

The iterative hole-particle method for excited states calculation: Application to tetratomic thiocarbonyls

MANAS BANERJEE* and ASIT KUMAR CHANDRA

Department of Chemistry, University of Burdwan, Burdwan 713 104, India

Abstract. The single configuration SCF calculation for excited states is proposed for the various differently optimized excited states. Different sets of occupied and unoccupied one-electron orbitals are obtained for the different excited states. Morokuma's model is extended to a semiempirical CNDO basis. The method predicts excited state geometry quite well. Qualitative agreement in the calculated transition energies, singlet-triplet splitting and barrier to inversion has been found and the results indicate no major deviation in the trends followed in similar non-iterative simple hole-potential calculation. As expected, convergence could not be achieved in all $^1\pi\pi^*$ calculations in the non-planar geometry. Calculations in the planar geometry, however, showed convergence with difficulty. One interesting feature is a gradual decrease in the energy difference between $^3n\pi^*$ and $^3\pi\pi^*$ states with successive fluorine substitution, ultimately leading to an inversion in the order in F_2CS . The prediction of $^3\pi\pi^*$ as the T_1 state in F_2CS is discussed in the context of photochemistry exhibited by certain aromatic carbonyl compounds. Probable extension of the present model to develop an average Fock operator for single excitations and also a one-electron operator for double excitations is proposed.

Keywords. Iterative hole-particle method; excited states calculation; tetratomic thiocarbonyls; singlet-triplet splitting.

1. Introduction

Features of molecular excited states can be explored rather satisfactorily in terms of single configuration (open shell) wavefunction (Roothaan 1960; Hunt and Goddard 1969). One-electron orbitals coming out from such open-shell Hartree Fock (HF) calculations are much superior to the usual ground state orbitals in giving the more correct CI expansion to the excited state wavefunction for which the open-shell single determinant serves as the reference configuration (Peyerimhoff and Buenker 1975). The V_{N-1} potential model, also referred to as the hole-potential model (HPM), provides one such means of describing the singly excited state (Huzinaga and Arnau 1970, 1971). Through a modification of only the HF virtual orbitals in the HPM, a considerable gain has been achieved in geometry, charge distribution, and transition energy of the singly excited states. This has been evident from earlier studies on the $^{1,3}n\pi^*$ and $^{1,3}\pi\pi^*$ states of some tetra-atomic thiocarbonyls (Banerjee and Bhattacharyya 1980, 1983). In an extended HF theory for excited states (Morokuma and Iwata 1972) some deficiency in the HPM theory was overcome to a great extent. The deficiency lies in the fact that the HPM theory allows a mixing among the virtual orbitals only and the 'occupied' subspace is

*To whom all correspondence should be addressed.

projected out unchanged. This model does not consider reorganization of the occupied or 'hole' orbitals under the influence of the excited electron. In the method of Morokuma and Iwata (1972) a further degree of freedom is added in which orbital reorganization is allowed within both the intraoccupied and intravirtual manifolds through a constrained variational minimization of the total electronic energy of the excited configuration. The 'hole' orbitals undergo reorganization under the influence of the excited electron in just the same way as the 'particle' orbitals are reorganized by the hole created in the occupied manifold. A convenient name for this method may be hole-particle potential model (HPPM). In actual computation this is achieved through the iterative SCF procedure. We perform the calculation with CNDO/2 formulation of the resulting LCAO-MO-SCF equation, employing only a valence AO basis set which is characteristic of such formulation. Use of a more extensive basis set would improve the results by giving more variational freedom to the orbitals.

One disadvantage of the HPPM theory stems from the fact that other configurations constructed from the optimized orbitals corresponding to a particular excited state are not optimized. Again the differently (singly excited) optimized configurations are not strictly orthogonal. In this situation one usually thinks in terms of an average Fock operator. We indicate the possibility of formulating such an operator, but in the present work we prefer to stick to the simple HPPM.

2. Theory

Let us partition the total space spanned by the closed-shell HF orbitals $\{\phi_i\}$ into two subspaces A and B which, for the present, represent the occupied and virtual manifolds respectively. We now define the Hermitian operator

$$V = \sum_{kl}^A a_{kl} |\phi_k\rangle \langle \phi_l| + \sum_{rs}^B b_{rs} |\phi_r\rangle \langle \phi_s| = V_2 + V_1, \quad (1)$$

where the numbers a_{kl} and b_{rs} constitute Hermitian matrices. It is obvious that

$$V|\phi_i\rangle = \sum_k^A a_{ki} |\phi_k\rangle = \psi_i, \quad \text{for } i \in A, \quad (2a)$$

$$V|\phi_m\rangle = \sum_r^B b_{rm} |\phi_r\rangle = \psi_m, \quad \text{for } m \in B. \quad (2b)$$

Equations (2) bring about intra- A space and intra- B space mixing. The quantities a_{ki} and b_{rm} may be chosen as matrix elements of the Hermitian operators Ω_2 and Ω_1 on the subspaces A and B , respectively, where such operators may be assumed with a certain degree of arbitrariness. If we assume the particular choice of $\Omega_{1\alpha}$ and $\Omega_{2\mu}$ and the subspace projection operators P_A and P_B are defined in terms of the Hartree Fock MO $\{\phi_i\}$ so that

$$P_A = \sum_k^A |\phi_k\rangle \langle \phi_k|, \quad (3)$$

(1) can be expressed as

$$V = P_A^\dagger \Omega_{2\mu} P_A + P_B^\dagger \Omega_{1\alpha} P_B. \quad (4)$$

In view of formulating singlet or triplet excited states arising out of the singly excited configuration alone, we make the following choices:

$$\begin{aligned} \Omega_{1\alpha} &= a_1 J_\alpha + b_1 K_\alpha, \\ \Omega_{2\mu} &= a_2 J_\mu + b_2 K_\mu, \end{aligned} \quad (5)$$

where for the triplet

$$a_1 = -1, b_1 = 0, a_2 = 1, b_2 = 0$$

and for the singlet

$$a_1 = -1, b_1 = 2, a_2 = 1, b_2 = -2. \quad (6)$$

Such ground and excited state wavefunctions are represented by the usual normalized determinantal functions

$$\Psi_0 = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \dots \phi_N \bar{\phi}_N|, \quad (7a)$$

and ${}^{1,3}\Psi_{(\alpha \rightarrow \mu)} = |\psi_1 \bar{\psi}_1 \dots \frac{1}{\sqrt{2}} (\psi_\alpha \bar{\psi}_\mu \mp \bar{\psi}_\alpha \psi_\mu) \dots \psi_N \bar{\psi}_N|.$ (7b)

Here $\{\psi_i\}$ are the new orbitals appropriate to the excited state configuration. If instead of (7b) one writes the configuration

$${}^{1,3}\Psi_{(\alpha \rightarrow \mu)} = |\phi_1 \bar{\phi}_1 \phi_2 \dots \frac{1}{\sqrt{2}} (\phi_\alpha \bar{\psi}_\mu \mp \bar{\phi}_\alpha \psi_\mu) \dots \phi_N \bar{\phi}_N|,$$

where ψ_μ is some modified upper orbital which can be obtained by a unitary mixing of the HF orbitals $\{\phi_B\}$, then one can readily write the energy expression as (Roothaan 1951)

$${}^{1,3}E = E_0 + \langle \psi_\mu | F | \psi_\mu \rangle - \langle \phi_\alpha | F | \phi_\alpha \rangle + (-J_{\alpha\mu} + K_{\alpha\mu} \pm K_{\alpha\mu}). \quad (8)$$

Variational minimization of (8) with respect to the expansion coefficients of ψ_μ leads to a one-electron equation described by the operator

$$F^b = F + P_B^\dagger \Omega_{1\alpha} P_B = F + V_1. \quad (9)$$

In (9) the projector P_B is added to ensure no mixing with A -space orbitals. This follows from the situation when $a_{kl} = 0$ for all $k, l \in A$ in the potential V of (1). Obviously, the A -space orbitals are directly eigenfunctions of F^b , but the B -space functions are not. The present situation produces the HPM theory. Similarly, the operator

$$F^a = F + P_A^\dagger \Omega_{2\mu} P_A = F + V_2, \quad (10)$$

generates modified 'hole' orbitals as eigenfunctions, but the B -space orbitals are directly eigenfunctions to it. This emerges from $b_{rs} = 0$ for all $r, s \in B$. Now, a variational minimization of the energy expression, corresponding to the configuration mentioned in (7b), generates the one-electron equations,

$$F' \psi_i = \lambda_i \psi_i,$$

where $F' = F + P_B^\dagger \Omega_{1\alpha} P_B + P_A^\dagger \Omega_{2\mu} P_A = F + V_1 + V_2.$ (11)

The entire eigenspectrum of F' contains 'new' orbitals which consider electron reorganization in both subspaces A and B in the excited state. Using the AO basis set $\{\chi_p\}$ representation of (11),

$$F' C_i = \lambda_i S C_i. \quad (12)$$

Defining $R = C C^\dagger$ and noting that $R^\dagger S R = R$ and $C^\dagger S C = I$ we can express

$$F' = F + V_1 - S R V_1 - V_1 R S + S R V_1 R S + S R V_2 R S, \quad (13)$$

where $V_1 = X^\dagger \Omega_{1\alpha} X$ and $V_2 = X^\dagger \Omega_{2\mu} X$.

Under CNDO approximations the overlap is neglected in normalization. Thus, $S = I$ and $R \equiv P$ which is the matrix representation of projector P_A in the orthonormalized basis. Equation (13) is simplified to

$$F' = F + (I - P) V_1 (I - P) + P V_2 P. \quad (14)$$

Simplification from CNDO entails

$$(V_1)_{pq} = a_1 \sum_r c_{r\alpha}^2 g_{pr} \delta_{pq} + b_1 c_{p\alpha} c_{q\alpha} g_{pq},$$

$$(V_2)_{pq} = a_2 \sum_r c_{r\mu}^2 g_{pr} \delta_{pq} + b_2 c_{p\mu} c_{q\mu} g_{pq}.$$

It should be noted that the two operators $\Omega_{1\alpha}$ and $\Omega_{2\mu}$ have a mutual interdependence and that (12) and (14) must be solved iteratively. At convergence the excited state energy is calculated as

$$E = E_0 + \lambda_\mu - \lambda_\alpha - a_1 J_{\alpha\mu} + b_1 K_{\alpha\mu}. \quad (15)$$

With the objective of removing the nonorthogonality problem in the HPPM theory it is convenient to formulate the average Fock operator

$$F' = F + P_B^\dagger (\Omega_{1\alpha} + \Omega_{1\beta}) P_B + P_A^\dagger (\Omega_{2\mu} + \Omega_{2\nu}) P_A + \sum_{\alpha}^{n_A} f_{\alpha} [P_B^\dagger (J_{\alpha} - K_{\alpha} \mp K_{\alpha}) P_B], \quad (16)$$

where f_{α} and f_{μ} are orbital weight parameters.

In quite a similar manner the Fock operator corresponding to the doubly excited configuration $\Psi_{(\alpha\beta \rightarrow \mu\nu)}$ can be formulated as

$$F' = F + P_B^\dagger (\Omega_{1\alpha} + \Omega_{1\beta}) P_B + P_A^\dagger (\Omega_{2\mu} + \Omega_{2\nu}) P_A. \quad (17)$$

Our present work concerns singly excited configurations only and (11) and (14) are employed in computing excited states of the thiocarbonyls.

3. Results and discussion

We present the results of our calculation and the related discussion about the chosen thiocarbonyl molecules under three headings. Firstly, we discuss the salient features of techniques employed in computation, difficulties encountered and their origin are given some rationale in terms of known information. Secondly, we present our results of molecular excited state conformation together with a comparison with the HPM results and the available experimental values. Since the

molecules H_2CS , HFCS and F_2CS have already been studied in the context of HPM theory, it is pertinent to consider the same ones in order to judge the merit of the present HPPM theory. Thirdly, electronic transition energies and relative ordering of the low lying $n\pi^*$ and $\pi\pi^*$ states are investigated.

3.1 Computational approach

As it is apparent that the quantities a_{kl} and b_{rs} in (1) represent coupling between orbitals belonging to different subspaces, it is expected that eigenvalues from operator F' in (11) includes a double correction in considering the interaction between orbitals ψ_α and ψ_μ . Hence the need for the correction made in (15). While not giving the eigenvalues from (14) the same significance as orbital energies in the Koopman's sense, it is found that the modified upper orbital eigenvalues λ_μ are lower in magnitude than λ_α , the corresponding eigenvalues of the lower orbitals in a particular excited state. This situation requires a constant level shifting up (Saunders and Hillier 1973) of the upper orbitals during the iteration and after each diagonalization the shift amount is subtracted from all the transformed upper orbital eigenvalues. This resulted in a smooth convergence in most cases due to prevention of the undesirable inter-subspace orbital swapping.

In cases of substantial orbital reorganization in either or both subspaces there occurs intra-subspace orbital swapping during the iteration. As for example, the n -orbital may be the HOMO and the immediately underlying orbital may be a π , whereas LUMO is a π^* in the ground state wavefunction of some carbonyl compound. To start with, the $n\pi^*$ excitation is from HOMO to LUMO. After some iterations the n -orbital may go down below the π orbital which then becomes the 'HOMO'. In order to keep the correct configuration for the excited state throughout the entire calculation, arrangement must be done to identify the appropriate ψ_α and ψ_μ before each iteration. Since the symmetry of each MO is uniquely defined under the molecular point group, an account of the symmetry of all the MO belonging to both subspaces are stored in the memory in the form of character string arrays. At the beginning of each iteration particular orbital pairs are located by their symmetry by comparison of such arrays. In table 1 we present a SCF convergence profile for the ${}^3A''(n\pi^*)$ state of F_2CS molecule at a near equilibrium (40° bent out of plane) geometry. In the beginning, the n -orbital was 12th in the usual ordering, but at convergence it became the 11th, while the

Table 1. Convergence profile for the ${}^3A''(n\pi^*)$ state of the F_2CS molecule in a 40° bent out-of-plane geometry.

Iteration number	Electronic energy (a.u.)	$(\lambda_\mu - \lambda_\alpha)$	$J_{n\pi^*}$	$K_{n\pi^*}$
1	-73.0031988	-0.2404079	0.3727068	0.0003076
2	-73.0155678	-0.2530753	0.3730054	0.0002899
3	-73.0157237	-0.2533755	0.3731497	0.0002893
4	-73.0158648	-0.2535198	0.3731528	0.0002891
5	-73.0158665	-0.2535230	0.3731543	0.0002891
6	-73.0158679	-0.2535245	0.3731543	0.0002891
7	-73.0158680	-0.2535245	0.3731543	0.0002891

π -orbital became 12th in position. The lowest π^* orbital, however, retained its position unaltered as the 13th.

In all our calculations the singlet multiplicity state has always been found to be energetically higher than the corresponding triplet counterpart arising from a similar orbital configuration, except for the $n\pi^*$ states in the planar geometry. This unfortunate situation arises due to the neglect of all one centre exchange integrals in the CNDO approximation. The singlet-triplet degeneracy in the planar geometry occurs due to vanishing of the $K_{n\pi^*}$ integral under such approximation.

One remarkable feature was explored when our HPPM SCF method was employed for the calculation of $^1\pi\pi^*$ species which cannot be distinguished on the basis of orbital symmetry characteristics from other lower energy species, including the ground state. Whereas the $^3\pi\pi^*$ species converged smoothly at all conformations of bending, the corresponding $^1\pi\pi^*$ state did not converge even at the slightest departure from planarity. The planar $^1\pi\pi^*$ species converged, however, with difficulty after a very extensive reorganization of the orbitals, accompanied in all cases with drifting of both the π and π^* orbitals to a greater blue shift region (see table 5 below). The resulting excitation energies show a higher magnitude and cannot be reasonably accepted unless corrected for the loss of orthogonality with the ground state. It may be noted that excited states arising from $\pi \rightarrow \pi^*$ or $\sigma \rightarrow \sigma^*$ excitations with singlet spin coupling are generally described as semidiffuse in character (Peyerimhoff and Buenker 1975) rather than as valence species type. Such a situation requires incorporation of long range diffuse functions in the basis set (Huzinaga 1962) for an adequate representation of the excited state. It is felt, therefore, that in calculating such semidiffuse states reliably, *ab initio* calculations with double-zeta basis, augmented with appropriate diffuse functions should be employed keeping in mind, however, the maintenance of the orthogonality of such states.

3.2 Structural results

In table 2 we present the equilibrium out-of-plane bending angles in $^{1,3}n\pi^*$, $^3\pi\pi^*$ states of H_2CS , HFCS and F_2CS . Results from unrestricted open-shell (^3UHF)

Table 2. Out-of-plane bending equilibrium angles in $^{1,3}n\pi^*$ and $^3\pi\pi^*$ states of tetra-atomic thiocarbonyls. Quantities within ()^a represent HPM calculated results and those within [] represent experimental/*ab initio* values.

Molecule	Bending angle (degrees)			
	$^3n\pi^*$	$^1n\pi^*$	$^3\pi\pi^*$	^3UHF
H_2CS	30(30) [24.2] ^b	20(20)	12(10) [13] ^d	0
HFCS	37(35) [35.2] ^b	33(35)	33(30)	25
F_2CS	38(40) [42] ^b [30.5-34.1] ^c	39(40)	40(40)	32

^aBanerjee and Bhattacharyya (1980, 1983); ^bKapur *et al* (1979);

^cMoule and Mehra (1970); ^dBruna *et al* (1974).

Table 3. *p*-electron and *s*-electron densities on the C-atom in planar and equilibrium nonplanar geometries in the $^1,^3n\pi^*$ and $^1,^3\pi\pi^*$ states of some thiocarbonyls.

Molecule	Geometry	C-atom orbital	One-electron density in			
			$^3n\pi^*$	$^1n\pi^*$	$^3\pi\pi^*$	$^1\pi\pi^*$
H ₂ CS	Planar	<i>p</i>	3.3610	3.3610	2.9966	2.9966
		<i>s</i>	1.1506	1.1506	1.1506	1.1506
	Equil ^a	<i>p</i>	3.3025	3.3234	2.9841	—
		<i>s</i>	1.1844	1.1722	1.1556	—
HFCS	Planar	<i>p</i>	3.1653	3.1653	2.9165	2.9428
		<i>s</i>	1.1478	1.1478	1.1486	1.1486
	Equil	<i>p</i>	2.9711	3.0282	2.8317	—
		<i>s</i>	1.2351	1.2226	1.2074	—
F ₂ CS	Planar	<i>p</i>	2.9810	2.9810	2.8239	2.8404
		<i>s</i>	1.1562	1.1562	1.1562	1.1562
	Equil	<i>p</i>	2.6510	2.6538	2.5582	—
		<i>s</i>	1.3172	1.3152	1.2866	—

^aEquil = Nonplanar equilibrium (adiabatic) geometry.

calculations are included for comparison. In all calculations *d*-orbitals were excluded from the basis set of the S-atom, as it was found in earlier HPM calculations (Banerjee and Bhattacharyya 1980) that inclusion of such basis functions destroy the geometrical features of excited states. It may be observed from table 2 that the equilibrium angles of non-planarity in our present calculation are almost comparable to those found by HPM calculations. In H₂CS the extent of nonplanarity is greater in the $^3n\pi^*$ state than in the $^1n\pi^*$ state. With gradual fluorine substitution the difference in their extents of nonplanarity decreased almost uniformly. The simple HPM results were rather insensitive in that they predicted equal amounts of bending in both singlet and triplet $n\pi^*$ states of HFCS and F₂CS. It is encouraging to note that the predicted bending (38°) in $^3A''$ of F₂CS has better agreement with experimental results (30.5°–34.1°) than the *ab initio* open-shell (STO-3G) calculated magnitude (42°). A decreasing trend of the electron density on the C-atom in the different equilibrium excited state conformations of the three molecules is observed (table 3) with increasing fluorine substitution. This is in keeping with the gradual electron-withdrawing effect by the electro-negative fluorine atoms. Close observation reveals that in spite of this gradual decrease in total electron density on the C-atom, there is an opposite increasing trend in the *s*-electron density in these molecules which, obviously, is compensated by a greater diminishing trend in *p*-electron density. The trend of increasing nonplanarity in a particular state in all the three molecules can be expected from the Walsh postulate (Walsh 1953) that 'whether or not an orbital becomes more tightly bound with change of angle is determined primarily by whether or not it changes from being built from a *p*-orbital (on an atom) to being built from an *s*-orbital (on that atom)'.

The barriers to inversion estimated by such semiempirical methods are always expected to predict high values due to the deficiency inherent in the CNDO theory. Still the present method yields barrier heights which are better than those predicted by the simple HPM theory (table 4). Successive fluorine substitution leading to gradual withdrawal of electron density from the C-atom seems to enhance the barrier height in all cases.

3.3 Spectral results

Adiabatic (with respect to nonplanar bending) and vertical transition energies for $A \leftarrow \tilde{X}$ transitions in the three molecules considered are presented together with the UHF-calculated results in table 5. In H_2CS the presently calculated magnitudes

Table 4. Barrier to planar inversion (in cm^{-1}) in excited states of thiocarbonyls; quantities within ()^a represent HPM results, those within [] are experimental/*ab initio* results.

Molecule	Planar inversion barrier in			
	$^1n\pi^*$	$^3n\pi^*$	$^3\pi\pi^*$	^3UHF
H_2CS	86 (285)	385 (394) [108] ^b	11 (≈ 0)	0
HFCS	1256 (4321)	2130 (5418) [843] ^b	972 (1082)	304
F_2CS	5934 (6032)	6230 (6186) [> 3100] ^b	4415 (4345) [> 3000] ^c	1786

^aBanerjee and Bhattacharyya (1980, 1983); ^bKapur *et al* (1979); ^cLessard and Moule (1973).

Table 5. $^1,^3n\pi^*$ and $^1,^3\pi\pi^*$ transition energies (eV) in some simple thiocarbonyls. Quantities within ()^a represent HPM calculated results, those within [] are experimental or *ab initio* values.

Molecule	Transition energy in eV							
	$^3n\pi^*$		$^1n\pi^*$		$^3\pi\pi^*$		$^1\pi\pi^*$	^3UHF
	Adiabatic	Vertical	Adiabatic	Vertical	Adiabatic	Vertical	Vertical	Vertical
H_2CS	3.11 (3.10) [2.3-2.5] ^b	3.15 (3.15)	3.14 (3.12)	3.15 (3.15)	3.73 (3.72) [3.28] ^c	3.73 (3.72)	20.48	1.86
HFCS	3.77 (4.34)	4.04 (5.01)	3.88 (4.48)	4.04 (5.01)	4.08 (4.03)	4.20 (4.17)	18.38	2.57
F_2CS	4.29 (4.29) [3.00] ^d	5.06 (5.05)	4.32 (4.30)	5.06 (5.05)	4.22 (4.17) [6.08] ^c	4.77 (4.80)	16.38	3.25

^aBanerjee and Bhattacharyya (1980, 1983); ^bPeyerimhoff and Buenker (1975); ^cBruna *et al* (1974); ^dMoule and Mehra (1970); ^eLessard and Moule (1973).

Table 6. Energy differences and decrease in electron population on C-atom in passing from ${}^3n\pi^*$ state to ${}^3\pi\pi^*$ state in the thiocarbonyls

Molecule	$E_{\pi\pi^*} - E_{n\pi^*}$ (eV)	Decrease in electron population on C (vertical)
H ₂ CS	0.620	0.3644
HFCS	0.305	0.2480
F ₂ CS	-0.064	0.1571

are in very close agreement with the simple HPM results. This reflects that hole orbitals reorganization should be small. The reasons for exceptionally high values for the ${}^1\pi\pi^*$ transition energies seem to have been explained in §3.1 and it appears (Peyerimhoff and Buenker 1975) that the corresponding CI calculated values, viz. 11.41 eV in H₂CO and 7.92 eV in H₂CS are large enough to find such states to be located high up in the spectrum. From a comparison of the HPM and HPPM results in all the three molecules it is observed that the effect of hole orbitals reorganization, which results in a difference in transition energies in the two methods, is most prominent in the case of $n\pi^*$ transitions in HFCS. It may be noted that unrestricted open-shell transition energies in H₂CS and F₂CS are in better agreement with the corresponding experimental values observed for their lowest triplets. While such betterment can be ascribed to a greater variational flexibility of the UHF method, compared to our HPPM, the former suffers from non-specificity of the particular excited state.

One can observe from tables 5 and 6 that the energy difference between ${}^3\pi\pi^*$ and ${}^3n\pi^*$ states decrease along the sequence H₂CS → HFCS → F₂CS, so much so that in F₂CS there is just a reversal in the order of $\pi\pi^*$ and $n\pi^*$ states. As the n -orbital is centred mainly upon the S-atom and the π^* orbital, although delocalized, has a greater amplitude on the C-atom, the $n \rightarrow \pi^*$ excitation leads to a flow of electron density from sulphur to carbon. On the other hand, the $\pi \rightarrow \pi^*$ excitation is well delocalized over the C=S region. In passing from a $n\pi^*$ state to a $\pi\pi^*$ state one finds from table 5 that there is a decrease in electron density on the carbon atom. Gradual attachment of the electronegative fluorine atoms with carbon is expected to withdraw the excess build-up of electron density on C in the $n\pi^*$ state, thereby levelling off the difference between ${}^3n\pi^*$ and ${}^3\pi\pi^*$ states. The predicted reversal in the order of low lying triplets in F₂CS is not quite unusual as it is evident that similar inversions are known to occur with some aromatic carbonyls. The failure to undergo photoreduction (Turro 1965) by 2-acetonaphthone and 1-naphthaldehyde with alcohols under the usual conditions is attributed to the existence of the ${}^3\pi\pi^*$ state as the lowest lying T_1 state. The reason has been the delocalization of electron density from the carbonyl region. It should, therefore, be worthwhile in the context of our present study to compare the relative ease of photoreduction of these thiocarbonyls.

4. Conclusion

Although the open-shell method of Morokuma is nothing new at the present time, its formulation in the framework of semiempirical model like the CNDO is

definitely substantial in the context of application to moderately large-sized molecular systems in retrieving at least qualitative information about the relative ordering of the various excited states and about the excited state geometry, barrier height etc. A serious limitation to improvement in this method is imposed by the extremely small size of the valence AO basis set employed in CNDO calculations. In future calculations employing extended basis sets, the results are expected to improve further. The most noteworthy point is that the one-electron orbitals thus obtained in calculating a particular excited state are more suitable in providing CI expansion for that state, rather than the usual Hartree Fock MO which sometimes fail to produce any improvement in such excited state calculations.

Acknowledgement

The authors wish to express their sincere thanks to Dr S P Bhattacharyya for helpful discussions. One of the authors (AKC) is grateful to the UGC for a fellowship. Computation facilities were extended by the personnel of the Computer Centre.

References

- Banerjee M and Bhattacharyya S P 1980 *J. Phys. Chem.* 2843
Banerjee M and Bhattacharyya S P 1983 *Indian J. Chem.* A22 457
Bruna P, Peyerimhoff S D, Buenker R J and Rosmus P 1974 *J. Chem. Phys.* 63 35
Hunt W J and Goddard III W A 1969 *Chem. Phys. Lett.* 3 414
Huzinaga S 1962 *J. Chem. Phys.* 36 453
Huzinaga S and Arnau C 1970 *Phys. Rev.* A1 1285
Huzinaga S and Arnau C 1971 *J. Chem. Phys.* 54 1948
Kapur A, Steer R P and Mezey P G 1979 *J. Chem. Phys.* 70 745
Lessard C R and Moule D C 1973 *Spectrochim Acta* A29 1055
Morokuma K and Iwata S 1972 *Chem. Phys. Lett.* 16 192
Moule D C and Mehra A K 1970 *J. Mol. Spectrosc.* 35 137
Peyerimhoff S D and Buenker R J 1975 in *Advances in quantum chemistry* (ed.) P O Lowdin (New York: Academic Press) vol. 9
Roothaan C C J 1960 *Rev. Mod. Phys.* 32 179
Saunders V R and Hillier I H 1973 *Int. J. Quantum Chem.* 7 699
Turro N J 1965 in *Molecular photochemistry* (New York: Benjamin) p. 152
Walsh A D 1953 *J. Chem. Soc.* 2260