VSEPR are reproduced faithfully by the complicated all electron MO scheme. However, the simple kinetic energy results obtained earlier by Takahata and Parr[9] were not found in our more elaborate studies, nor were the Walsh diagram type arguments effective. Other LMO energy partitions, however, showed minima near equilibrium, but any generalizations from these must await confirmation from similar applications to other molecules.

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Photochemical and Spectroscopic Applications of Approximate Molecular Orbital Theory. I. Averaged Field Approximate Open Shell Theory

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Abstract: An approximate procedure for obtaining self-consistent field wave functions for the first excited singlet state of polyatomic molecules is investigated. This procedure utilizes an averaged field Fock operator serving to reduce the three coupled SCF equations required in a normal singlet state open shell variational calculation to a single SCF equation within a slightly deorthogonalized basis field. The formalism, which is termed "average field approximate open shell" (AFAOS) theory, is applied to the CNDO and INDO procedures yielding favorable results. AFAOS calculations on a variety of molecules are presented. For polyatomic molecules containing 26 or more valence electrons, the AFAOS method yields wave functions of comparable accuracy to the more rigorous parent open shell theory of Kroto and Santry.

During the past decade, a number of approximate methods have been developed for obtaining self-consistent field molecular orbitals for all valence electrons of polyatomic molecules.[2-10] Although these procedures provide only qualitative information regarding the orbital nature and the density characteristics of the optical electrons, this information has often proved quite useful in rationalizing observed photochemical and spectroscopic phenomena.[11-13] While wave functions for the first excited triplet states of molecules (with closed shell ground states) can be generated using readily available unrestricted open shell procedures,[3,4,6] the complications involved in generating wave functions for the first excited singlet state (see below) have precluded the general use of wave functions optimized to the excited state singlet electron configuration. Accordingly, most LCAO investigations of excited singlets have relied on either virtual orbital techniques[7,12] or on the use of wave functions for the first excited triplet state when the differing symmetry of the open shell orbitals suggested that the singlet and triplet states would possess similar electron distributions.[13] The virtual orbital technique has the distinct disadvantage of optimizing the wave function for the ground state electron configuration. On the other hand, the use of triplet wave functions as an approximation for singlet wave functions, while often defended for CNDO calculations on σ,π^* (or n,π^*) states, is a dubious approach since many orbital interactions which are neglected in the unrestricted open shell calculation are important for the corresponding excited state singlet calculation.

Conventional SCF singlet state open shell variational procedures normally require the construction of three coupled SCF equations each requiring a separate Fock operator (see section I). These procedures require an approximate threefold increase in computation time relative to closed shell calculations and a computer code capable of monitoring the symmetries of the molecular orbitals since the order of the eigenvectors is occasionally different within the three orbital coefficient matrices.[8] The usual end result is a program limited to calculations on small basis set molecules.

In this article we investigate an approximate variational procedure for obtaining wave functions for the first excited singlet state of polyatomic molecules which utilizes an averaged field Fock operator serving to reduce the

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(2) Of the numerous approximate methods available, the CNDO and INDO procedures developed by Pople and coworkers[3-5] appear the more versatile and reliable.

(3) (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129, S136 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

(4) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967).

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three coupled SCF equations to a single SCF equation within a slightly deorthogonalized basis field.[14] This approach is named "averaged field approximate open shell (AFAOS) theory." The formalism is applied to the CNDO and INDO procedures yielding favorable results. The calculations presented in section III demonstrate that the approximations inherent in the CNDO and INDO procedures are of a comparable magnitude to the approximations introduced by the AFAOS formalism. Furthermore, for larger polyatomic molecules (26 or more valence electrons), the AFAOS method yields wave functions of comparable accuracy to the more rigorous parent open shell theory of Kroto and Santry utilizing three determinants.[8]

(I) Averaged Field Approximate Open Shell Theory

AFAOS theory is a reduced, simplified version of the approximate open shell theory (AOS) developed by Kroto and Santry,[8] and in order to facilitate comparison between the two theories, we shall adopt the symbolism of the above authors.

Assuming that the two open shell MO's are not degenerate, the wave function, ${}^1\Psi_{n\leftarrow m}$, for the first excited singlet state is given by eq 1 where $\psi_1 - \psi_l$ are

$$ {}^1\Psi_{n\leftarrow m} = \frac{1}{\sqrt{2}}\{|\psi_1(\alpha)\psi_1(\beta)\ldots\psi_l(\alpha)\psi_l(\beta)\psi_m(\alpha)\psi_n(\beta)| - |\psi_1(\alpha)\psi_1(\beta)\ldots\psi_l(\alpha)\psi_l(\beta)\psi_m(\beta)\psi_n(\alpha)|\} \quad (1) $$

the closed shell LCAO–MO's, and ψ_m and ψ_n are the two open shell LCAO–MO's

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

$$ \psi_n = \sum_\mu \chi_\mu b_{\mu n} \quad (3) $$

$$ \psi_m = \sum_\mu \chi_\mu a_{\mu m} \quad (4) $$

where χ_μ is the μth atomic orbital, $c_{\mu i}$ is the orbital coefficient associated with the μth atomic orbital and ith closed shell MO, and $a_{\mu m}$ and $b_{\mu n}$ are the orbital coefficients for the open shell MO's.

Application of the variational principle to the minimization of the energy of the excited state singlet with respect to the orbital coefficients generates three coupled SCF equations. Assuming an orthogonal basis set

$$ (\mathbf{F} + \mathbf{O})\mathbf{C} = \mathbf{SCE}_c \quad (5) $$

$$ (\mathbf{F} + \mathbf{N})\mathbf{A} = \mathbf{SAE}_m \quad (6) $$

$$ (\mathbf{F} + \mathbf{M})\mathbf{B} = \mathbf{SBE}_n \quad (7) $$

The **F** matrix is the Fock matrix of the closed shell electron configuration neglecting interactions associated with the two open shell electrons. The **O** matrix contains terms associated with the interactions between closed and open shell electrons, while the **N** and **M** matrices introduce the electron-repulsion terms associated with the electrons in ψ_n and ψ_m, respectively. The closed shell and total bond order charge density matrices are defined by eq 8 and 9, respectively.

$$ P_{\sigma\lambda}{}^c = 2 \sum_i^{\text{closed shell}} c_{\sigma i} c_{\lambda i} \quad (8) $$

$$ P_{\sigma\lambda}{}^T = P_{\sigma\lambda}{}^c + a_{\sigma m} a_{\lambda m} + b_{\sigma n} b_{\lambda n} \quad (9) $$

The closed shell Fock matrix, $F_{\mu\nu}$, is given by eq 10

$$ F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu}{}^c \quad (10) $$

where $H_{\mu\nu}$ is the one-electron Hamiltonian which includes the kinetic and the potential energy in the electrostatic field of the core and is given by

$$ H_{\mu\nu} = \int \chi_\mu \left[-\tfrac{1}{2}\nabla^2 - \sum_{\mathrm{A}} (Z_{\mathrm{A}}/R_{\mathrm{A}1}) \right] \chi_\nu \mathrm{d}\tau \quad (11) $$

where Z_{A} is the effective charge on the Ath nucleus. $G_{\mu\nu}{}^c$ is that portion of the closed shell Fock matrix associated with the effect of electron population on the potential due to other closed shell valence electrons and is given by

$$ G_{\mu\nu}{}^c = \sum_\sigma \sum_\lambda P_{\sigma\lambda}{}^c \{\langle\sigma\lambda|\mu\nu\rangle - \tfrac{1}{2}\langle\sigma\nu|\mu\lambda\rangle\} \quad (12) $$

where

$$ \langle\sigma\lambda|\mu\nu\rangle = \int \chi_\sigma(1)\chi_\lambda(1)(1/R_{12})\chi_\mu(2)\chi_\nu(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \quad (13) $$

The elements of the **O**, **N**, and **M** matrices are given by

$$ O_{\mu\nu} = \sum_\sigma \sum_\lambda (a_{\sigma m} a_{\lambda m} + b_{\sigma n} b_{\lambda n})\{\langle\sigma\lambda|\mu\nu\rangle - \tfrac{1}{2}\langle\sigma\nu|\mu\lambda\rangle\} \quad (14) $$

$$ N_{\mu\nu} = \sum_\sigma \sum_\lambda b_{\sigma n} b_{\lambda n}\{\langle\sigma\lambda|\mu\nu\rangle + \langle\sigma\nu|\mu\lambda\rangle\} \quad (15) $$

$$ M_{\mu\nu} = \sum_\sigma \sum_\lambda a_{\sigma m} a_{\lambda m}\{\langle\sigma\lambda|\mu\nu\rangle + \langle\sigma\nu|\mu\lambda\rangle\} \quad (16) $$

Inherent in the development of AFAOS theory is the knowledge that for polyatomic molecules, the elements of the **O**, **N**, and **M** matrices are small in magnitude relative to the remaining electron–electron repulsion matrix elements associated with the electrons occupying the closed shell orbitals. Kroto and Santry have discussed this observation in detail and have used this characteristic to justify their neglect of the off-diagonal elements associated with the $\mathbf{E}_c$, $\mathbf{E}_m$, and $\mathbf{E}_n$ matrices.[8] Accordingly, the three SCF equations can be reduced with good approximation to a single averaged field equation in which the **O**, **N**, and **M** matrices are replaced by an "averaged field" correction term, **L**

$$ (\mathbf{F} + \mathbf{L})\mathbf{C} = \mathbf{SCE} \quad (17) $$

where

$$ L_{\mu\nu} = \{(n - 2)O_{\mu\nu} + N_{\mu\nu} + M_{\mu\nu}\}/n \quad (18) $$

With respect to eq 17 and 18, the **C** matrix now contains the orbital coefficients of both the closed and open shell MO's, the **E** matrix is the eigenvalue matrix for both the closed and open shell MO's, and n is the total number of valence electrons.

The averaging of the matrix components in eq 18 might, upon initial inspection, appear arbitrarily weighted in favor of the **O** matrix resulting in an almost total distortion of the field encountered by the open shell electrons from an $n - 1$ electron potential field toward an (incorrect) n electron potential field. However, since the molecule contains more closed shell

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[14] G. A. Segal has developed a formalism for calculating SCF–LCAO–MO wave functions for open shell states which also utilizes a single determinant [*J. Chem. Phys.*, **52**, 3530 (1970)].

than open shell electrons, the optimization of the averaged field correction term in favor of the closed shell system is appropriate. Furthermore, we shall soon introduce in this section the AFAOS procedure for calculating the equilibrium geometry of the excited state. This procedure is also optimized to the closed shell system thereby reducing the error associated with the above weighting procedure.

As the number of valence electrons increases, the value of the AFAOS correction term, **L**, becomes dominated by the elements of the **O** matrix. Consequently, for large molecules, **L** can simply be set equal to **O**. Since AFAOS theory is primarily intended for calculations on large molecules (26 or more valence electrons), this simplification is appropriate. Accordingly, the averaged field Fock operator used in AFAOS formalism shall be given by eq 19. We

$$F_{\mu\nu}{}^{\mathrm{AFAOS}} = (F_{\mu\nu} + L_{\mu\nu}) = (F_{\mu\nu} + O_{\mu\nu}) \tag{19}$$

should emphasize that the use of eq 19 means that the eigenvectors and eigenvalues for the closed shell electrons will be calculated at a slightly better approximation than will the corresponding functions for the two open shell electrons. Furthermore, the accuracy of eq 19 relative to the more rigorous three equation approach is observed to improve with an increase in the number of valence electrons (n) (see section III). We attribute this observation to the increased importance of the closed shell electrons in the formation of the total charge density bond order matrix elements. Because of the importance of the closed shell electron densities in determining the SCF densities of the open shell electrons, one might expect that the use of eq 19 rather than eq 17 might also improve the quality of the open shell eigenvectors. This prediction was observed to hold for all of the larger ($n > 10$) molecules investigated in section III despite the fact that the open shell electrons are now calculated exclusively in an n, rather than an $n - 1$, electron potential.

In order to further simplify the calculations, the off-diagonal elements of the **E** matrix, which were neglected in the parent AOS method of Kroto and Santry, will also be neglected in AFAOS formalism. To partially counteract the error introduced by this approximation, and to take full advantage of the nature of the AFAOS approximation, the calculated equilibrium geometry of the excited state is determined by minimizing the excited state energy [$E_{n\leftarrow m}$ (eq 20)],

$$E_{n\leftarrow m} = {}^{1}\!/_{2} \sum_{\mu}\sum_{\nu} P_{\mu\nu}{}^{T}(H_{\mu\nu} + F_{\mu\nu}{}^{\mathrm{AFAOS}}) + \sum_{\mathrm{A}<\mathrm{B}}\sum Z_{\mathrm{A}}Z_{\mathrm{B}}/R_{\mathrm{AB}} - C_{nm} \tag{20}$$

assuming C_{nm} to be a constant. After the equilibrium geometry is theoretically determined, the contribution of C_{nm} (eq 21) is then included in calculating the energy

$$C_{nm} = {}^{1}\!/_{2}(J_{mm} + J_{nn} - J_{nm}) - K_{nm} \tag{21}$$

of the excited state. This procedure minimizes the error associated with the neglect of the off-diagonal elements by optimizing the calculation of equilibrium geometry to the SCF closed shell electron configuration. Since the closed shell system is treated more accurately than the open shell system under the AFAOS approximation, the above procedure has dual benefits within the AFAOS formalism. By optimizing both our AFAOS Fock operator and our SCF energy equation to the closed shell system, we minimize the importance of calculating the open shell electrons in an n electron potential. We have essentially constrained the open shell electron densities to conform with patterns dictated by the more accurately calculated closed shell system (see also section IV).

The use of an averaged field Fock operator coupled with the neglect of the off-diagonal elements of the eigenvalue matrix removes the orthogonality constraint between open shell and closed shell orbitals of the same symmetry. The approximate nature of the AFAOS Fock operator, however, and the use of this operator in approximate procedures such as CNDO and INDO, relegates the possible error associated with the use of a slightly deorthogonalized basis set to relative unimportance. As discussed in detail by Kroto and Santry, the extra computational difficulties associated with maintaining a totally orthogonal basis set are not warranted by the level of approximation inherent in the wave functions even for the more rigorous, three equation AOS method.[8] Even in the worst cases investigated in this paper, CO_2 (section IIIA3) and CH_3CHO (IIIB1), the resulting deviation of the eigenvectors from orthogonality is too small (scalar product <0.2) to be significant relative to other sources of error inherent in the approximations. In support of this statement, the AFAOS calculation on the first excited singlet state of CO_2 was the most successful of the small basis set calculations (see section IIIA). This observation provides some support for Kroto and Santry's supposition that the error associated with the neglect of orthogonality constraints is outweighed by the improvement in the treatment of electron repulsion.[8]

(II) Reduction to the CNDO and INDO Approximations

The AFAOS formalism is of an approximate nature and should have its most useful application when applied to approximate procedures such as the CNDO/2 and INDO–SCF methods developed by Pople and coworkers.[3–5] We shall observe in section III that the approximations inherent in CNDO and INDO theory are of a comparable magnitude to the approximations introduced by the AFAOS formalism. A sufficient number of articles on both CNDO[3,5,7,8] and INDO[4,10] procedures have been published to preclude a review here. Briefly, therefore, the CNDO/2 approximation to $\mathbf{F}^{\mathrm{AFAOS}}$ is given by eq 22 and 23, where $U_{\mu\mu}$

$$F_{\mu\mu}{}^{\mathrm{AFAOS}} = U_{\mu\mu} - 0.5(P_{\mu\mu}{}^{T})\gamma_{\mathrm{AA}} + P_{\mathrm{A}}{}^{T}\gamma_{\mathrm{AA}} + \sum_{\mathrm{B}(\neq \mathrm{A})} (P_{\mathrm{B}}{}^{T} - Z_{\mathrm{B}})\gamma_{\mathrm{AB}} \tag{22}$$

$$F_{\mu\nu}{}^{\mathrm{AFAOS}} = \beta_{\mathrm{AB}}S_{\mu\nu} - 0.5P_{\mu\nu}{}^{T}\gamma_{\mathrm{AB}} \tag{23}$$

and β_{AB} are empirical parameters given the same values as defined in ref 3b, γ_{AB} is the coulomb integral between the s orbitals on atoms A and B (eq 24), and $S_{\mu\nu}$

$$\gamma_{\mathrm{AB}} = \iint s_{\mathrm{A}}{}^{2}(1)\frac{1}{r_{12}}s_{\mathrm{B}}{}^{2}(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{24}$$

is the overlap integral between the μth and νth atomic orbitals χ_μ and χ_ν (eq 25). $P_{\mu\nu}{}^{T}$ is the total bond order

Table I. Theoretical and Experimental Excited State Geometries[a] (degrees)

Molecule	No. of valence electrons	CNDO virtual orbital[b]	CNDO–AOS[c]	CNDO–AFAOS	INDO–AFAOS	Exptl[d]
1. HCN	10		128	110	112	125
2. H_2C_2	10	135	130	134	132	120
3. HCF	12	130	129	128	126	127
4. H_2CO	12	0	15	38	37	31
5. CO_2	16	<90	110	118	120	122

[a] Bond angles for molecules 1, 2, 3, and 5; out of plane angle for molecule 4. Bond lengths have been held at experimental values (ref 15): HCN (R_{HC} = 1.14 Å, R_{CN} = 1.297), H_2C_2 (R_{HC} = 1.030, R_{CC} = 1.388), HCF (R_{HC} = 1.121, R_{CF} = 1.297), H_2CO (R_{CH} = 1.093, R_{CO} = 1.323, ∠HCH = 119°), CO_2 (R_{CO} = 1.246). [b] Reference 7. [c] Reference 8. [d] Reference 15.

$$S_{\mu\nu} = \int \chi_\mu \chi_\nu \mathrm{d}\tau \tag{25}$$

charge density matrix element as defined by eq 9, $P_{\mathrm{A}}{}^T$ is the total valence electron density on atom A (eq 26),

$$P_{\mathrm{A}}{}^T = \sum_{\mu(\mathrm{A})} P_{\mu\mu}{}^T \tag{26}$$

and Z_{A} is the total valence electron density on the neutral atom A.

The INDO approximation to $\mathbf{F}^{\mathrm{AFAOS}}$ is given by eq 27

$$F_{\mu\mu}{}^{\mathrm{AFAOS}} = U_{\mu\mu} + \sum_{\lambda}{}^{A} P_{\lambda\lambda}{}^T[\langle\mu\mu|\lambda\lambda\rangle - 0.5\langle\mu\lambda|\mu\lambda\rangle] + \sum_{\mathrm{B}(\neq\mathrm{A})}\left[\sum_{\lambda}{}^{B} P_{\lambda\lambda}{}^T - Z_{\mathrm{B}}\right]\gamma_{\mathrm{AB}} \tag{27}$$

and 28, where the symbols have the same meaning as for

$$F_{\mu\nu}{}^{\mathrm{AFAOS}} = \beta_{\mathrm{AB}} S_{\mu\nu} + 0.5 P_{\mu\nu}{}^T[3\langle\mu\nu|\mu\nu\rangle - \langle\mu\mu|\nu\nu\rangle] \tag{28}$$

the CNDO equations and the one-center integrals are defined as in ref 4. As in all CNDO and INDO calculations, neglect of overlap is assumed (eq 29).

$$\mathbf{F}^{\mathrm{AFAOS}}\mathbf{C} = \mathbf{CE} \tag{29}$$

The method of generating AFAOS wave functions is straightforward since only a single SCF equation is required. If there are n electrons, the lowest $[(n/2) - 1]$ eigenvectors form the closed shell set, and the $(n/2)$th and $[(n/2) + 1]$th eigenvectors form the set associated with the two singly occupied open shell orbitals. The energy of the excited state is calculated using eq 20 (assuming C_{nm} to be a constant), and the SCF iteration is continued until the difference in successive energies is equal to or less than a given value (10^{-6} au for the calculations reported in section III). If the iterative procedure fails to produce monotonically falling energies, the result is usually due to an oscillation between two oppositely polarized structures. This problem is consistently remedied by averaging the most recent Fock matrix with the previous Fock matrix and using this averaged matrix in the subsequent iteration.

(III) AFAOS Calculations on Excited Singlet State Molecular Parameters

As discussed in section I, the quality of the AFAOS approximations improves with increasing number of valence electrons in the molecule whose wave function is being calculated. Consequently, the most severe test of the AFAOS approximations would involve calculations on small basis set molecules. The molecules investigated in part A are sufficiently small to test the quality of the AFAOS approximations and have the advantage that their excited state geometries have been both spectroscopically determined and theoretically calculated using other molecular orbital techniques. Comparison of the AFAOS calculations with the latter calculations will prove useful in evaluating our simplified procedure. In part B, some representative calculations on some larger polyatomic molecules are reported. Although the AFAOS procedures perform well even with small basis set systems (part A), this formalism was developed primarily to permit rapid calculations on large polyatomic molecules normally out of the range of more sophisticated procedures. The calculations in part B are presented as an example of the versatility of AFAOS theory.

(A) Small Basis Set Molecules. A comparison of CNDO–AFAOS and INDO–AFAOS geometries with those calculated using the parent AOS procedures and virtual orbital techniques is present in Table I. As can be seen with reference to Table I, the AFAOS procedure calculates excited state geometries with roughly the same degree of accuracy (or inaccuracy) as the parent AOS theory. As expected, both the CNDO–AFAOS and INDO–AFAOS calculations improve in accuracy relative to the parent AOS calculations as the number of valence electrons in the molecule increases. This observation is in accord with the nature of the averaged field Fock operator which is optimized to the closed shell portion of the molecule. In all cases, the AFAOS technique performed better than the virtual orbital technique.

A comparison of calculated and observed transition energies is shown in Table II. The AFAOS method, while usually matching the performance of the AOS method, occasionally magnifies certain errors characteristic of both CNDO and INDO wave functions. Specifically, the invariance of the wave functions requires that both σ and π resonance integrals $[\beta_{\mu\nu} = 0.5(\beta_{\mathrm{A}}{}^0 + \beta_{\mathrm{B}}{}^0)S_{\mu\nu}]$ have a value determined solely by the nature of atoms A and B. Hence, there is no differentiation between σ and π electron mobility. As a result, AFAOS transition energies tend to be calculated too high for $\pi^* \leftarrow \pi$ transitions (*e.g.*, H_2C_2) and too low for $\pi^* \leftarrow n$ transitions (*e.g.*, H_2CO). This type of error could be considerably reduced by including configuration interaction in the calculation.[10] We do not suggest, however, that the increased computational effort would be an appropriate addition to the computationally reduced AFAOS formalism.

A brief discussion of specific molecular calculations follows.

(1) HCN, H_2C_2, HNO, and HCF. Reference to Tables I and II indicates that there is a significant improvement in the quality of the AFAOS calculations on 12 valence electron molecules (HNO, HCF) over those on 10 valence electron molecules (HCN, H_2C_2).

Table II. Theoretical and Experimental $S_1 \leftarrow S_0$ Transition Energies[a] (eV)

Molecule	No. of valence electrons	CNDO virtual orbital[b]	CNDO-AOS[c]	CNDO-AFAOS	INDO-AFAOS	Exptl[d]
1. HCN	10		7.87	8.88	8.46	6.47
2. H_2C_2	10	9.59	9.67	9.95	10.84	5.23
3. H_2CO	12	4.63	3.21	1.80	2.06	3.49
4. HNO[e]	12	2.41		1.73	1.65	1.63
5. HCF	12	2.66	2.54	2.42	2.31	2.14
6. CO_2	16		6.07	5.57	4.91	5.70

[a] Theoretical transition energies calculated assuming geometries of Table I for excited state singlet and geometries as given in ref 15 for ground state. [b] Reference 7. [c] Reference 8. [d] Reference 15. [e] Assuming known excited state geometry (ref 15).

Considering the poor quality of the calculations on HCN and H_2C_2, 12 valence electron molecules should be considered the lower limit molecular size for analysis by AFAOS procedures.

A comparison of charge densities for the $^1A''$ state of HCF calculated using virtual orbital AOS and AFAOS theories is shown in Table III.

Table III. Charge Density for the $^1A''$ State of HCF

Assignment	Atom	Virtual orbital[a]	CNDO-AOS[a]	CNDO-AFAOS	INDO-AFAOS
a''	F	−0.100	−0.127	−0.116	−0.122
	C	−0.900	−0.873	−0.884	−0.878
	H	0.0	0.0	0.0	0.0
a'	F	−0.172	−0.145	−0.133	−0.144
	C	−0.707	−0.737	−0.726	−0.716
	H	−0.121	−0.118	−0.141	−0.140
Core	F	−6.752	−6.822	−6.818	−6.819
	C	−2.484	−2.357	−2.377	−2.356
	H	−0.764	−0.821	−0.805	−0.825
Total charge	F	−0.024	−0.094	−0.067	−0.084
	C	−0.091	+0.033	+0.013	+0.050
	H	+0.115	+0.061	+0.054	+0.034

[a] Reference 8.

Table IV. Dipole Moment and Charge Density in the $^1A_2$ State of Formaldehyde

Assignment	Atom	Virtual orbital[a]	CNDO-AOS[a]	CNDO-AFAOS	INDO-AFAOS
$b_1(\pi^*)$	O	−0.413	−0.203	−0.221	−0.230
	C	−0.537	−0.776	−0.739	−0.726
	H	−0.025	−0.011	−0.020	−0.022
$b_2(n)$	O	−0.658	−0.761	−0.778	−0.776
	C	−0.090	−0.055	−0.018	−0.017
	H	−0.126	−0.092	−0.102	−0.104
Core	O	−4.867	−5.089	−5.085	−5.103
	C	−3.660	−3.200	−3.269	−3.229
	H	−0.735	−0.856	−0.823	−0.834
Total charge	O	+0.060	−0.053	−0.084	−0.108
	C	−0.287	−0.031	−0.026	+0.027
	H	+0.113	+0.042	+0.055	+0.040
Dipole moment,[b] D		0.81	1.04	1.61	1.59

[a] Reference 8. [b] Experimental value = 1.56 D: D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **45**, 52 (1966).

(2) H_2CO. While the ground state of formaldehyde is planar with a dipole moment of 2.34 D (ref 15), the excited singlet state is pyrimidal with an out-of-plane angle of 31° (ref 15) and a dipole moment of 1.56 D.[16] The significant decrease in dipole moment is attributed to the charge transfer characteristics of $\pi^* \leftarrow n$ transitions. Since the virtual orbital technique optimizes the electron distribution to the ground state orbital population, it is incapable of properly accounting for the electron redistribution accompanying transitions involving large transfer of charge. Both the AOS and AFAOS methods, however, optimize the wave function to the excited state electron configuration and predict a significant redistribution of core electron density accompanying excitation (see Table IV). This redistribution partially compensates for the excitation of an electron from a nonbonding orbital principally localized on oxygen to a π^* orbital principally localized on carbon and results in a larger and more accurate calculated dipole moment.

If the HCH bond angle and CO and CH bond lengths are fixed at the experimental values (footnote *a*, Table I), virtual orbital theory predicts a planar excited state,[7] AOS theory predicts a pyramidal geometry with an out-of-plane angle of 15° and a barrier of 0.0004 eV,[8] and CNDO- and INDO-AFAOS theories both predict a pyramidal geometry with an out-of-plane angle of ~37° and a barrier of 0.1 eV. While experimental values for the out-of-plane angle range from 20 to 38°, we have chosen for comparison an intermediate value of 31° favored by Herzberg.[15] The barrier to inversion has been experimentally observed to be roughly 0.04 eV.[17] If only the bond lengths are fixed at experimental values, the most stable geometry predicted by AOS theory is planar with an HCH angle of 124°. CNDO- and INDO-AFAOS theories both predict equilibrium geometries for the excited state which are strongly pyramidal with an out-of-plane angle of ~40° and an HCH angle of ~114°. (The observed HCH angle for the first excited singlet state is 119°.[15]) Figure 1 shows the trend in INDO-AFAOS excited state energy with changes in out-of-plane and HCH angles. This figure should be compared with Figure 2 of Kroto and Santry's article on AOS theory (ref 8). The differences between the geometries predicted by AOS and AFAOS theory are primarily associated with the difference in approach to the neglect of the off-diagonal elements of the orbital energy matrices. Only AFAOS theory attempts to offset this error by modifying the calculation of equilibrium geometry (see section I).

(3) CO_2. A comparison of the potential energy curves for the first excited $^1B_2$ singlet state of carbon dioxide as calculated by virtual orbital, AOS, and AFAOS theories is shown in Figure 2. The loss of orthogonality constraints associated with the neglect of the off-diagonal elements of the orbital energy matrix **E** is more serious in CO_2 than in any of the other

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(15) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, Van Nostrand, Princeton N. J., 1966.

(16) D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **45**, 52 (1966).

(17) J. B. Coon, *et al.*, *J. Mol. Spectrosc.*, **20**, 107 (1966).

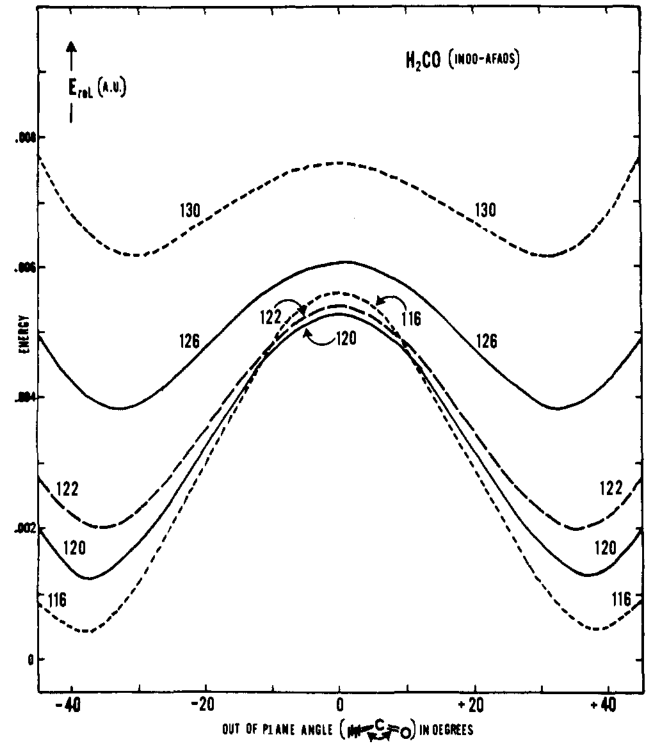

Figure 1. INDO–AFAOS potential energy curves for the first excited $^1A_2(n,\pi^*)$ singlet state of formaldehyde calculated for various angles of the HCH bond.

molecules evaluated in part A.[8] The neglect of these elements, however, does not seem to impair the quality of either the AOS or AFAOS calculations. As can be seen with reference to Tables I and II, the results for the calculation on CO_2 are better than for any of the smaller molecules. This observation suggests that the considerable reduction in computational effort associated with the loss of orthogonality constraints is justified and does not lead to significant error.

The charge densities for the $^1B_2$ state of CO_2 calculated using virtual orbital AOS and AFAOS theories are shown in Table V.

Table V. Charge Density for the $^1B_2$ State of Carbon Dioxide

Assignment	Atom	Virtual orbital[a]	CNDO–AOS[a]	CNDO–AFAOS	INDO–AFAOS
a_1	O	−0.268	−0.278	−0.278	−0.253
	C	−0.464	−0.445	−0.445	−0.495
b_2	O	−0.500	−0.489	−0.494	−0.495
	C	0.0	−0.023	−0.012	−0.010
Core	O	−5.219	−5.431	−5.349	−5.403
	C	−3.563	−3.137	−3.302	−3.194
Total charge	O	+0.013	−0.198	−0.120	−0.151
	C	−0.027	+0.395	+0.241	+0.301

[a] Reference 8.

B. Large Basis Set Molecules. Since AFAOS formalism was developed as an economical and reasonably accurate procedure for obtaining open shell wave functions for polyatomic systems, some examples of large basis set calculations are presented in this section. The following examples were chosen to illustrate the versatility of AFAOS theory, but before we investigate these specific molecular calculations we should mention why no transition energy calculations are presented.

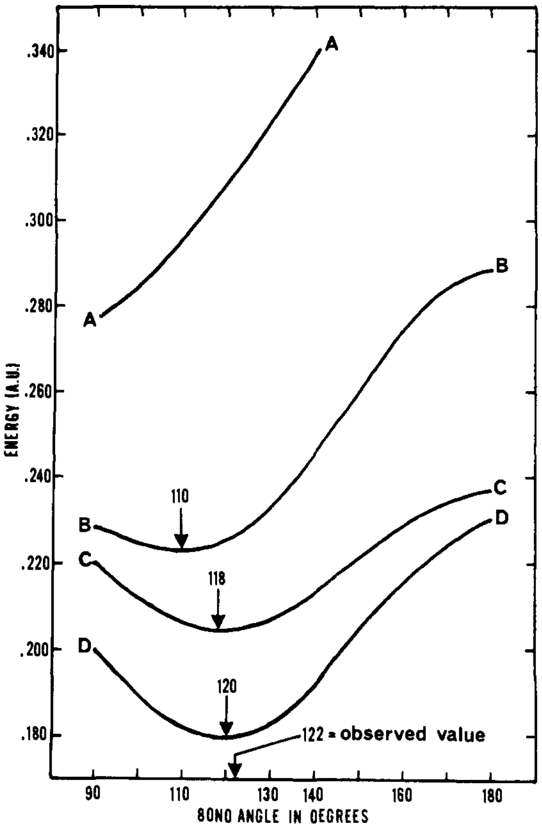

Figure 2. Potential energy curves for the first excited $^1B_2$ singlet state of carbon dioxide as calculated by virtual orbital (A), CNDO–AOS (B), CNDO–AFAOS (C), and INDO–AFAOS (D) theories.

While AFAOS theory provides reliable information on excited state geometries and electron distributions [provided significant state mixing is not present (see IIIB3)], it is unreliable for the calculation of transition energies. As mentioned in section IIIA, AFAOS formalism magnifies errors inherent in the CNDO and INDO procedures in that $\pi^* \leftarrow n$ and $\pi^* \leftarrow \sigma$ transition energies are calculated to be smaller than observed, while $\pi^* \leftarrow \pi$ transition energies are calculated to be considerably larger than observed. This situation is only marginally improved for large basis set calculations. Accordingly, we do not suggest that AFAOS theory be used for calculating transition energies unless one is interested in calculating relative differences among transition energies for a chromophorically homologous series of molecules.

(1) Vibrational Activity in the Electronic Spectrum of Acetaldehyde. For the purposes of this discussion, the "activity" of a given vibration in an electronic spectrum shall be defined as proportional to the progressional development of that vibration in the vibronic band system. Accordingly, our use of the term "vibrational activity" is directly related to the Franck–Condon activity associated with a given vibrational mode. If we restrict our analysis to only those vibronic transitions which are symmetry allowed, then the calculation of *relative* vibrational activity reduces to the analysis of the theoretically predicted changes in geometry upon excitation.

Although AFAOS theory is far too approximate to warrant its use as the source of geometrical data for a complete Franck–Condon analysis, it can often provide sufficiently accurate structural information to permit qualitative prediction of vibrational activity. For example, if the A–B bond length is calculated to significantly increase on excitation relative to other bond lengths, we would predict that the A–B stretching vibration would exhibit strong activity in the electronic spectrum. A similar relationship is expected for calculated changes in the in-plane and out-of-plane bond angles and the vibronic activity of their corresponding bending modes (provided those modes are symmetry allowed). If the excitation-induced change in the equilibrium geometry is small, and the fundamental vibrations in both ground and excited states can be described in terms of relatively pure, isolated group frequencies (minimal mixing of coordinates), then the above procedure will usually lead to meaningful, vibrational activity predictions. Alternatively, should the calculations predict significant changes in geometry upon excitation, vibronic activity can usually be assumed for those vibrations whose coordinates are reflected in the nuclear motion required to relax from the Franck–Condon to the equilibrium excited state geometry. Unfortunately, the intermediate cases represent the bulk of the observed situations, and these are the most difficult to analyze using the above, simplified assumptions. The following example describes the use of the above procedure to analyze vibrational activity in a molecule whose geometry is predicted to markedly change on excitation.

Acetaldehyde is planar in the ground state, but INDO–AFAOS theory predicts the first excited (n,π^*) singlet state to be nonplanar with an out-of-plane angle of approximately 25°. The calculated energy of the excited state is very sensitive to changes in the $\angle$CCO and out-of-plane bond angles in a fashion similar to that calculated for the $\angle$HCH and out-of-plane bond angles in formaldehyde (Figure 1). Accordingly, a significant vibrational coupling between the molecular out-of-plane deformation and $\angle$CCO bending is to be expected in the electronic spectrum, and these two fundamentals should exhibit strong, and relatively equal, vibrational activity.

The largest calculated excitation-induced change in bond length involves lengthening of the carbonyl bond (~0.1 Å), and, therefore, the carbonyl stretching vibration should exhibit strong vibrational activity.

Finally, the barrier to methyl rotation is calculated to slightly increase upon excitation, but the change is relatively small and little, if any, vibrational activity is predicted for the methyl torsion.

A recent analysis of the vibrational-electronic spectrum of acetaldehyde by the author indicated that only three excited state fundamentals [the carbonyl stretching ($\nu_4' = 1127$ cm^{-1}), the out-of-plane deformation (see next paragraph; $\nu_{14}' = 450$ cm^{-1}), and the methyl torsion ($\nu_{15}' = 191$ cm^{-1})] and one ground state fundamental ($\nu_{15}'' = 143$ cm^{-1}) are active in the formation of the low resolution vibronic band system.[18] The out-of-plane deformation vibration exhibits the strongest progressional activity and provides strong evidence for a nonplanar excited state. Furthermore, the fact that no inversion doubling is observed in the low resolution spectrum suggests that the barrier to inversion is high and that the out-of-plane angle is greater than 20°.[18,19] Both the carbonyl stretching and methyl torsion vibrations show considerable, and relatively equal, vibronic activity, the activity of the methyl torsion being considerably higher than predicted. This latter discrepancy might be due to the predictable failure of CNDO and INDO procedures to adequately predict barriers to internal rotation or might result from strong mixing of the torsional vibration with the out-of-plane deformation.

The absence of the $\angle$CCO bending vibration in the vibronic spectrum is surprising and might indicate, as our calculations suggest, that the ν_{14}' fundamental is a very "impure" vibration comprising a mixture of the two coordinates associated with the $\angle$CCO and out-of-plane bending motions.

(2) The Excited State Geometry of Propynal. The strength of a given bond is theoretically proportional to the calculated bond population given by the product of the bond order ($P_{\mu\nu}$) and the overlap ($S_{\mu\nu}$). The changes in bond populations calculated between ground and excited state electron configurations can therefore be related to the direction and magnitude of changes in bond length observed upon excitation. Such a comparison for the ground and first excited n,π^* singlet states of propynal is shown in Table VI.

Table VI. Changes in Bond Populations and Bond Lengths on Excitation for the $S_1(n,\pi^*) \leftarrow S_0$ Transition in Propynal[a,b] [$H_6C_4{\equiv}C_3C_2H_5O_1$]

Bond	Change in bond length on excitation,[a] Å	Change in bond population on excitation[b]
$C_2{=}O_1$	+0.110	+0.062
$C_3{-}C_2$	−0.081	−0.011
$C_4{\equiv}C_3$	+0.029	+0.027
$C_2{-}H_5$	−0.015	+0.037
$C_4{-}H_6$	+0.020	+0.001

[a] Bond length changes were taken from the data of D. R. Williams [*J. Chem. Phys.*, **55**, 4578 (1971)] which were derived from the spectroscopic analyses of J. C. D. Brand, *et al.*[20] [b] Bond population changes were calculated as follows:

change in bond population on excitation =

$$\sum_{\mu(A)} \sum_{\nu(B)} S_{\mu\nu}''P_{\mu\nu}''(\text{INDO}) - \sum_{\mu(A)} \sum_{\nu(B)} S_{\mu\nu}'P_{\mu\nu}'(\text{INDO–AFAOS})$$

where ('') indicates ground state, (') indicates excited state, and the equation applies to the change in bond population between atoms A and B. The ground state nuclear configuration was assumed for both the INDO and INDO–AFAOS calculations.

For all but one bond, the calculations qualitatively correlate with the changes in bond length predicted using Badger and Clark's force constant relationships.[20] In the case of the formyl CH bond, however, the INDO–AFAOS calculations indicate a lengthening of the bond on excitation, which is contrary to the decrease predicted using force constant relationships. This observation is significant in light of Lin and Moule's analysis of the n,π^* triplet state geometry of propynal

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(18) R. R. Birge, results to be published.

(19) (a) HCOF, which is isoelectronic with CH_3CHO, also exhibits no inversion doubling, and Giddings and Innes fix the out-of-plane angle in the excited state of HCOF to be greater than 20° based on the absence of inversion doubling.[19b] Identical arguments can be used to fix the same lower limit for the out-of-plane angle in the n,π^* state of acetaldehyde. (b) L. E. Giddings, Jr., and K. Keith Innes, *J. Mol. Spectrosc.*, **6**, 528 (1961).

(20) J. C. D. Brand, J. H. Calloman, and J. K. G. Watson, *Discuss. Faraday Soc.*, **35**, 175 (1963).

based on a more reliable Franck–Condon calculation.[21] These authors calculated an increase in the formyl CH bond upon excitation. Considering the observed and expected similarities in the geometries predicted for the singlet and triplet states of propynal,[20,21] this one discrepancy is surprising and may indicate a failure in the force constant calculation. Such failures (albeit infrequent) can be rationalized in terms of strong mixing of the coordinates associated with a second vibrational mode with the coordinates of the vibration whose frequency is being utilized in the force constant calculation.

(3) **Singlet–Triplet Mixing in Benzophenone.** The dipole moments of benzophenone in the lowest n,π^* singlet and triplet states have been spectroscopically determined by Hochstrasser and Noe to be 1.46 and 1.79 D, respectively[22] (the ground state dipole moment of benzophenone is 2.98 D).[23] The dipole moments for the corresponding three states in formaldehyde have also been determined,[15,16,24] and the observed dipole moments for the two molecules are compared in Table VII to calculated values based on INDO procedures. As can be seen with reference to Table VII, the trend in calculated values for both formaldehyde and benzophenone following the pattern $S_0 > S_1 > T_1$. While the observed dipole moments for formaldehyde follow this pattern, the observed values for benzophenone show the triplet n,π^* state dipole moment to be larger than that found for the singlet n,π^* state. Hochstrasser and Noe attribute the increased dipole moment in $T_1(n,\pi^*)$ relative to $S_1(n,\pi^*)$ to be due to mixing of higher excited states into T_1. The INDO–AFAOS calculations support this hypothesis for the following reasons.

Table VII. Calculated and Observed Values for the Dipole Moments[a] for the S_0, $S_1(n,\pi^*)$, and $T_1(n,\pi^*)$ States of Benzophenone and Formaldehyde

	Benzophenone		Formaldehyde	
State	Calcd[b]	Obsd	Calcd[b]	Obsd
S_0	2.96	2.98[c]	1.94	2.34[e]
$S_1(n,\pi^*)$	1.78	1.46[d]	1.59	1.56[f]
$T_1(n,\pi^*)$	1.07	1.79[d]	1.35	1.29[g]
$\Delta\mu(S_1 - T_1)$[h]	+0.71	−0.33	+0.24	+0.27

[a] All dipole moments are given in Debye units. [b] Ground state dipole moments were calculated using closed shell INDO procedures (ref 4), excited state singlet dipole moments were calculated using INDO–AFAOS procedures, and excited state triplet dipole moments were calculated using INDO unrestricted open shell procedures (ref 4). [c] Reference 23. [d] Reference 22. [e] Reference 15. [f] Reference 16. [g] Reference 24. [h] Difference between excited state singlet and excited state triplet dipole moments.

The calculated values for the S_1 and T_1 dipole moments of formaldehyde follow observation with almost quantitative precision. Since the calculations on both formaldehyde and benzophenone correctly predict the lowest S_1 and T_1 states to be of n,π^* orbital nature, the differential between observed and calculated dipole moments for S_1 and T_1 in benzophenone cannot be attributed to an incorrect calculated orbital occupation. Accordingly, the calculated discrepancy is most likely due to the misrepresentation of the triplet excited state resulting from the neglect of configuration interaction and spin-orbit coupling. Based on simple one-electron singlet–triplet mixing theory, the most likely spin-orbit coupling interaction would involve mixing of $S_2(\pi,\pi^*)$ into T_1, because the two states differ in orbital occupancy by only one electron and the energy differential between these two states is small.[11] Since the π,π^* singlet is predicted to have a dipole moment similar to the ground state ($\pi^* \leftarrow \pi$ transitions exhibit relatively little charge transfer character), the mixing of $S_2(\pi,\pi^*)$ into $T_1(n,\pi^*)$ would increase the dipole moment of the triplet state. The large T_1 dipole moment could also result from configuration interaction between $T_2(\pi,\pi^*)$ and $T_1(n,\pi^*)$ (note that the out-of-plane rotation of the phenyl groups would permit these configurations to interact).

(IV) Comments and Conclusions

Averaged field approximate open shell (AFAOS) theory is a computationally reduced version of Kroto and Santry's approximate open shell (AOS) theory and is primarily intended for use on large basis set molecules. While AFAOS theory provides reliable information on excited state geometries and electron distributions, it is unreliable for the calculation of transition energies. The principal features of AFAOS theory are: (1) the use of an averaged field Fock operator optimized to the closed shell system (serving to reduce the three coupled SCF equations used in AOS theory to a single AFAOS-SCF equation); (2) the neglect of the off-diagonal elements of the eigenvalue matrix (resulting in a slightly deorthogonalized basis set); and (3) the optimization of the calculation of excited state equilibrium geometry to the closed shell system. As a consequence of features 1 and 3, the quality of the AFAOS approximation improves with an increase in the number of valence electrons in the molecule whose wave function is being calculated.

The approximations inherent in AFAOS theory are partially self-compensating. For example, the error associated with the use of an averaged field Fock operator (an error which misrepresents the field encountered by the open shell electrons) is partially compensated by feature 3 above. Nevertheless, the magnitude of the AFAOS approximations restricts the use of this procedure to approximate, semiempirical SCF schemes such as CNDO and INDO.

The AFAOS Fock operator is optimized to the closed shell system on the assumption that a sufficient number of closed shell orbitals will effectively buffer the error associated with the misrepresented open shell system. For example, if a molecule whose wave function is to be calculated contains 12 valence electrons [the lower limit suggested for AFAOS calculations (see section IIIA1)], and the correct field for the open shell ψ_a orbital is represented as $\psi_a(1)\psi_b(1)\psi_c^2(10)$, the AFAOS field for the ψ_a orbital is misrepresented as $\psi_a^2(1)$-$\psi_b(1)\psi_c^2(10)$. If the closed shell orbitals were frozen during AOS- or AFAOS-SCF iteration, the magnitude of the difference in the AFAOS ψ_a eigenvector field relative to the more correct AOS representation would

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(21) C. T. Lin and D. C. Moule, *J. Mol. Spectrosc.*, **38**, 136 (1971).

(22) R. M. Hochstrasser and L. J. Noe, *ibid.*, **38**, 175 (1971).

(23) P. H. Gore, J. A. Hosteins, R. J. W. LeFevre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. B*, 741 (1967).

(24) A. D. Buckingham, D. A. Ramsey, and J. Tyrell, *Can. J. Phys.*, **48**, 1242 (1970).

Table VIII. CNDO Open Shell Orbital Coefficients for the First Excited ${}^1A_2(n,\pi^*)$ Singlet State of Formaldehyde[a]

Atom	Orbital	$b_2(n)$			$b_1(\pi^*)$		
		AOS[b]	AFAOS[c]	Virtual orbital[d]	AOS[b]	AFAOS[c]	Virtual orbital[d]
O	2s	0.0	0.0	0.0	0.010	0.010	0.005
	$2p_x$	0.0	0.0	0.0	−0.081	−0.084	−0.123
	$2p_y$	−0.872	−0.883	−0.817	0.0	0.0	0.0
	$2p_z$	0.0	0.0	0.0	0.443	0.458	0.629
C	2s	0.0	0.0	0.0	−0.131	−0.131	−0.139
	$2p_x$	0.0	0.0	0.0	0.160	0.160	0.111
	$2p_y$	0.235	0.129	0.291	0.0	0.0	0.0
	$2p_z$	0.0	0.0	0.0	−0.856	−0.853	−0.735
H_1	1s	−0.303	−0.320	−0.352	0.105	0.079	0.093
H_2	1s	0.303	0.320	0.352	0.105	0.079	0.093
Percentage difference from AOS[e]		0.0	15.1	20.9	0.0	7.3	43.5

[a] The molecular coordinates were identical for each calculation: R_{CO} = 1.323 Å, R_{CH} = 1.093 Å, ∠HCH = 119°, δ (out of plane angle) = 15°. The x axis is parallel to the carbonyl bond; the z axis is perpendicular to the plane formed by the carbon and hydrogen atoms. [b] CNDO–approximate open shell theory (ref 8). [c] CNDO–averaged field approximate open shell theory. [d] CNDO–virtual orbital theory (ref 7). [e] Percentage difference of eigenvectors from AOS eigenvectors as calculated using the formula $100[\Sigma_\mu|(a_\mu - a_\mu^{AOS})|]$ where a_μ is the μth atomic orbital coefficient.

be roughly 15%.[25] Correspondingly, if the molecule contained 26 valence electrons, the error would be reduced to roughly 5%.[25]

However, the closed shell orbitals are not frozen during AFAOS–SCF iterative convergence, and it is imperative that the averaged field procedure prevent the misrepresented open shell field from "contaminating" the eigenvector set associated with the closed shell electrons. AFAOS procedures minimize such "contamination" by setting the AFAOS Fock correction term, **L**, equal to **O** rather than to $[(n-2)\mathbf{O} + \mathbf{N} + \mathbf{M}]/n$, thereby assuring that (1) the closed shell system is treated as correctly as possible (see section I), and (2) the open shell electrons, while influencing the closed shell electron density patterns, are themselves constrained to realistic density patterns (subject to sufficient closed shell orbital buffering[26]).

It should be noted that this apparent preoccupation with the quality of the closed shell field does not introduce errors in the open shell eigenvectors of a comparable magnitude as observed in virtual orbital theory. Although AFAOS open shell orbital coefficients are consistently less accurate than the corresponding functions for the closed shell orbitals, as we have shown in section III, the open shell coefficients are always more accurate than those calculated using virtual orbital theory. In virtual orbital theory, the molecular orbitals are optimized to the ground state electron configuration and any electron redistribution accompanying excitation is totally ignored. In AFAOS theory, on the other hand, the closed shell orbitals are optimized to the correct excited state electron configuration while the open shell orbitals are superficially optimized toward an incorrect electron configuration corresponding to two different states of a negative ion. Through a combination of open shell orbital constrainment and closed shell orbital buffering inherent in the use of eq 19 and 20, the open shell orbitals are influenced away from the unrealistic negative ion configuration and toward the correct $n - 1$ electron configuration. In short, even though the open shell electrons are placed into an incorrect field, the domination of the closed shell orbitals on the resultant total self-consistent field is sufficient to force the open shell electrons into realistic density patterns.

We shall include one final example to demonstrate the efficacy of this approximation. A comparison of the CNDO open shell orbital coefficients as calculated for the first excited singlet state of formaldehyde using AOS, AFAOS, and virtual orbital theories is presented in Table VIII. The molecular dimensions were identical for each calculation (R_{CO} = 1.323 Å, R_{CH} = 1.093 Å, ∠HCH = 119°, δ = 15°) so that the difference in eigenvectors could be directly related to the method of generating the wave functions. The AFAOS orbital coefficients are clearly more accurate than those calculated using virtual orbital theory.[27] Furthermore, judging from the dipole moments calculated for the AFAOS and AOS excited state electron distributions, the AFAOS electron densities may be physically more realistic than those calculated using AOS theory (see Table IV). Since the computational times and complexities are virtually identical for AFAOS and virtual orbital calculations, it seems apparent that the continued use of virtual orbital theory for the calculation of first excited singlet state properties can no longer be justified solely for reasons of computational speed or simplicity.

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(25) The percentage errors given are approximate since the observed errors will be a function of the nature of the ψ_a orbital (principally its degree of polarity) and will therefore differ for various molecular calculations.

(26) The calculations reported in Section III suggest that molecules containing less than 12 valence electrons do not provide sufficient closed shell orbital buffering and that AFAOS wave functions calculated for such molecules are usually unreliable.

(27) Formaldehyde contains 12 valence electrons which is the lower limit basis set size suggested for AFAOS calculations. Consequently, the formaldehyde calculation provides an appropriate test of AFAOS procedures. In contrast to the differences between AFAOS and AOS eigenvectors calculated for formaldehyde, AFAOS open shell eigenvectors calculated for benzophenone (68 valence electrons) correspond to three significant figures with those calculated using AOS procedures (for identical molecular geometries). The computational time for the AFAOS calculation, however, was roughly one-third that required for the AOS calculation.