014	0.0	0.0	0.0	0.0
	Y'	-0.014776	0.014091	-0.005107	-0.045640	-0.027211	0.0	0.0	0.0	0.0
	Z	-0.273666	0.473980	0.112003	-0.000667	-0.022044	0.0	0.0	0.0	0.0
	Z'	0.018164	-0.013321	0.012419	0.013957	-0.012417	0.0	0.0	0.0	0.0
O2	S	-0.476827	-0.435910	0.030443	-0.057331	0.137540	0.0	0.0	0.0	0.0
	S'	-0.254760	-0.259672	0.022420	-0.037972	0.088448	0.0	0.0	0.0	0.0
	S''	0.018364	-0.022346	0.009316	-0.014726	0.036187	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.670634	-0.096809	-0.727376	0.095275
	X'	0.0	0.0	0.0	0.0	0.0	-0.005208	-0.023121	-0.014785	0.024647
	Y	0.021910	0.048961	0.013066	-0.432065	0.707014	0.0	0.0	0.0	0.0
	Y'	-0.014776	0.014091	-0.005107	-0.045640	-0.027211	0.0	0.0	0.0	0.0
	Z	0.273666	-0.473980	-0.112003	0.000667	0.022044	0.0	0.0	0.0	0.0
	Z'	-0.018164	0.013321	-0.012419	-0.013957	0.012417	0.0	0.0	0.0	0.0
H1	S	-0.038261	0.019337	0.196919	0.000479	-0.026697	0.075839	0.284638	-0.096519	0.305121
	S'	-0.008321	0.009592	-0.034037	-0.019939	-0.008993	0.021208	-0.018028	-0.028478	-0.016835
H2	S	-0.038261	0.019337	0.196919	0.000479	-0.026697	-0.075839	-0.284638	0.096519	-0.305121
	S'	-0.008321	0.009592	-0.034037	-0.019939	-0.008993	-0.021208	0.018028	0.028478	0.016835
H3	S	0.038261	-0.019337	-0.196919	-0.000479	0.026697	0.075839	0.284638	0.096519	-0.305121
	S'	0.008321	-0.009592	0.034037	0.019939	0.008993	0.021208	-0.018028	0.028478	0.016835
H4	S	0.038261	-0.019337	-0.196919	-0.000479	0.026697	-0.075839	-0.284638	-0.096519	0.305121
	S'	0.008321	-0.009592	0.034037	0.019939	0.008993	-0.021208	0.018028	-0.028478	-0.016835

Table 64. CMO's and NRO's for 1,2-dioxetane at R_{CC} = 4.0369 a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	1.560500	1.861700	2.000000	2.000000
C1	S	0.000478	-0.669989	-0.041576	0.085152	0.160670	0.052972	-0.044683	0.000406	0.671847
	S'	-0.000588	-0.123690	0.139160	-0.222624	-0.426223	-0.122201	0.119232	-0.000358	0.119905
	S''	-0.000112	-0.004586	-0.009911	0.000328	-0.005050	-0.018588	0.012137	0.000105	0.002157
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000162	0.001369	0.028715	-0.039135	0.136862	-0.354148	0.492247	0.000140	-0.003268
	Y'	0.000263	0.000556	0.009777	-0.004398	-0.000866	0.087499	-0.073615	0.000083	0.000506
	Z	-0.000360	-0.001999	-0.160993	0.182038	-0.184982	-0.038506	0.147083	-0.000520	0.002199
	Z'	-0.000517	-0.000319	-0.029283	0.006983	-0.013464	0.007270	-0.010155	-0.000550	0.000089
C2	S	0.000478	-0.669989	-0.041576	0.085152	0.160670	0.052972	-0.044683	-0.000406	-0.671847
	S'	-0.000588	-0.123690	0.139160	-0.222624	-0.426223	-0.122201	0.119232	0.000358	-0.119905
	S''	-0.000112	-0.004586	-0.009911	0.000328	-0.005050	-0.018588	0.012137	-0.000105	-0.002157
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000162	-0.001369	-0.028715	0.039135	-0.136862	0.354148	-0.492247	0.000140	-0.003268
	Y'	-0.000263	-0.000556	-0.009777	0.004398	0.000866	-0.087499	0.073615	0.000083	0.000506
	Z	-0.000360	-0.001999	-0.160993	0.182038	-0.184982	-0.038506	0.147083	0.000520	-0.002199
	Z'	-0.000517	-0.000319	-0.029283	0.006983	-0.013464	0.007270	-0.010155	0.000550	-0.000089
O1	S	-0.333361	0.000238	-0.467406	-0.383631	-0.022192	0.025807	0.049570	-0.335071	-0.000867
	S'	0.618195	0.000116	-0.244852	-0.229013	-0.017805	0.016618	0.030663	0.617118	-0.000750
	S''	-0.003050	0.000224	0.026541	-0.029340	-0.011827	-0.001377	0.001138	-0.003147	-0.001058
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000003	0.000427	-0.011036	0.015172	0.005707	0.615950	0.266254	-0.001079	-0.000271
	Y'	0.000246	0.000082	0.000770	-0.005974	-0.004590	0.031828	-0.025374	0.000344	-0.000049
	Z	-0.002570	-0.003432	0.229048	-0.441394	0.119823	0.125999	-0.073214	-0.003046	0.004624
	Z'	0.000576	-0.000246	-0.019112	0.021791	0.009463	0.025917	-0.001216	0.000624	0.000735
O2	S	-0.333361	0.000238	-0.467406	-0.383631	-0.022192	0.025807	0.049570	0.335071	0.000867
	S'	0.618195	0.000116	-0.244852	-0.229013	-0.017805	0.016618	0.030663	-0.617118	0.000750
	S''	-0.003050	0.000224	0.026541	-0.029340	-0.011827	-0.001377	0.001138	0.003147	0.001058
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000003	-0.000427	0.011036	-0.015172	-0.005707	-0.615950	-0.266254	-0.001079	-0.000271
	Y'	-0.000246	-0.000082	-0.000770	0.005974	0.004590	-0.031828	0.025374	0.000344	-0.000049
	Z	-0.002570	-0.003432	0.229048	-0.441394	0.119823	0.125999	-0.073214	0.003046	-0.004624
	Z'	0.000576	-0.000246	-0.019112	0.021791	0.009463	0.025917	-0.001216	-0.000624	-0.000735
H1	S	0.000409	0.004800	0.034186	-0.024221	0.188662	-0.063340	0.039080	0.000571	-0.005797
	S'	0.000044	0.000076	0.007246	-0.011110	-0.032816	0.004239	-0.004395	0.000056	-0.000248
H2	S	0.000409	0.004800	0.034186	-0.024221	0.188662	-0.063340	0.039080	0.000571	-0.005797
	S'	0.000044	0.000076	0.007246	-0.011110	-0.032816	0.004239	-0.004395	0.000056	-0.000248
H3	S	0.000409	0.004800	0.034186	-0.024221	0.188662	-0.063340	0.039080	-0.000571	0.005797
	S'	0.000044	0.000076	0.007246	-0.011110	-0.032816	0.004239	-0.004395	-0.000056	0.000248
H4	S	0.000409	0.004800	0.034186	-0.024221	0.188662	-0.063340	0.039080	-0.000571	0.005797
	S'	0.000044	0.000076	0.007246	-0.011110	-0.032816	0.004239	-0.004395	-0.000056	0.000248

Table 64. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.136600	0.441200	2.000000	2.000000	2.000000	2.000000
C1	S	0.053830	-0.085981	0.163027	-0.109456	-0.055184	0.0	0.0	0.0	0.0
	S'	-0.167450	0.217532	-0.431575	0.258313	0.132807	0.0	0.0	0.0	0.0
	S''	0.004562	0.001082	-0.004349	0.009123	0.006518	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.063523	0.417441	0.089981	0.428257
	X'	0.0	0.0	0.0	0.0	0.0	0.021292	0.009266	-0.046757	0.006038
	Y	-0.032371	0.030213	0.145384	0.751990	0.310116	0.0	0.0	0.0	0.0
	Y'	0.000945	-0.005371	0.001445	-0.092793	-0.019222	0.0	0.0	0.0	0.0
	Z	0.180797	-0.179973	-0.186559	0.228639	0.097873	0.0	0.0	0.0	0.0
	Z'	0.036098	-0.006332	-0.013609	-0.014442	0.011077	0.0	0.0	0.0	0.0
C2	S	-0.053830	0.085981	-0.163027	0.109456	0.055184	0.0	0.0	0.0	0.0
	S'	0.167450	-0.217532	0.431575	-0.258313	-0.132807	0.0	0.0	0.0	0.0
	S''	-0.004562	-0.001082	0.004349	-0.009123	-0.006518	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.063523	0.417441	-0.089981	-0.428257
	X'	0.0	0.0	0.0	0.0	0.0	0.021292	0.009266	0.046757	-0.006038
	Y	-0.032371	0.030213	0.145384	0.751990	0.310116	0.0	0.0	0.0	0.0
	Y'	0.000945	-0.005371	0.001445	-0.092793	-0.019222	0.0	0.0	0.0	0.0
	Z	-0.180797	0.179973	0.186559	-0.228639	-0.097873	0.0	0.0	0.0	0.0
	Z'	-0.036098	0.006332	0.013609	0.014442	-0.011077	0.0	0.0	0.0	0.0
O1	S	0.475611	0.435477	-0.029746	0.054267	-0.121527	0.0	0.0	0.0	0.0
	S'	0.253109	0.259482	-0.022003	0.035203	-0.077468	0.0	0.0	0.0	0.0
	S''	-0.021147	0.022913	-0.009226	0.011367	-0.029628	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.672640	-0.098218	0.723822	-0.096142
	X'	0.0	0.0	0.0	0.0	0.0	-0.005286	-0.023284	0.012747	-0.024528
	Y	0.021999	0.037557	0.012310	-0.445401	0.688094	0.0	0.0	0.0	0.0
	Y'	-0.012560	0.013541	-0.005026	-0.047077	-0.025261	0.0	0.0	0.0	0.0
	Z	-0.271185	0.472260	0.112609	-0.003334	-0.015686	0.0	0.0	0.0	0.0
	Z'	0.019374	-0.015011	0.012043	0.012861	-0.010772	0.0	0.0	0.0	0.0
O2	S	-0.475611	-0.435477	0.029746	-0.054267	0.121527	0.0	0.0	0.0	0.0
	S'	-0.253109	-0.259482	0.022003	-0.035203	0.077468	0.0	0.0	0.0	0.0
	S''	0.021147	-0.022913	0.009226	-0.011367	0.029628	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.672640	-0.098218	-0.723822	0.096142
	X'	0.0	0.0	0.0	0.0	0.0	-0.005286	-0.023284	-0.012747	0.024528
	Y	0.021999	0.037557	0.012310	-0.445401	0.688094	0.0	0.0	0.0	0.0
	Y'	-0.012560	0.013541	-0.005026	-0.047077	-0.025261	0.0	0.0	0.0	0.0
	Z	0.271185	-0.472260	-0.112609	0.003334	0.015686	0.0	0.0	0.0	0.0
	Z'	-0.019374	0.015011	-0.012043	-0.012861	0.010772	0.0	0.0	0.0	0.0
H1	S	-0.038196	0.019998	0.197127	0.001202	-0.026591	0.076782	0.285524	-0.096019	0.304618
	S'	-0.008391	0.009848	-0.033875	-0.019364	-0.009064	0.021644	-0.017845	-0.028328	-0.016889
H2	S	-0.038196	0.019998	0.197127	0.001202	-0.026591	-0.076782	-0.285524	0.096019	-0.304618
	S'	-0.008391	0.009848	-0.033875	-0.019364	-0.009064	-0.021644	0.017845	0.028328	0.016889
H3	S	0.038196	-0.019998	-0.197127	-0.001202	0.026591	0.076782	0.285524	0.096019	-0.304618
	S'	0.008391	-0.009848	0.033875	0.019364	0.009064	0.021644	-0.017845	0.028328	0.016889
H4	S	0.038196	-0.019998	-0.197127	-0.001202	0.026591	-0.076782	-0.285524	-0.096019	0.304618
	S'	0.008391	-0.009848	0.033875	0.019364	0.009064	-0.021644	0.017845	-0.028328	-0.016889

Table 65. CMO's and NRO's for 1,2-dicxetane at R_{CC} = 4.0754 a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	1.387600	1.856000	2.000000	2.000000
C1	S	0.000457	-0.670048	-0.044699	-0.090216	0.155243	0.047266	-0.043520	0.000566	0.671592
	S'	-0.000531	-0.123577	0.145909	0.234012	-0.414597	-0.109452	0.117418	-0.000676	0.120397
	S''	-0.000095	-0.004570	-0.009092	-0.000563	-0.004170	-0.016849	0.009935	-0.000099	0.002404
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000153	0.001272	0.022265	0.031345	0.129037	-0.370915	0.485418	0.000323	-0.003042
	Y'	0.000247	0.000525	0.010150	0.005479	-0.001484	0.092785	-0.074739	-0.000137	0.000424
	Z	-0.000408	-0.002040	-0.168365	-0.191624	-0.202210	-0.049912	0.124425	-0.000238	0.001963
	Z'	-0.000496	-0.000278	-0.027161	-0.005594	-0.009751	0.008726	-0.007270	-0.000774	-0.000197
C2	S	0.000457	-0.670048	-0.044699	-0.090216	0.155243	0.047266	-0.043520	-0.000566	-0.671592
	S'	-0.000531	-0.123577	0.145909	0.234012	-0.414597	-0.109452	0.117418	0.000676	-0.120397
	S''	-0.000095	-0.004570	-0.009092	-0.000563	-0.004170	-0.016849	0.009935	0.000099	-0.002404
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000153	-0.001272	-0.022265	-0.031345	-0.129037	0.370915	-0.485418	0.000323	-0.003042
	Y'	-0.000247	-0.000525	-0.010150	-0.005479	0.001484	-0.092785	0.074739	-0.000137	0.000424
	Z	-0.000408	-0.002040	-0.168365	-0.191624	-0.202210	-0.049912	0.124425	0.000238	-0.001963
	Z'	-0.000496	-0.000278	-0.027161	-0.005594	-0.009751	0.008726	-0.007270	0.000774	0.000197
O1	S	-0.333366	0.000295	-0.468059	0.384092	-0.016489	0.028935	0.055005	-0.335039	-0.000792
	S'	0.618190	0.000167	-0.244707	0.230566	-0.012724	0.018270	0.034196	0.617145	-0.000670
	S''	-0.003030	0.000287	0.027711	0.031372	-0.006720	0.001017	0.003041	-0.003120	-0.000906
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000243	0.000569	-0.012854	-0.032357	0.006977	0.612504	0.286662	-0.000938	-0.000409
	Y'	0.000225	0.000063	0.001687	0.006803	-0.003901	0.027382	-0.025374	-0.000251	-0.000084
	Z	-0.002633	-0.003640	0.218244	0.436603	0.117026	0.125905	-0.060053	-0.003052	0.004447
	Z'	0.000553	-0.000291	-0.017928	-0.019453	0.009224	0.021325	0.000068	0.000689	0.000600
O2	S	-0.333366	0.000295	-0.468059	0.384092	-0.016489	0.028935	0.055005	0.335039	0.000792
	S'	0.618190	0.000167	-0.244707	0.230566	-0.012724	0.018270	0.034196	-0.617145	0.000670
	S''	-0.003030	0.000287	0.027711	0.031372	-0.006720	0.001017	0.003041	0.003120	0.000906
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000243	-0.000569	0.012854	0.032357	-0.006977	-0.612504	-0.286662	-0.000938	-0.000409
	Y'	-0.000225	-0.000063	-0.001687	-0.006803	0.003901	-0.027382	0.025374	-0.000251	-0.000084
	Z	-0.002633	-0.003640	0.218244	0.436603	0.117026	0.125905	-0.060053	0.003052	-0.004447
	Z'	0.000553	-0.000291	-0.017928	-0.019453	0.009224	0.021325	0.000068	-0.000689	-0.000600
H1	S	0.000383	0.004761	0.033540	0.024693	0.189981	-0.061933	0.036632	0.000441	-0.005722
	S'	0.000036	0.000066	0.007282	0.011974	-0.033058	0.004250	-0.004245	0.000024	-0.000186
H2	S	0.000383	0.004761	0.033540	0.024693	0.189881	-0.061933	0.036632	0.000441	-0.005722
	S'	0.000036	0.000066	0.007282	0.011974	-0.033058	0.004250	-0.004245	0.000024	-0.000186
H3	S	0.000383	0.004761	0.033540	0.024693	0.189881	-0.061933	0.036632	-0.000441	0.005722
	S'	0.000036	0.000066	0.007282	0.011974	-0.033058	0.004250	-0.004245	-0.000024	0.000186
H4	S	0.000383	0.004761	0.033540	0.024693	0.189881	-0.061933	0.036632	-0.000441	0.005722
	S'	0.000036	0.000066	0.007282	0.011974	-0.033058	0.004250	-0.004245	-0.000024	0.000186

Table 65. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.142600	0.613800	2.000000	2.000000	2.000000	2.000000
C1	S	0.055078	0.092170	0.159216	0.108211	-0.053663	0.0	0.0	0.0	0.0
	S'	-0.169724	-0.232473	-0.423478	-0.255704	0.130929	0.0	0.0	0.0	0.0
	S''	0.004150	-0.001638	-0.005247	-0.008158	0.005642	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.064942	0.416859	0.089526	0.427877
	X'	0.0	0.0	0.0	0.0	0.0	0.021509	0.009940	-0.045852	0.006597
	Y	-0.025540	-0.021076	0.137402	-0.757238	0.319533	0.0	0.0	0.0	0.0
	Y'	-0.000772	-0.000803	0.006955	0.092376	-0.022396	0.0	0.0	0.0	0.0
	Z	0.182997	0.199404	-0.203360	-0.194453	0.089182	0.0	0.0	0.0	0.0
	Z'	0.033321	0.000713	-0.006928	0.008829	0.007562	0.0	0.0	0.0	0.0
C2	S	-0.055078	-0.092170	-0.159216	-0.108211	0.053663	0.0	0.0	0.0	0.0
	S'	0.169724	0.232473	0.423478	0.255704	-0.130929	0.0	0.0	0.0	0.0
	S''	-0.004150	0.001638	0.005247	0.008158	-0.005642	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.064942	0.416859	-0.089526	-0.427877
	X'	0.0	0.0	0.0	0.0	0.0	0.021509	0.009940	0.045852	-0.006597
	Y	-0.025540	-0.021076	0.137402	-0.757238	0.319533	0.0	0.0	0.0	0.0
	Y'	-0.000772	-0.000803	0.006955	0.092376	-0.022396	0.0	0.0	0.0	0.0
	Z	-0.182997	-0.199404	0.203360	0.194453	-0.089182	0.0	0.0	0.0	0.0
	Z'	-0.033321	-0.000713	0.006928	-0.008829	-0.007562	0.0	0.0	0.0	0.0
O1	S	0.479315	-0.433206	-0.023121	-0.054010	-0.099417	0.0	0.0	0.0	0.0
	S'	0.253939	-0.260872	-0.016535	-0.035100	-0.063433	0.0	0.0	0.0	0.0
	S''	-0.023079	-0.029005	-0.005749	-0.009964	-0.024492	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.675187	-0.099777	0.719970	-0.096971
	X'	0.0	0.0	0.0	0.0	0.0	-0.005483	-0.023407	0.010655	-0.024317
	Y	0.022320	-0.015341	0.011602	0.444602	0.675069	0.0	0.0	0.0	0.0
	Y'	-0.009734	-0.008891	-0.005405	0.047467	-0.022797	0.0	0.0	0.0	0.0
	Z	-0.250128	-0.465622	0.109972	0.017682	-0.001075	0.0	0.0	0.0	0.0
	Z'	0.018046	0.014191	0.010782	-0.009641	-0.013613	0.0	0.0	0.0	0.0
O2	S	-0.479315	0.433206	0.023121	0.054010	0.099417	0.0	0.0	0.0	0.0
	S'	-0.253939	0.260872	0.016535	0.035100	0.063433	0.0	0.0	0.0	0.0
	S''	0.023079	0.029005	0.005749	0.009964	0.024492	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	-0.675187	-0.099777	-0.719970	0.096971
	X'	0.0	0.0	0.0	0.0	0.0	-0.005483	-0.023407	-0.010655	0.024317
	Y	0.022320	-0.015341	0.011602	0.444602	0.675069	0.0	0.0	0.0	0.0
	Y'	-0.009794	-0.008891	-0.005405	0.047467	-0.022797	0.0	0.0	0.0	0.0
	Z	0.250128	0.465622	-0.109972	-0.017682	0.001075	0.0	0.0	0.0	0.0
	Z'	-0.018046	-0.014191	-0.010782	0.009641	0.013613	0.0	0.0	0.0	0.0
H1	S	-0.038230	-0.023493	0.199195	0.005915	-0.029512	0.077101	0.286815	-0.094816	0.304705
	S'	-0.008587	-0.010922	-0.033529	0.021104	-0.009940	0.021867	-0.017456	-0.027975	-0.016761
H2	S	-0.038230	-0.023493	0.199195	0.005915	-0.029512	-0.077101	-0.286815	0.094816	-0.304705
	S'	-0.008587	-0.010922	-0.033529	0.021104	-0.009940	-0.021867	0.017456	0.027975	0.016761
H3	S	0.038230	0.023493	-0.199195	-0.005915	0.029512	0.077101	0.286815	0.094816	-0.304705
	S'	0.008587	0.010922	0.033529	-0.021104	0.009940	0.021867	-0.017456	0.027975	0.016761
H4	S	0.038230	0.023493	-0.199195	-0.005915	0.029512	-0.077101	-0.286815	-0.094816	0.304705
	S'	0.008587	0.010922	0.033529	-0.021104	0.009940	-0.021867	0.017456	-0.027975	-0.016761

Table 66. CMO's and NBO's for 1,2-dioxetane at R_{CC} = 4.1754 a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	0.159800	1.908000	2.000000	2.000000
C1	S	0.000503	-0.669694	-0.075980	-0.093599	0.143873	0.005423	-0.003613	0.000366	0.671858
	S'	-0.000373	-0.124479	0.227513	0.229596	-0.388219	-0.014390	0.010395	-0.000044	0.120260
	S''	-0.000192	-0.005054	-0.011800	-0.004669	-0.004171	-0.016450	0.005015	0.000024	0.001890
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000290	-0.000657	-0.039409	-0.020534	-0.042793	-0.487478	0.387523	0.000011	-0.001523
	Y'	-0.000026	0.000316	-0.003109	-0.001720	0.003038	0.101213	-0.046022	-0.000228	0.001131
	Z	-0.000971	-0.001993	-0.220032	-0.147327	-0.258093	0.088938	-0.068847	-0.000894	0.002718
	Z'	-0.000461	0.000093	-0.038437	-0.012829	-0.008401	-0.029675	0.010970	-0.000628	-0.000062
C2	S	0.000503	-0.669694	-0.075980	-0.093599	0.143873	0.005423	-0.003613	-0.000366	-0.671858
	S'	-0.000373	-0.124479	0.227513	0.229596	-0.388219	-0.014390	0.010395	0.000044	-0.120260
	S''	-0.000192	-0.005054	-0.011800	-0.004669	-0.004171	-0.016450	0.005015	-0.000024	-0.001890
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000290	0.000657	0.039409	0.020534	0.042793	0.487478	-0.387523	0.000011	-0.001523
	Y'	0.000026	-0.000316	0.003109	0.001720	-0.003038	-0.101213	0.046022	-0.000228	0.001131
	Z	-0.000971	-0.001993	-0.220032	-0.147327	-0.258093	0.088938	-0.068847	0.000894	-0.002718
	Z'	-0.000461	0.000093	-0.038437	-0.012829	-0.008401	-0.029675	0.010970	0.000628	0.000062
O1	S	-0.333598	0.000787	-0.381033	0.478222	-0.000754	-0.031172	0.025885	-0.333886	-0.001387
	S'	0.618044	0.000421	-0.184600	0.287803	0.000760	-0.018222	0.017266	0.617886	-0.001049
	S''	-0.003069	0.000169	0.053443	0.042143	0.005968	0.014651	0.006732	-0.003059	-0.001023
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000525	-0.000380	0.043062	0.063393	0.033201	0.580623	0.426537	-0.000692	0.001021
	Y'	0.000085	0.000104	-0.007755	-0.005175	0.003992	-0.082861	-0.002207	-0.000049	0.000286
	Z	-0.003511	-0.004406	0.261812	0.396335	0.106784	-0.074477	-0.097811	-0.003473	0.004773
	Z'	0.000415	-0.000301	-0.044503	-0.025332	0.001539	0.012999	0.004075	0.000540	0.000463
O2	S	-0.333598	0.000787	-0.381033	0.478222	-0.000754	-0.031172	0.025885	0.333886	0.001387
	S'	0.618044	0.000421	-0.184600	0.287803	0.000760	-0.018222	0.017266	-0.617886	0.001049
	S''	-0.003069	0.000169	0.053443	0.042143	0.005968	0.014651	0.006732	0.003059	0.001023
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000525	0.000380	-0.043062	-0.063393	-0.033201	-0.580623	-0.426537	-0.000692	0.001021
	Y'	-0.000085	-0.000104	0.007755	0.005175	-0.003992	0.082861	0.002207	-0.000049	0.000286
	Z	-0.003511	-0.004406	0.261812	0.396335	0.106784	-0.074477	-0.097811	0.003473	-0.004773
	Z'	0.000415	-0.000301	-0.044503	-0.025332	0.001539	0.012999	0.004075	-0.000540	-0.000463
H1	S	0.000245	0.003782	0.035139	0.015470	0.175428	-0.061272	0.032374	0.000452	-0.006086
	S'	-0.000042	-0.000253	0.008813	0.012608	-0.035539	-0.001840	0.001539	0.000015	-0.000174
H2	S	0.000245	0.003782	0.035139	0.015470	0.175428	-0.061272	0.032374	0.000452	-0.006086
	S'	-0.000042	-0.000253	0.008813	0.012608	-0.035539	-0.001840	0.001539	0.000015	-0.000174
H3	S	0.000245	0.003782	0.035139	0.015470	0.175428	-0.061272	0.032374	-0.000452	0.006086
	S'	-0.000042	-0.000253	0.008813	0.012608	-0.035539	-0.001840	0.001539	-0.000015	0.000174
H4	S	0.000245	0.003782	0.035139	0.015470	0.175428	-0.061272	0.032374	-0.000452	0.006086
	S'	-0.000042	-0.000253	0.008813	0.012608	-0.035539	-0.001840	0.001539	-0.000015	0.000174

Table 66. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.085200	1.847000	2.000000	2.000000	2.000000	2.000000
C1	S	-0.077904	0.092089	0.164303	-0.024216	-0.030717	0.0	0.0	0.0	0.0
	S'	0.231092	-0.222997	-0.432315	0.063344	0.076210	0.0	0.0	0.0	0.0
	S''	-0.007729	0.001853	-0.006679	0.009243	0.006024	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.151943	0.379264	0.151015	0.411139
	X'	0.0	0.0	0.0	0.0	0.0	-0.041449	0.024165	-0.051103	0.023086
	Y	-0.034405	0.024592	-0.013996	0.727994	0.383698	0.0	0.0	0.0	0.0
	Y'	-0.011864	0.006810	0.007715	-0.037124	-0.065544	0.0	0.0	0.0	0.0
	Z	-0.217075	0.153378	-0.269712	-0.082150	-0.032858	0.0	0.0	0.0	0.0
	Z'	-0.048785	0.012591	-0.009528	0.005354	-0.002756	0.0	0.0	0.0	0.0
C2	S	0.077904	-0.092089	-0.164303	0.024216	0.030717	0.0	0.0	0.0	0.0
	S'	-0.231092	0.222997	0.432315	-0.063344	-0.076210	0.0	0.0	0.0	0.0
	S''	0.007729	-0.001853	0.006679	-0.009243	-0.006024	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.151943	0.379264	-0.151015	-0.411139
	X'	0.0	0.0	0.0	0.0	0.0	-0.041449	0.024165	0.051103	-0.023086
	Y	-0.034405	0.024592	-0.013996	0.727994	0.383698	0.0	0.0	0.0	0.0
	Y'	-0.011864	0.006810	0.007715	-0.037124	-0.065544	0.0	0.0	0.0	0.0
	Z	0.217075	-0.153378	0.269712	0.082150	0.032858	0.0	0.0	0.0	0.0
	Z'	0.048785	-0.012591	0.009528	-0.005354	0.002756	0.0	0.0	0.0	0.0
O1	S	-0.386313	-0.482646	-0.010249	-0.014165	-0.030522	0.0	0.0	0.0	0.0
	S'	-0.188435	-0.290324	-0.005872	-0.007655	-0.019688	0.0	0.0	0.0	0.0
	S''	0.051956	-0.041942	0.004183	0.007376	-0.005118	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.665072	-0.163980	0.680400	-0.156969
	X'	0.0	0.0	0.0	0.0	0.0	0.009797	-0.035477	0.010394	-0.035776
	Y	0.040102	-0.068916	0.021878	-0.455164	0.566290	0.0	0.0	0.0	0.0
	Y'	-0.011063	0.002893	0.000365	0.058065	0.020075	0.0	0.0	0.0	0.0
	Z	0.272855	-0.403942	0.094601	0.095537	-0.099427	0.0	0.0	0.0	0.0
	Z'	-0.043846	0.027831	0.002729	-0.022280	-0.005586	0.0	0.0	0.0	0.0
O2	S	0.386313	0.482646	0.010249	0.014165	0.030522	0.0	0.0	0.0	0.0
	S'	0.188435	0.290324	0.005872	0.007655	0.019688	0.0	0.0	0.0	0.0
	S''	-0.051956	0.041942	-0.004183	-0.007376	0.005118	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.665072	-0.163980	-0.680400	0.156969
	X'	0.0	0.0	0.0	0.0	0.0	0.009797	-0.035477	-0.010394	0.035776
	Y	0.040102	-0.068916	0.021878	-0.455164	0.566290	0.0	0.0	0.0	0.0
	Y'	-0.011063	0.002893	0.000365	0.058065	0.020075	0.0	0.0	0.0	0.0
	Z	-0.272855	0.403942	-0.094601	-0.095537	0.099427	0.0	0.0	0.0	0.0
	Z'	0.043846	-0.027831	-0.002729	0.022280	0.005586	0.0	0.0	0.0	0.0
H1	S	0.042004	-0.017297	0.201995	-0.071465	-0.041761	-0.108322	0.318955	-0.116332	0.338649
	S'	0.009938	-0.010881	-0.034239	-0.017515	-0.009072	-0.039246	-0.007917	-0.039171	-0.009023
H2	S	0.042004	-0.017297	0.201995	-0.071465	-0.041761	0.108322	-0.318955	0.116332	-0.338649
	S'	0.009938	-0.010881	-0.034239	-0.017515	-0.009072	0.039246	0.007917	0.039171	0.009023
H3	S	-0.042004	0.017297	-0.201995	0.071465	0.041761	-0.108322	0.318955	0.116332	-0.338649
	S'	-0.009938	0.010881	0.034239	0.017515	0.009072	-0.039246	-0.007917	0.039171	0.009023
H4	S	-0.042004	0.017297	-0.201995	0.071465	0.041761	0.108322	-0.318955	-0.116332	0.338649
	S'	-0.009938	0.010881	0.034239	0.017515	0.009072	0.039246	0.007917	-0.039171	-0.009023

Table 67. CMO's and NRO's for 1,2-dicxetane at R_{CC} = 4.3754 a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	0.114100	1.920400	2.000000	2.000000
C1	S	0.000431	-0.669944	-0.081125	-0.087557	0.143097	0.000753	-0.001903	0.000327	0.671871
	S'	-0.000091	-0.124085	0.243906	0.211535	-0.385763	-0.002656	0.004996	0.000138	0.120404
	S''	-0.000202	-0.005043	-0.012796	-0.006259	-0.004181	-0.015011	0.003658	-0.000044	0.002147
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000458	-0.000927	-0.067616	-0.034992	-0.074187	-0.486114	0.364237	-0.000289	-0.000832
	Y'	-0.000086	0.000385	-0.010286	-0.004610	0.001900	0.087332	-0.034950	-0.000214	0.001069
	Z	-0.001293	-0.002048	-0.223359	-0.125677	-0.249393	0.141649	-0.110572	-0.001266	0.002880
	Z'	-0.000445	0.000149	-0.043255	-0.016198	-0.010386	-0.037180	0.012106	-0.000563	-0.000076
C2	S	0.000431	-0.669944	-0.081125	-0.087557	0.143097	0.000753	-0.001903	-0.000327	-0.671871
	S'	-0.000091	-0.124085	0.243906	0.211535	-0.385763	-0.002656	0.004996	-0.000138	-0.120404
	S''	-0.000202	-0.005043	-0.012796	-0.006259	-0.004181	-0.015011	0.003658	0.000044	-0.002147
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000458	0.000927	0.067616	0.034992	0.074187	0.486114	-0.364237	-0.000289	-0.000832
	Y'	0.000086	-0.000385	0.010286	0.004610	-0.001900	-0.087332	0.034950	-0.000214	0.001069
	Z	-0.001293	-0.002048	-0.223359	-0.125677	-0.249393	0.141649	-0.110572	0.001266	-0.002880
	Z'	-0.000445	0.000149	-0.043255	-0.016198	-0.010386	-0.037180	0.012106	0.000563	0.000076
O1	S	-0.333424	0.001118	-0.356304	0.491172	-0.003940	-0.023731	0.015932	-0.333540	-0.001574
	S'	0.618194	0.000645	-0.164435	0.295951	-0.001003	-0.013438	0.010551	0.618133	-0.001162
	S''	-0.003006	0.000266	0.067542	0.045524	0.006994	0.011467	0.003603	-0.002984	-0.001051
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.001022	-0.000984	0.076299	0.108723	0.041096	0.558392	0.433330	-0.001128	0.001634
	Y'	0.000139	0.000088	-0.015889	-0.009425	0.004025	-0.102764	-0.000830	0.000039	0.000387
	Z	-0.003653	-0.004579	0.268265	0.385214	0.092146	-0.156648	-0.139408	-0.003596	0.004647
	Z'	0.000342	-0.000358	-0.057936	-0.029470	-0.001332	0.030183	0.002994	0.000424	0.000433
O2	S	-0.333424	0.001118	-0.356304	0.491172	-0.003940	-0.023731	0.015932	0.333540	0.001574
	S'	0.618194	0.000645	-0.164435	0.295951	-0.001003	-0.013438	0.010551	-0.618133	0.001162
	S''	-0.003006	0.000266	0.067542	0.045524	0.006994	0.011467	0.003603	0.002984	0.001051
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.001022	0.000984	-0.076299	-0.108723	-0.041096	-0.558392	-0.433330	-0.001128	0.001634
	Y'	-0.000139	-0.000088	0.015889	0.009425	-0.004025	0.102764	0.000830	0.000039	0.000387
	Z	-0.003653	-0.004579	0.268265	0.385214	0.092146	-0.156648	-0.139408	0.003596	-0.004647
	Z'	0.000342	-0.000358	-0.057936	-0.029470	-0.001332	0.030183	0.002994	-0.000424	-0.000433
H1	S	0.000270	0.003741	0.035944	0.013158	0.176584	-0.052349	0.025710	0.000448	-0.006098
	S'	-0.000054	-0.000277	0.009284	0.012237	-0.035368	-0.001282	0.001050	-0.000002	-0.000197
H2	S	0.000270	0.003741	0.035944	0.013158	0.176584	-0.052349	0.025710	0.000448	-0.006098
	S'	-0.000054	-0.000277	0.009284	0.012237	-0.035368	-0.001282	0.001050	-0.000002	-0.000197
H3	S	0.000270	0.003741	0.035944	0.013158	0.176584	-0.052349	0.025710	-0.000448	0.006098
	S'	-0.000054	-0.000277	0.009284	0.012237	-0.035368	-0.001282	0.001050	0.000002	0.000197
H4	S	0.000270	0.003741	0.035944	0.013158	0.176584	-0.052349	0.025710	-0.000448	0.006098
	S'	-0.000054	-0.000277	0.009284	0.012237	-0.035368	-0.001282	0.001050	0.000002	0.000197

Table 67. (Continued)

	(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO	2.000000	2.000000	2.000000	0.074100	1.891400	2.000000	2.000000	2.000000	2.000000
C1 S	0.080662	0.086240	0.163312	-0.024406	-0.024750	0.0	0.0	0.0	0.0
S'	-0.242893	-0.206883	-0.429713	0.061827	0.062742	0.0	0.0	0.0	0.0
S''	0.010199	0.003256	-0.006260	0.007488	0.005605	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	0.167046	0.369553	0.161941	0.409315
X'	0.0	0.0	0.0	0.0	0.0	-0.032405	0.023961	-0.040312	0.019570
Y	0.059340	0.032743	-0.049192	0.686732	0.372714	0.0	0.0	0.0	0.0
Y'	0.019236	0.010411	0.002895	-0.036662	-0.052604	0.0	0.0	0.0	0.0
Z	0.218050	0.127479	-0.265891	-0.172134	-0.075877	0.0	0.0	0.0	0.0
Z'	0.055450	0.018300	-0.013717	0.004056	0.003195	0.0	0.0	0.0	0.0
C2 S	-0.080662	-0.086240	-0.163312	0.024406	0.024750	0.0	0.0	0.0	0.0
S'	0.242893	0.206883	0.429713	-0.061827	-0.062742	0.0	0.0	0.0	0.0
S''	-0.010199	-0.003256	0.006260	-0.007488	-0.005605	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	0.167046	0.369553	-0.161941	-0.409315
X'	0.0	0.0	0.0	0.0	0.0	-0.032405	0.023961	0.040312	-0.019570
Y	0.059340	0.032743	-0.049192	0.686732	0.372714	0.0	0.0	0.0	0.0
Y'	0.019236	0.010411	0.002895	-0.036662	-0.052604	0.0	0.0	0.0	0.0
Z	-0.218050	-0.127479	0.265891	0.172134	0.075877	0.0	0.0	0.0	0.0
Z'	-0.055450	-0.018300	0.013717	-0.004056	-0.003195	0.0	0.0	0.0	0.0
O1 S	0.361040	-0.491953	-0.012688	-0.006867	-0.015449	0.0	0.0	0.0	0.0
S'	0.168850	-0.295772	-0.007534	-0.002187	-0.010237	0.0	0.0	0.0	0.0
S''	-0.063921	-0.043846	0.004343	0.010665	-0.004049	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	0.661339	-0.187490	0.671822	-0.184735
X'	0.0	0.0	0.0	0.0	0.0	0.007499	-0.040167	0.007707	-0.042241
Y	-0.073871	-0.111914	0.028863	-0.470086	0.528213	0.0	0.0	0.0	0.0
Y'	0.020735	0.008777	-0.000880	0.079404	0.012549	0.0	0.0	0.0	0.0
Z	-0.276550	-0.388552	0.088203	0.129790	-0.159466	0.0	0.0	0.0	0.0
Z'	0.056182	0.030595	0.001323	-0.031742	-0.004503	0.0	0.0	0.0	0.0
O2 S	-0.361040	0.491953	0.012688	0.006867	0.015449	0.0	0.0	0.0	0.0
S'	-0.168850	0.295772	0.007534	0.002187	0.010237	0.0	0.0	0.0	0.0
S''	0.063921	0.043846	-0.004343	-0.010665	0.004049	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	0.661339	-0.187490	-0.671822	0.184735
X'	0.0	0.0	0.0	0.0	0.0	0.007499	-0.040167	-0.007707	0.042241
Y	-0.073871	-0.111914	0.028863	-0.470086	0.528213	0.0	0.0	0.0	0.0
Y'	0.020735	0.008777	-0.000880	0.079404	0.012549	0.0	0.0	0.0	0.0
Z	0.276550	0.388552	-0.088203	-0.129790	0.159466	0.0	0.0	0.0	0.0
Z'	-0.056182	-0.030595	-0.001323	0.031742	0.004503	0.0	0.0	0.0	0.0
H1 S	-0.042591	-0.015601	0.203343	-0.063507	-0.034404	-0.103992	0.331126	-0.114918	0.347984
S'	-0.009980	-0.011051	-0.033878	-0.015240	-0.007343	-0.038697	-0.004121	-0.039814	-0.005764
H2 S	-0.042591	-0.015601	0.203343	-0.063507	-0.034404	0.103992	-0.331126	0.114918	-0.347984
S'	-0.009980	-0.011051	-0.033878	-0.015240	-0.007343	0.038697	0.004121	0.039814	0.005764
H3 S	0.042591	0.015601	-0.203343	0.063507	0.034404	-0.103992	0.331126	0.114918	-0.347984
S'	0.009980	0.011051	0.033878	0.015240	0.007343	-0.038697	-0.004121	0.039814	0.005764
H4 S	0.042591	0.015601	-0.203343	0.063507	0.034404	0.103992	-0.331126	-0.114918	0.347984
S'	0.009980	0.011051	0.033878	0.015240	0.007343	0.038697	0.004121	-0.039814	-0.005764

Table 68. CMO's and NRO's for 1,2-dioxetane at R_{CC} = 5.8754 a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	0.097000	1.913100	2.000000	2.000000
C1	S	0.000379	-0.670117	-0.078210	-0.083703	0.151466	-0.004594	0.002763	0.000427	0.670634
	S'	0.000040	-0.123786	0.238097	0.202797	-0.403871	0.010666	-0.007688	-0.000041	0.122850
	S''	-0.000182	-0.004716	-0.012398	-0.007453	-0.003308	-0.005005	0.001665	-0.000212	0.003948
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000135	-0.000277	-0.015724	-0.008037	-0.021286	-0.541735	0.360865	-0.000092	0.000018
	Y'	-0.000008	0.000115	-0.002176	-0.001202	0.001186	0.065333	-0.033623	-0.000030	0.000234
	Z	-0.001523	-0.002421	-0.228631	-0.138499	-0.256533	0.040392	-0.028383	-0.001342	0.002661
	Z'	-0.000436	0.000031	-0.046415	-0.021416	-0.013185	-0.012538	0.002461	-0.000610	-0.000049
C2	S	0.000379	-0.670117	-0.078210	-0.083703	0.151486	-0.004594	0.002763	-0.000427	-0.670634
	S'	0.000040	-0.123786	0.238097	0.202797	-0.403871	0.010666	-0.007688	0.000041	-0.122850
	S''	-0.000182	-0.004716	-0.012398	-0.007453	-0.003308	-0.005005	0.001665	0.000212	-0.003948
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000135	0.000277	0.015724	0.008037	0.021286	0.541735	-0.360865	-0.000092	0.000018
	Y'	0.000008	-0.000115	0.002176	0.001202	-0.001186	-0.065333	0.033623	-0.000030	0.000234
	Z	-0.001523	-0.002421	-0.228631	-0.138499	-0.256533	0.040392	-0.028383	0.001342	-0.002661
	Z'	-0.000436	0.000031	-0.046415	-0.021416	-0.013185	-0.012538	0.002461	0.000610	0.000049
O1	S	-0.333369	0.001093	-0.369310	0.479387	-0.020002	-0.014283	0.006127	-0.333540	-0.001271
	S'	0.618255	0.000662	-0.172025	0.289482	-0.011406	-0.007342	0.003990	0.618124	-0.000865
	S''	-0.002937	0.000359	0.067543	0.046028	0.004875	0.010329	0.001149	-0.003013	-0.000683
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000245	-0.000225	0.017195	0.027684	0.007198	0.547091	0.486390	-0.000337	0.000369
	Y'	0.000054	0.000028	-0.002733	-0.002367	0.001369	-0.126955	0.006980	-0.000062	0.000058
	Z	-0.003688	-0.004544	0.271219	0.411741	0.087591	-0.039320	-0.031128	-0.003676	0.004632
	Z'	0.000334	-0.000357	-0.060822	-0.032906	0.000321	0.011018	0.001299	0.000421	0.000436
O2	S	-0.333369	0.001093	-0.369310	0.479387	-0.020002	-0.014283	0.006127	0.333540	0.001271
	S'	0.618255	0.000662	-0.172025	0.289482	-0.011406	-0.007342	0.003990	-0.618124	0.000865
	S''	-0.002937	0.000359	0.067543	0.046028	0.004875	0.010329	0.001149	0.003013	0.000683
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000245	0.000225	-0.017195	-0.027684	-0.007198	-0.547091	-0.486390	-0.000337	0.000369
	Y'	-0.000054	-0.000028	0.002733	0.002367	-0.001369	0.126955	-0.006980	-0.000062	0.000058
	Z	-0.003688	-0.004544	0.271219	0.411741	0.087591	-0.039320	-0.031128	0.003676	-0.004632
	Z'	0.000334	-0.000357	-0.060822	-0.032906	0.000321	0.011018	0.001299	-0.000421	-0.000436
H1	S	0.000314	0.004454	0.037452	0.019461	0.188669	-0.013172	0.009390	0.000384	-0.005061
	S'	-0.000051	-0.000133	0.009458	0.011950	-0.034493	-0.000522	0.000143	-0.000009	-0.000045
H2	S	0.000314	0.004454	0.037452	0.019461	0.188669	-0.013172	0.009390	0.000384	-0.005061
	S'	-0.000051	-0.000133	0.009458	0.011950	-0.034493	-0.000522	0.000143	-0.000009	-0.000045
H3	S	0.000314	0.004454	0.037452	0.019461	0.188669	-0.013172	0.009390	-0.000384	0.005061
	S'	-0.000051	-0.000133	0.009458	0.011950	-0.034493	-0.000522	0.000143	0.000009	0.000045
H4	S	0.000314	0.004454	0.037452	0.019461	0.188669	-0.013172	0.009390	-0.000384	0.005061
	S'	-0.000051	-0.000133	0.009458	0.011950	-0.034493	-0.000522	0.000143	0.000009	0.000045

Table 68. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.087300	1.902600	2.000000	2.000000	2.000000	2.000000
C1	S	0.077052	0.085058	0.154808	-0.008578	-0.004125	0.0	0.0	0.0	0.0
	S'	-0.235766	-0.205101	-0.411751	0.019375	0.010648	0.0	0.0	0.0	0.0
	S''	0.013660	0.005087	-0.002997	0.003194	0.000559	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.154702	0.386666	0.152137	0.396936
	X'	0.0	0.0	0.0	0.0	0.0	-0.032262	0.021891	-0.033179	0.019661
	Y	0.014652	0.007202	-0.017501	0.622318	0.375653	0.0	0.0	0.0	0.0
	Y'	0.003080	0.002962	0.001387	-0.053052	-0.037674	0.0	0.0	0.0	0.0
	Z	0.223492	0.141939	-0.259240	-0.044842	-0.016370	0.0	0.0	0.0	0.0
	Z'	0.053384	0.019275	-0.014157	0.001686	-0.000817	0.0	0.0	0.0	0.0
C2	S	-0.077052	-0.085058	-0.154808	0.008578	0.004125	0.0	0.0	0.0	0.0
	S'	0.235766	0.205101	0.411751	-0.019375	-0.010648	0.0	0.0	0.0	0.0
	S''	-0.013660	-0.005087	0.002997	-0.003194	-0.000559	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.154702	0.386666	-0.152137	-0.396936
	X'	0.0	0.0	0.0	0.0	0.0	-0.032262	0.021891	0.033179	-0.019661
	Y	0.014652	0.007202	-0.017501	0.622318	0.375653	0.0	0.0	0.0	0.0
	Y'	0.003080	0.002962	0.001387	-0.053052	-0.037674	0.0	0.0	0.0	0.0
	Z	-0.223492	-0.141939	0.259240	0.044842	0.016370	0.0	0.0	0.0	0.0
	Z'	-0.053384	-0.019275	0.014157	-0.001686	0.000817	0.0	0.0	0.0	0.0
O1	S	0.371872	-0.483129	-0.020169	-0.002108	-0.013450	0.0	0.0	0.0	0.0
	S'	0.174530	-0.292324	-0.011716	0.001040	-0.008089	0.0	0.0	0.0	0.0
	S''	-0.065323	-0.047379	0.004089	0.009812	-0.000821	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.668644	-0.172710	0.673243	-0.171998
	X'	0.0	0.0	0.0	0.0	0.0	0.008216	-0.040771	0.008479	-0.041472
	Y	-0.015461	-0.030684	0.005187	-0.519151	0.520957	0.0	0.0	0.0	0.0
	Y'	0.005791	0.000523	0.000731	0.111051	0.012485	0.0	0.0	0.0	0.0
	Z	-0.272885	-0.411701	0.086693	0.026023	-0.037295	0.0	0.0	0.0	0.0
	Z'	0.060453	0.034802	0.000641	-0.008370	-0.001155	0.0	0.0	0.0	0.0
O2	S	-0.371872	0.483129	0.020169	0.002108	0.013450	0.0	0.0	0.0	0.0
	S'	-0.174530	0.292324	0.011716	-0.001040	0.008089	0.0	0.0	0.0	0.0
	S''	0.065323	0.047379	-0.004089	-0.009812	0.000821	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.668644	-0.172710	-0.673243	0.171998
	X'	0.0	0.0	0.0	0.0	0.0	0.008216	-0.040771	-0.008479	0.041472
	Y	-0.015461	-0.030684	0.005187	-0.519151	0.520957	0.0	0.0	0.0	0.0
	Y'	0.005791	0.000523	0.000731	0.111051	0.012485	0.0	0.0	0.0	0.0
	Z	0.272885	0.411701	-0.086693	-0.026023	0.037295	0.0	0.0	0.0	0.0
	Z'	-0.060453	-0.034802	-0.000641	0.008370	0.001155	0.0	0.0	0.0	0.0
H1	S	-0.039172	-0.019195	0.193864	-0.015424	-0.006717	-0.113863	0.337084	-0.114037	0.337860
	S'	-0.010122	-0.011123	-0.034476	-0.003249	-0.000541	-0.038699	-0.004190	-0.037365	-0.006112
H2	S	-0.039172	-0.019195	0.193864	-0.015424	-0.006717	0.113863	-0.337084	0.114037	-0.337860
	S'	-0.010122	-0.011123	-0.034476	-0.003249	-0.000541	0.038699	0.004190	0.037365	0.006112
H3	S	0.039172	0.019195	-0.193864	0.015424	0.006717	-0.113863	0.337084	0.114037	-0.337860
	S'	0.010122	0.011123	0.034476	0.003249	0.000541	-0.038699	-0.004190	0.037365	0.006112
H4	S	0.039172	0.019195	-0.193864	0.015424	0.006717	0.113863	-0.337084	-0.114037	0.337860
	S'	0.010122	0.011123	0.034476	0.003249	0.000541	0.038699	0.004190	-0.037365	-0.006112

Table 69. CMO's and NRO's for 1,2-dioxetane at R_{CC} = 8.8754 a.u.

		(1a1)	(2a1)	(3a1)	(4a1)	(5a1)	(6a1)	(7a1)	(1b2)	(2b2)
ETCGAO		2.000000	2.000000	2.000000	2.000000	2.000000	0.090200	1.910800	2.000000	2.000000
C1	S	0.000177	-0.674932	-0.070069	0.155921	-0.029600	0.000020	0.000452	0.000189	0.674962
	S'	-0.000274	-0.110208	0.247450	-0.446573	0.074663	0.000531	-0.001468	-0.000296	0.110150
	S''	-0.000089	-0.004655	-0.008868	0.000860	-0.011997	-0.000792	0.000323	-0.000102	0.004620
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000000	-0.000004	-0.000455	-0.002442	-0.003390	-0.576795	0.362007	-0.000001	-0.000009
	Y'	-0.000002	0.000001	-0.000506	0.000098	0.000515	0.054215	-0.032342	0.000003	0.000021
	Z	-0.000053	-0.000838	-0.126038	-0.172426	-0.303143	0.007013	-0.004281	-0.000045	0.000836
	Z'	-0.000028	-0.000447	-0.036181	-0.004762	-0.041392	-0.003070	0.000434	-0.000036	0.000454
C2	S	0.000177	-0.674932	-0.070069	0.155921	-0.029600	0.000020	0.000452	-0.000189	-0.674962
	S'	-0.000274	-0.110208	0.247450	-0.446573	0.074663	0.000531	-0.001468	0.000296	-0.110150
	S''	-0.000089	-0.004655	-0.008868	0.000860	-0.011997	-0.000792	0.000323	0.000102	-0.004620
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000000	0.000004	0.000455	0.002442	0.003390	0.576795	-0.362007	-0.000001	-0.000009
	Y'	0.000002	-0.000001	0.000506	-0.000098	-0.000515	-0.054215	0.032342	0.000003	0.000021
	Z	-0.000053	-0.000838	-0.126038	-0.172426	-0.303143	0.007013	-0.004281	0.000045	-0.000836
	Z'	-0.000028	-0.000447	-0.036181	-0.004762	-0.041392	-0.003070	0.000434	0.000036	-0.000454
O1	S	-0.318367	0.000175	-0.485582	-0.260360	0.270258	-0.003025	0.000720	-0.318373	-0.000181
	S'	0.626194	0.000862	-0.227939	-0.147117	0.173166	-0.002146	0.000609	0.626187	-0.000869
	S''	-0.003264	0.001562	0.050371	-0.014929	0.063423	-0.000251	0.000587	-0.003277	-0.001575
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	-0.000003	0.000001	0.000529	-0.001205	0.002048	0.532797	0.505603	-0.000003	0.000005
	Y'	0.000004	-0.000004	-0.000159	0.000207	0.000162	-0.124764	0.011978	0.000002	0.000016
	Z	-0.000936	-0.000078	0.121755	-0.104704	0.476871	-0.003027	-0.001640	-0.000930	0.000084
	Z'	0.000797	-0.001416	-0.048907	0.013331	-0.048219	0.001981	-0.000211	0.000803	0.001422
O2	S	-0.318367	0.000175	-0.485582	-0.260360	0.270258	-0.003025	0.000720	0.318373	0.000181
	S'	0.626194	0.000862	-0.227939	-0.147117	0.173166	-0.002146	0.000609	-0.626187	0.000869
	S''	-0.003264	0.001562	0.050371	-0.014929	0.063423	-0.000251	0.000587	0.003277	0.001575
	X	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	X'	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Y	0.000003	-0.000001	-0.000529	0.001205	-0.002048	-0.532797	-0.505603	-0.000003	0.000005
	Y'	-0.000004	0.000004	0.000159	-0.000207	-0.000162	0.124764	-0.011978	0.000002	0.000016
	Z	-0.000936	-0.000078	0.121755	-0.104704	0.476871	-0.003027	-0.001640	0.000930	-0.000084
	Z'	0.000797	-0.001416	-0.048907	0.013331	-0.048219	0.001981	-0.000211	-0.000803	-0.001422
H1	S	-0.000001	0.001151	-0.006956	0.162097	0.110846	-0.000036	0.001068	-0.000003	-0.001173
	S'	0.000017	0.000895	0.012326	-0.035457	-0.001519	0.000433	-0.000171	0.000017	-0.000906
H2	S	-0.000001	0.001151	-0.006956	0.162097	0.110846	-0.000036	0.001068	-0.000003	-0.001173
	S'	0.000017	0.000895	0.012326	-0.035457	-0.001519	0.000433	-0.000171	0.000017	-0.000906
H3	S	-0.000001	0.001151	-0.006956	0.162097	0.110846	-0.000036	0.001068	0.000003	0.001173
	S'	0.000017	0.000895	0.012326	-0.035457	-0.001519	0.000433	-0.000171	-0.000017	0.000906
H4	S	-0.000001	0.001151	-0.006956	0.162097	0.110846	-0.000036	0.001068	0.000003	0.001173
	S'	0.000017	0.000895	0.012326	-0.035457	-0.001519	0.000433	-0.000171	-0.000017	0.000906

Table 69. (Continued)

		(3b2)	(4b2)	(5b2)	(6b2)	(7b2)	(1b1)	(2b1)	(1a2)	(2a2)
ETCGAO		2.000000	2.000000	2.000000	0.089300	1.909700	2.000000	2.000000	2.000000	2.000000
C1	S	0.068935	0.156509	0.030063	0.002186	0.000187	0.0	0.0	0.0	0.0
	S'	-0.245366	-0.447787	-0.075425	-0.004382	-0.000426	0.0	0.0	0.0	0.0
	S''	0.009889	0.000364	0.011226	-0.002692	0.000139	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.392760	-0.152852	0.393663	-0.152476
	X'	0.0	0.0	0.0	0.0	0.0	-0.005488	-0.036067	-0.006365	-0.037034
	Y	0.000541	-0.002382	0.001378	-0.588293	0.364370	0.0	0.0	0.0	0.0
	Y'	-0.000058	0.000620	0.000628	0.055654	-0.032637	0.0	0.0	0.0	0.0
	Z	0.124053	-0.171908	0.303705	0.005200	-0.000450	0.0	0.0	0.0	0.0
	Z'	0.038328	-0.005182	0.041197	0.000005	-0.000912	0.0	0.0	0.0	0.0
C2	S	-0.068935	-0.156509	-0.030063	-0.002186	-0.000187	0.0	0.0	0.0	0.0
	S'	0.245366	0.447787	0.075425	0.004382	0.000426	0.0	0.0	0.0	0.0
	S''	-0.009889	-0.000364	-0.011226	0.002692	-0.000139	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.392760	-0.152852	-0.393663	0.152476
	X'	0.0	0.0	0.0	0.0	0.0	-0.005488	-0.036067	0.006365	0.037034
	Y	0.000541	-0.002382	0.001378	-0.588293	0.364370	0.0	0.0	0.0	0.0
	Y'	-0.000058	0.000620	0.000628	0.055654	-0.032637	0.0	0.0	0.0	0.0
	Z	-0.124053	0.171908	-0.303705	-0.005200	0.000450	0.0	0.0	0.0	0.0
	Z'	-0.038328	0.005182	-0.041197	-0.000005	0.000912	0.0	0.0	0.0	0.0
O1	S	0.486736	-0.260731	-0.270637	-0.001065	-0.002125	0.0	0.0	0.0	0.0
	S'	0.229222	-0.147524	-0.173551	-0.001088	-0.001427	0.0	0.0	0.0	0.0
	S''	-0.048503	-0.015500	-0.063934	-0.001162	-0.000523	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.323620	0.613350	0.323653	0.613153
	X'	0.0	0.0	0.0	0.0	0.0	-0.024385	0.035141	-0.024649	0.034754
	Y	-0.000419	-0.000803	-0.003794	0.530334	0.508661	0.0	0.0	0.0	0.0
	Y'	0.000540	0.000252	0.000019	-0.121362	0.011781	0.0	0.0	0.0	0.0
	Z	-0.122449	-0.104716	-0.476598	-0.001277	-0.003762	0.0	0.0	0.0	0.0
	Z'	0.048241	0.013609	0.048514	0.000952	0.000358	0.0	0.0	0.0	0.0
O2	S	-0.486736	0.260731	0.270637	0.001065	0.002125	0.0	0.0	0.0	0.0
	S'	-0.229222	0.147524	0.173551	0.001088	0.001427	0.0	0.0	0.0	0.0
	S''	0.048503	0.015500	0.063934	0.001162	0.000523	0.0	0.0	0.0	0.0
	X	0.0	0.0	0.0	0.0	0.0	0.323620	0.613350	-0.323653	-0.613153
	X'	0.0	0.0	0.0	0.0	0.0	-0.024385	0.035141	0.024649	-0.034754
	Y	-0.000419	-0.000803	-0.003794	0.530334	0.508661	0.0	0.0	0.0	0.0
	Y'	0.000540	0.000252	0.000019	-0.121362	0.011781	0.0	0.0	0.0	0.0
	Z	0.122449	0.104716	0.476598	0.001277	0.003762	0.0	0.0	0.0	0.0
	Z'	-0.048241	-0.013609	-0.048514	-0.000952	-0.000358	0.0	0.0	0.0	0.0
H1	S	0.006594	0.162138	-0.111164	-0.000381	0.000194	0.172740	-0.308869	0.172061	-0.309344
	S'	-0.012464	-0.035463	0.001582	-0.000110	0.000248	-0.029416	-0.023732	-0.029735	-0.023662
H2	S	0.006594	0.162138	-0.111164	-0.000381	0.000194	-0.172740	0.308869	-0.172061	0.309344
	S'	-0.012464	-0.035463	0.001582	-0.000110	0.000248	0.029416	0.023732	0.029735	0.023662
H3	S	-0.006594	-0.162138	0.111164	0.000381	-0.000194	0.172740	-0.308869	-0.172061	0.309344
	S'	0.012464	0.035463	-0.001582	0.000110	-0.000248	-0.029416	-0.023732	0.029735	0.023662
H4	S	-0.006594	-0.162138	0.111164	0.000381	-0.000194	-0.172740	0.308869	0.172061	-0.309344
	S'	0.012464	0.035463	-0.001582	0.000110	-0.000248	0.029416	0.023732	-0.029735	-0.023662