MINIMAL BASIS CALCULATIONS FOR

SOME SULPHUR COMPOUNDS

PARTICIPATION OF d ORBITALS
IN BONDING OF SULPHUR
BY MINIMAL BASIS CALCULATIONS

By

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The involvement of d orbitals in the coordination of sulphur in three simple sulphur compounds is investigated using an ab initio approach. Comparison of minimal and extended basis set results for molecular properties such as dipole moment, molecular geometry, and force constants provides a means of establishing the importance of d orbitals in sulphur compounds and probably other second row compounds. Excited states of sulphur dioxide and ozone are studied in the hope of elucidating the respective spectra on a theoretical basis. These investigations also provide initial data for the parametrization of the semi-empirical CNDO approach for second row atoms.

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INTRODUCTION

To date, numerous ab initio studies of first row atom containing molecules have been performed. One of the objectives of these calculations has been the determination of an optimum basis set for use in further studies. Since ab initio calculations involve large numbers of complex integrals, the use of gaussian expansions of Slater type orbitals has evolved[1-5]. The main advantage of gaussian functions is the relative ease of integral evaluation in this basis as compared with Slater orbitals. The validity of such expansions has been judged on the basis of agreement between theoretically calculated molecular properties and experimental values.

Of the many ab initio calculations involving first row atoms, a fair proportion has involved the use of a minimal basis set. Such a basis set is defined[6] to consist of only those atomic orbitals which are occupied in the ground state of each atom constituting the molecule. Pople and various co-workers[2,7-9] have been responsible for a significant portion of the exploratory work in this field. Their investigations have been focused on first row molecules in an attempt to extend ab initio calculations to relatively large organic systems. An immediate problem encountered in such an extension is the choice of a suitable gaussian expansion for the basis set. Some investigators have used fairly large gaussian representations and have consequently been limited to small molecular systems. Pople and co-workers have optimised the size of expansion appropriate for future work with large molecules and have found that the minimum size required for an adequate representation in such calculations consists of three gaussian functions per Slater orbital. These findings provided the basic incentive for the calculations to be reported in this thesis.

A natural extension of these minimal basis calculations is to second row atom containing molecules. In this work the use of a minimal basis for second row molecule calculations has been investigated. Preliminary calculations have been limited to three sulphur containing molecules - carbon monosulphide, hydrogen sulphide, and sulphur dioxide - with the assumption that these molecules should be fairly representative of the behaviour of second row atoms in general.

There exists an ever-increasing need for the extension of theoretical calculations to second row systems, since the majority of molecules of biological and geological significance contain elements such as phosphorus, sulphur, chlorine, and silicon. Ab initio calculations are impractical where large molecular systems are concerned, since the size of system which may be studied is limited both by the nature of computing facilities required and financial considerations. Consequently, ab initio calculations are often not appropriate for the large biologically important molecules or large silicate molecules which are of interest to the geologist. However, a potentially rather attractive method of molecular orbital studies applicable to these classes of compounds is available in the form of the semi-empirical treatment which has proven quite successful for large first row molecules[10]. Although an attempt has been made to extend methods such as CNDO and INDO to second row atoms,[11] initial results have been discouraging. There exists an obvious need for improved parametrization in such calculations. This could be achieved if a variety of reference ab initio wave functions for second row molecules were available for comparison. One of the aims of the present series of calculations is to provide at least a fraction of such reference wave functions. Those wave functions obtained in the course of this work are for minimal basis, and minimal basis extended to include d, ab initio calculations.

An additional factor of considerable interest in this type of computation is the effect of extension of the minimal basis to include 3d functions centred on the second row atom. Some preliminary calculations have been attempted[12] in an effort to ascertain the suitability of the minimal basis set for second row molecules. These however, made no consideration of the effects of 3d functions. It is nevertheless widely believed that these orbitals are probably required, even in the most naive treatments, for a satisfactory description of the electronic properties of second row molecules.

In order to assess the importance of d orbitals in the molecular bonding of some sulphur compounds, it was decided to compare results of two series of calculations. One series involved only the minimal basis set, the other an extended set in which the exponents of the included d orbitals had been optimised. The criterion chosen for assessing the involvement of d functions was the agreement between theoretically computed molecular properties - such as dipole moment, ionization potential, optimum bond lengths and bond stretching force constants - and the experimentally observed values.

The results presented in this work should be of particular interest, as for some time there has existed a dispute pertaining to the exact nature of the contribution made by d orbitals to the molecular bonding. This problem has been studied theoretically by both electrostatic and molecular orbital approaches. Using a point charge model, Craig[13] determined that d orbitals do contract in the presence of a potential field due to ligand charges. The extent of contraction found is considered sufficient to make plausible the participation of these functions in the molecular bonding of second row molecules. More recently, there has been considerable effort made to determine whether d functions are utilized in bonding and also to establish more definitely the nature of their role. Several ab initio studies have indicated that d orbitals are indeed essential to bonding of second row atoms[14-18].

The major source of dissension has been provided by results of various experimental investigations concerned with aromatic sulphides and heteroatomic compounds of divalent sulphur. For instance, the interpretation of the hyperfine splitting constants obtained in electron spin resonance studies of the dibenzothiophene, dibenzoselenophene and dibenzofuran radical anions has been made using two models[19]. It was found that the correct interpretation of the spectrum for both dibenzofuran and dibenzothiophene could be obtained without inclusion of d orbitals. In fact, the model in which d orbitals of π symmetry were considered produced incorrect spin distributions.

A more extensive spectroscopic study of this type of sulphur compound[20] has indicated that 3d orbital participation, if it exists at all, does not modify the molecular properties significantly. One notable exception is thiophene, in which the sulphur 3d orbitals are thought to be involved in the π system. However, ab initio calculations[21] in which the effects of inclusion of d orbitals on sulphur in thiophene were studied, have indicated that the role of d orbitals is a minor one, which in fact is probably overestimated by the nature of the basis set.

It is hoped that the present series of calculations will provide further insight into the resolution of this dichotomy.

CHAPTER I

THEORETICAL BACKGROUND

Theoretical calculations presently in use for the investigation of molecular properties by the molecular orbital method fall into one of two categories - designated as ab initio and semi-empirical. In ab initio calculations, all electrons are considered simultaneously and the exact non relativistic Hamiltonian is used to obtain a solution to the Schrödinger equation. Those integrals involved in obtaining a solution are evaluated either explicitly or by numerical methods, but this approach entails the evaluation of all integrals, both one- and two-electron. In semi-empirical calculations, only the electrons considered to be the most important to the molecular bonding are considered explicitly. Integral evaluation is simplified by use of various approximations. Certain integrals may be neglected altogether, while others are assigned values on the basis of experimental data. Thus, although the fundamental ideology is the same in these two approaches, the mathematical treatment differs in both complexity and scope. These differences should become apparent as the methods are described in the following outline.

1.1. ROOTHAAN'S EQUATIONS AND SELF CONSISTENT FIELD THEORY

The purpose of any molecular orbital calculation is to obtain a solution of Schrödinger's equation, which is normally stated in its time independent form as:

$$\mathcal{H}\Psi = E\Psi \qquad (1.1)$$

In this equation, $\mathcal{H}$ is the Hamiltonian operator, which consists of a sum of one and two electron contributions, Ψ is the wave function, depending on the electronic co-ordinates and E is the energy.

The method of solution in the case of a polyatomic, multi-electron molecular system is based on Fock's procedure for solving a multielectron closed shell atomic problem. An outline of the derivation of Fock's equations is given in Roothaan's classical paper[22] which presents a mathematical formulation of the linear combination of atomic orbitals approach within the Hartree-Fock method.

In the derivation of the Hartree-Fock equations, the molecular wave function is represented by an antisymmetrized product of one electron molecular spin orbitals. The usual notation for the wave function is:

$$\Psi = (N!)^{-\frac{1}{2}} \left| \phi_1(1)\, \overline{\phi_1}(2)\, \phi_2(3)\, \overline{\phi_2}(4) \ldots\, \phi_n(2n-1)\overline{\phi_n}(2n) \right| \qquad (1.2)$$

where $N = 2n$ is the total number of electrons and the ϕ_i are molecular orbitals, with $\overline{\phi_i}$ denoting a β spin.

$\mathcal{H}$, the total Hamiltonian operator occurring in equation (1.1) is given by the sum of one and two electron contributions, $\mathcal{H}_1$ and $\mathcal{H}_2$ respectively; in atomic units:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$$

$$\mathcal{H} = \left[- \sum_q (\tfrac{1}{2}\nabla_q^2) - \sum_A \sum_q \frac{Z_A}{r_{Aq}}\right] + \sum_{q>s} \sum r_{qs}^{-1} \qquad (1.3)$$

The one electron contributions consist of kinetic energy and nuclear electronic attraction terms, and the two electron term represents electronic repulsions. ∇^2 is the differential operator for kinetic energy, Z_A refers to nuclear charge on centre A, r_{Aq} and r_{qs} represent nucleus to electron and inter-electron distances.

To calculate the total energy of the system it is necessary to evaluate the integral, over both space and spin coordinates of all the electrons:

$$\int \Psi^* \, (\mathcal{H}_1 + \mathcal{H}_2) \, \Psi \, d\tau \qquad (1.4)$$

Considering first the one electron contributions:

$$\mathcal{H}_1 = \sum_q \left(- \tfrac{1}{2}\nabla_q^2 - \frac{Z_A}{r_{Aq}} \right) = \sum_q H(q) \qquad (1.5)$$

$$\begin{aligned}\int \Psi^* \, H(q) \, \Psi \, d\tau = \frac{1}{(2n)!} \sum_P \sum_{P'} (-1)^P (-1)^{P'} \; P\{\phi_1(1) \, \overline{\phi_1}(2) \ldots \\ \ldots \overline{\phi_n}(2n)\} \, H(q) \, P'\{\phi_1(1) \, \overline{\phi_1}(2) \ldots \overline{\phi_n}(2n)\} d\tau\end{aligned} \qquad (1.6)$$

where P, P' are operators which permute electrons among the molecular orbitals.

Since it is simpler to work with an orthonormal set, it may be assumed without loss of generality that the MO satisfy the following condition:

$$\int \phi_i^* \, \phi_j \, d\tau = \delta_{ij} \quad \text{, the Kronecker delta} \qquad (1.7)$$

Because of this condition, the only non zero contributions to the one electron terms are those for which P and P' are identical, and since the electrons are indistinguishable, the value of this integral is identical for all 2n electrons:

$$\int \Psi^* H(1)\ \Psi\ d\tau \ = \ \frac{2n}{(2n)!} \sum_{P} \int P\{\phi_1(1)\ \overline{\phi_1}(2) \ldots \overline{\phi_n}(2n)\} \times H(1)\ P\{\phi_1(1)\ \overline{\phi_1}(2) \ldots \overline{\phi_n}(2n)\}\ d\tau \qquad (1.8)$$

$$\int \Psi^* \mathcal{H}_1\ \Psi\ d\tau \ = \ 2 \sum_{i=1}^{n} H_{ii} \qquad (1.9)$$

where $$H_{ii} \ = \ \int \phi_i^*(1)\ H\ \phi_i(1)\ d\tau_1 \qquad (1.10)$$

Similarly for the two electron terms, because of indistinguishability of electrons, each contribution is identical and the total number of these terms is $\frac{1}{2}(2n)(2n-1)$

$$\int \Psi^* \mathcal{H}_2\ \Psi\ d\tau \ = \ \frac{(2n)(2n-1)}{(2n)!\ 2} \sum_{P} \sum_{P'} (-1)^{P}(-1)^{P'} \int P\{\phi_1(1)\ \overline{\phi_1}(2) \ldots \ldots \overline{\phi_n}(2n)\}\ r_{12}^{-1}\ P'\{\phi_1(1)\ \overline{\phi_1}(2) \ldots \overline{\phi_n}(2n)\} d\tau \qquad (1.11)$$

This integral evaluation is more complicated than that for the single electron terms since now the non zero terms include permutations which differ by the interchange of two electrons.

For the case where the two electrons are assigned to the same orbitals in both permutations - that is where the permutations are identical, there are four contributions in total:

$$\iint \overline{\phi}_i^*(1)\, \overline{\phi}_j^*(2)\; r_{12}^{-1}\; \overline{\phi}_i(1)\, \overline{\phi}_j(2)\; d\tau_1\, d\tau_2 \qquad (1.12)$$

and the corresponding α spin integral, and:

$$\iint \overline{\phi}_i^*(1)\; \phi_j^*(2)\; r_{12}^{-1}\; \overline{\phi}_i(1)\; \phi_j(2)\; d\tau_1\, d\tau_2 \qquad (1.13)$$

$$\iint \phi_i^*(1)\; \overline{\phi}_j^*(2)\; r_{12}^{-1}\; \phi_i(1)\; \overline{\phi}_j(2)\; d\tau_1\, d\tau_2 \qquad (1.14)$$

Integrals of this kind are coulomb integrals and generally denoted:

$$J_{ij} = \iint \phi_i^*(1)\; \phi_j^*(2)\; r_{12}^{-1}\; \phi_i(1)\; \phi_j(2)\; d\tau_1\, d\tau_2 \qquad (1.15)$$

If the two electrons are assigned to the same molecular orbital, their spins must be different, and only two of the above contributions occur.

The other type of non zero two electron integral occurs when the spatial orbitals of electrons i and j are interchanged in the two permutations. Here only two contributions arise:

$$\iint \phi_i^*(1)\; \phi_j^*(2)\; r_{12}^{-1}\; \phi_j(1)\; \phi_i(2)\; d\tau_1\, d\tau_2 \qquad (1.16)$$

and $\iint \overline{\phi}_i^*(1)\; \overline{\phi}_j^*(2)\; r_{12}^{-1}\; \overline{\phi}_j(1)\; \overline{\phi}_i(2)\; d\tau_1\, d\tau_2 \qquad (1.17)$

These are the exchange integrals, symbolized by K_{ij}; these always occur with a negative sign since the two permutations are of different parity.

The complete expression for the electronic energy becomes:

$$\varepsilon = 2\sum_{i=1}^{n} H_{ii} + \sum_{i} J_{ii} + \sum_{i\neq j} (2J_{ij} - K_{ij})$$

$$\text{or} \quad \varepsilon = 2\sum_{i=1}^{n} H_{ii} + \sum_{i}^{n}\sum_{j}^{n} (2J_{ij} - K_{ij}) \tag{1.18}$$

Now that the energy expression has been derived, the variational method is applied, and the energy is minimized with respect to the molecular orbitals ϕ_i by use of the method of undetermined multipliers. This procedure results in a set of differential equations:

$$[H^{\text{core}} + \sum_{j} (2J_j - K_j)]\,\phi_i = \sum_{j}\varepsilon_{ij}\phi_j \quad i=1,2....n \tag{1.19}$$

where H^{core} is the $H(q)$ defined by equation (1.5),

and
$$J_j\phi_i(\mu) = [\int \frac{\phi_j^*(\nu)\phi_j(\nu)}{r_{\mu\nu}}d\tau\,]\,\phi_i(\mu)$$

$$K_j\phi_i(\mu) = [\int \frac{\phi_i^*(\nu)\phi_j(\nu)}{r_{\mu\nu}}d\tau\,]\,\phi_j(\mu)$$

The quantity represented by the square brackets in equation (1.19) is the Fock operator F and the equations themselves are known as the Hartree-Fock equations.

Roothaan, in order to simplify the solution of these equations proposed the use of the linear combination of atomic orbitals (χ_μ) to represent molecular orbitals (ϕ_i).

$$\phi_i = \sum_\mu \chi_\mu c_{\mu i} \tag{1.20}$$

The $c_{\mu i}$ refer to the coefficients of the μth atomic orbital in the ith molecular orbital. In this approach the energy is expressed in terms of the set of coefficients $\{c_{\mu i}\}$ and the energy is minimized in accordance with the variational method, with respect to the coefficients. The energy expression in the LCAO-MO SCF procedure is:

$$\varepsilon = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} - \tfrac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} [(\mu\nu/\lambda\sigma) - \tfrac{1}{2}(\mu\lambda/\nu\sigma)]$$

$$P_{\mu\nu} = 2 \sum_{i=1}^{occ} c_{\mu i}^{*} c_{\nu i}$$

$$H_{\mu\nu} = \int \chi_\mu(1)\, H^{core} \chi_\nu(1)\, d\tau_1 \tag{1.21}$$

$$(\mu\nu/\lambda\sigma) = \iint \chi_\mu(1)\, \chi_\nu(1) \frac{1}{r_{12}} \chi_\lambda(2)\, \chi_\sigma(2)\, d\tau_1\, d\tau_2$$

Upon application of the variational method to the above energy expression, the set of resulting equations in the LCAO-MO SCF procedure is:

$$\sum_\nu (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) c_{\nu i} = 0 \tag{1.22}$$

where $F_{\mu\nu}$, the Fock operator:

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu/\lambda\sigma) - \tfrac{1}{2}(\mu\lambda/\nu\sigma) \right] \qquad (1.23)$$

In order that a solution exist , the secular determinant must equal zero:

$$| F - S\varepsilon | = 0 \qquad (1.24)$$

Therefore, the problem consists of solving a set of equations non - linear in c_i for both the c_i and ε_i. The usual procedure involves assumption of an initial set of c_i to be used in evaluation of the initial Fock matrix. This Fock matrix is then used to solve the secular equations for a new set of c_i. This series of operations is repeated until the new set of coefficients yields an energy which agrees with that from the previous cycle within the limits of a specified criterion. The molecular orbitals are then said to have reached self consistency and the procedure is therefore known as the self consistent field method. It is usual to use as an initial guess, the one electron Hamiltonian matrix elements.

This type of calculation applies to all closed shell ground state configurations and may be extended to excited states. Roothaan[22] explains the differences between the two types of calculation and presents formulae for the triplet and singlet state energies.

Pople and Nesbet[23] have developed an open shell theory applicable to the ground states of radical ions as well as to excited states; the wave function used for this calculation is of the unrestricted type - one in which the alpha and beta spin electrons are assigned to independent sets of molecular orbitals, $\{\phi_i^\alpha\}$ and $\{\phi_i^\beta\}$. For M alpha spin electrons and N beta spin electrons the wave function is given as:

$$\Psi^\circ = [(M+N)!]^{-\frac{1}{2}} \sum_P (-1)^P \, P\{\phi_1^\alpha(1)\,\alpha(1)\,\phi_2^\alpha(2)\,\alpha(2)\ldots\ldots\phi_M^\alpha(M)\,\alpha(M)\,\phi_{M+1}^\beta(M+1)\,\beta(M+1)\ldots\ldots\phi_{M+N}^\beta(M+N)\,\beta(M+N)\} \tag{1.25}$$

By applying the standard procedure, as outlined for closed shell ground states, to this type of wave function, it may be shown that the energy for the open shell system of (M+N) electrons is given by:

$$E = \sum_i^\alpha H_i + \sum_i^\beta H_i + \tfrac{1}{2}\Big(\sum_i^{\alpha+\beta}\sum_j^{\alpha+\beta} J_{ij}\Big) - \tfrac{1}{2}\Big(\sum_i^\alpha\sum_j^\alpha + \sum_i^\beta\sum_j^\beta\Big) K_{ij} \tag{1.26}$$

Then, by use of the variation theorem, it is found that a solution for the open shell case is dependent on two sets of matrix equations:

$$\begin{aligned}(\underline{F}^\alpha - \varepsilon_i^\alpha \underline{S})\,\underline{C}_i^\alpha &= 0\\ (\underline{F}^\beta - \varepsilon_i^\beta \underline{S})\,\underline{C}_i^\beta &= 0\end{aligned} \tag{1.27}$$

where

$$\begin{aligned}\underline{F}^\alpha &= \underline{H} + \underline{J} - \underline{K}^\alpha\\ \underline{F}^\beta &= \underline{H} + \underline{J} - \underline{K}^\beta\end{aligned} \tag{1.28}$$

The results reported in this thesis were for ab initio calculations using the POLYATOM[24] system of programmes; the open shell calculations were of the unrestricted type.

1.2 BASIS SETS:- GAUSSIAN VERSUS SLATER FUNCTIONS:

Two types of function are most often used to comprise the basis set in the LCAO approach; one possible choice is the set consisting of nodeless Slater type exponential functions, having the general form:

$$S_i = r^{n-1} Y_{lm}(\theta, \phi) e^{-\alpha_i r} \qquad (1.29)$$

where $Y_{lm}(\theta, \phi)$ are spherical harmonics, r the radial distance, l, m, n the quantum numbers and α_i the exponential parameter which may be optimized within the molecular calculation or assigned an a priori value on the basis of Slater's rules[25]. These functions have been widely used since their analytical form represents adequately the atomic orbital, the cusp condition being reproduced at the nucleus. Furthermore, calculations using a Slater basis converge fairly rapidly. The major disadvantage of these STO is the intractable nature of the complex multi-electron, multi-centre integral evaluation.

Boys,[26] in 1950 first suggested and formulated the use of gaussian type functions as an alternative basis set. In his work, he derived equations necessary for evaluation of integrals over gaussian functions.

A gaussian type function, on a centre A is normally represented:

$$g_i(r_A) = x^l y^m z^n \exp(-\alpha_i r_A^2) \qquad (1.30)$$

where α_i is the exponential parameter, either chosen on the basis of previous atomic calculations or else optimized within the calculation.

$$r_A^2 = (x_A^2 + y_A^2 + z_A^2)$$

$$= (x - A_x)^2 + (y - A_y)^2 + (z - A_z)^2 \qquad (1.31)$$

(x, y, z) representing co-ordinates of an arbitrary point in space, and (A_x, A_y, A_z) the co-ordinates of centre A.

l, m, n are parameters, the value of which is determined by the orbital type:

s type: $l = m = n = 0$

p type: $l = 1;\ m = n = 0$ etc.

d type: $l = 2;\ m = n = 0$ etc.

With recent advances in computing facilities, Boys' approach has since been extended and applied to various problems, including molecular calculations. In his review article, Shavitt[27] discusses the methods used to implement this approach and presents the formulae required for integral evaluations in a more comprehensible form. The great advantage of these gaussian functions over Slater type functions is realized in the comparative ease with which multi-centre integrals may be evaluated. The simplification is due to the fundamental property of gaussian functions which permits reduction of a product of two gaussians $g_i(r_A)$ and $g_j(r_B)$ centred on atoms A and B, respectively, to a single gaussian with centre C on the line segment between A and B.

$$\begin{aligned} g_i(r_A)\, g_j(r_B) &= \exp(-\alpha_i r_A^2 - \alpha_j r_B^2) \\ &= \exp\{-\frac{\alpha_i\,\alpha_j}{\alpha_i+\alpha_j}\,\overline{AB}^2 - (\alpha_i+\alpha_j)\, r_C^2\} \\ &\equiv K \exp(-\alpha_k r_C^2) = K g_k(r_C) \end{aligned} \tag{1.32}$$

where $\overline{AB} = [(B_x - A_x)^2 + (B_y - A_y)^2 + (B_z - A_z)^2]^{\frac{1}{2}}$

The usefulness of this and other characteristic properties of the gaussian function is illustrated in appendix I where the necessary formulae for the computation of dipole moments are derived.

Although gaussians are mathematically superior to Slater functions for these computations, early calculations by Boys[26] using a basis set consisting of gaussian functions proved that such a representation is inferior to the analogous Slater representation. This deficiency results from the inadequacy of single gaussians to reproduce the radial distribution of the atomic orbital. The representation using gaussians is especially poor at the nucleus, where the cusp behaviour is not obtained and also at large distances from the nucleus where the gaussian function drops off too rapidly. To improve the gaussian to Slater fit, the use of linear combinations of gaussian type functions (LC GTF) has been proposed. This approach requires an optimization of the gaussian function coefficients and exponential parameters which occur in the linear combination fitting the gaussian functions to either an atomic Slater type function or a Hartree-Fock atomic orbital. One method used for these optimizations is the least squares fit, which has been applied by several workers who have tabulated their results in the literature[3,4,5].

By use of this LCGTF-AO approximation, it is possible to simulate the radial behaviour of Slater type functions and therefore approximate the exact orbitals to the same degree of accuracy. This procedure introduces a large number of additional integrals, increasing both the length of time required for evaluation of molecular integrals and also the complexity of the programming. In addition it has been found that the wave function obtained with a gaussian basis set exhibits much poorer convergence properties than does a comparable Slater basis set wave function. However, these difficulties are more than compensated for by the facility of multi-centre integral evaluation.

The computations to be reported in this work are results of ab initio molecular orbital calculations for gaussian expansions of Slater type orbitals. The programmes involved are versions of POLYATOM[24] modified for use at McMaster University.

From the discussion presented above, it may be seen that such a calculation provides a potentially powerful technique for theoretical investigation of small polyatomic molecules. Whether these calculations may be successfully extended to larger systems and the changes required to make such studies possible are questions which remain to be settled.

1.3 SEMI-EMPIRICAL METHODS

Semi-empirical methods avoid the problem of evaluation of complex multi-centre integrals but at the same time provide a means of studying larger polyatomic systems. This approach usually involves a series of approximations made in the process of setting up the problem, coupled with the incorporation of experimentally obtained parameters. To date, methods depending on a wide range of approximations have been developed; their success has been determined by the reliability of the calculated molecular properties. The various semi-empirical methods available to the experimentalist and the nature of approximations encompassed by each of these have been described in a recent review article[28].

One such semi-empirical method, perhaps the most widely applied, is the CNDO or complete neglect of differential overlap approximation developed by Pople and co-workers[10,11,29]. Although this approach has been quite successful and therefore widely applied for first row molecules, extension to second row atoms has been neglected because of the lack of experimental data required for parametrization. The calculations performed in the course of this work were designed with the objective of contributing towards the parametrization of CNDO/2 for second row atoms. Consequently, it seems appropriate to present briefly the concepts involved in this approximation. Further details are available in a recently published monograph by Pople and Beveridge[30].

The fundamental approximation made in CNDO theory involves neglect of all integrals in which products $\chi_\mu(1)\ \chi_\nu(1)$ occur, $\mu \neq \nu$, for a basis set consisting of valence shell orbitals only. This approximation imposes the following constraint on single centre overlap integrals:

$$S_{\mu\nu} = \int \chi_\mu(1)\ \chi_\nu(1)\ d\tau = \delta_{\mu\nu} \qquad (1.33)$$

The constraint of neglect of differential overlap eliminates contribution from all two electron integrals $(\mu\nu/\lambda\sigma)$, as defined by equation (1.21), except those in which $\mu = \nu$ and $\lambda = \sigma$.

Furthermore, those two electron integrals which do make a contribution depend not on the type of atomic orbital, but rather on the atom on which the orbital is centred. These two electron integrals are evaluated explicitly for s type functions, on the two atomic centres:

$$(\mu\mu/\lambda\lambda) = \gamma_{AB}, \text{ the coulomb integral}$$

$$= \int \chi_s^A(1)\ \chi_s^B(2)\ r_{12}^{-1}\ \chi_s^A(1)\ \chi_s^B(2)\ d\tau_1\ d\tau_2 \qquad (1.34)$$

In the case of one electron integrals, differential overlap is not neglected since it is essentially a measure of the extent of bonding due to overlap of electron distribution on adjacent atoms. The contributions to single electron energy are the following:

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B\neq A} (\mu/V_B/\mu)$$

where

$$U_{\mu\mu} = (\mu/-\tfrac{1}{2}\nabla^2 - V_A/\mu) \qquad (1.35)$$

$U_{\mu\mu}$ represents the energy of an electron in the orbital ϕ_μ in the presence of its own core, the quantity $(-\frac{1}{2}\nabla^2)$ being the kinetic energy and V_A the potential due to the core of atom A.

$H_{\mu\nu}$ is zero if μ and ν are on the same centre. Otherwise, the one electron contribution to the electronic energy is given by:

$$H_{\mu\nu} = (\mu/-\tfrac{1}{2}\nabla^2 - V_A - V_B/\nu)$$

$$= \beta_{\mu\nu} = \beta^\circ_{AB}\ S_{\mu\nu} \qquad (1.36)$$

which is effectively the energy of an electron moving simultaneously in the field of two nuclei. This contribution is termed the resonance integral and given the symbol $\beta_{\mu\nu}$. The contributing overlap integrals, $S_{\mu\nu}$, are evaluated according to standard formulae[31].

Both $\beta_{\mu\nu}$ and $U_{\mu\mu}$ are assigned numerical values dependent on experimental data and are not obtained directly through integral evaluation. These are the parameters in this semi-empirical method. In CNDO/2, the $U_{\mu\mu}$ values are assigned as explained elsewhere[30] on the basis of atomic spectroscopic data[32]. The resonance integrals β°_{AB} are approximated by:

$$\beta^{\circ}_{AB} = \tfrac{1}{2}(\beta^{\circ}_{A} + \beta^{\circ}_{B}) \tag{1.37}$$

where the β°_{A} are optimized by fitting CNDO wave functions to more accurate self consistent field calculations. In CNDO/2, the final expression for the Fock operator is:

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2}P_{\mu\mu})\gamma_{AA} + \sum_{\substack{B\neq A\\ \mu\neq\nu}} [-Q_B\, \gamma_{AB} + (Z_B\, \gamma_{AB} - V_{AB})]$$

$$P_{AA} = \sum_{\mu}^{A} P_{\mu\mu} \quad \text{and} \quad P_{\mu\nu} = 2\sum_{i=1}^{occ} C_{\mu i}\, C_{\nu i}$$

$$Q_B = Z_B - P_{BB} \tag{1.38}$$

Q_B being the net charge on atom B

Z_B, the core charge on B

$$V_{AB} = Z_B \int \chi^{A2}(1)\, r_{1B}^{-1}\, d\tau_1$$

$$F_{\mu\nu} = \beta^{\circ}_{AB}\, S_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\, \gamma_{AB}$$

In the CNDO/2 approximation, and similar related methods, the major problem is the lack of more accurate wave functions which are essential to the parametrization for second row and heavier atoms. It is hoped that this work will at least partially alleviate this difficulty.

CHAPTER II

COMPARISON OF MINIMAL AND EXTENDED BASIS SET CALCULATIONS FOR THE SERIES OF COMPOUNDS: HYDROGEN SULPHIDE, CARBON MONOSULPHIDE AND SULPHUR DIOXIDE

The purpose of this work was to determine whether the minimal basis set is adequate for second row atoms or whether it requires extension to include d orbitals. This question was investigated by an ab initio study of the molecular properties of three sulphur containing compounds. The effects of inclusion of 3d orbitals on sulphur were determined by performing two parallel studies:- one without d functions, that is the minimal basis set, and the other with d functions - here referred to as the extended basis set computation. The importance of d functions was evaluated by a comparison of the computed values of bond lengths, dipole moments and force constants for the two series. Agreement of calculated values with experimentally determined ones was also an important factor in deciding the extent of d orbital participation.

II.1 BASIS SET:

The type of basis set used in these calculations was chosen so as to provide a reasonably accurate description of the molecular situation and at the same time remain economically viable. This basis set consisted of linear combinations of gaussian type functions to effect a representation of Slater type orbitals. The core orbitals 1s, in the case of first row atoms, and 1s, 2s and 2p for second row were represented by two gaussians each, and the valence orbitals - 2s and 2p for first row atoms and 3s and 3p for second row atoms, were each represented by four gaussians. Hydrogen 1s orbitals were represented by four gaussians, and the 3d orbitals by 2 gaussians. This basis is similar in constitution to that used in other calculations for CS, H_2S and SO_2 which consisted of three gaussian functions for the representation of each Slater type function[16,43]. However, both the basis set used in these calculations and the 3 gaussian set are inferior in magnitude to the set used in most ab initio calculations. For instance, results have been reported[15] for SO_2 calculations in which the sulphur atom is represented by 12s- type and 9p- type gaussians and the oxygen atom by 10s-type and 5p-type gaussians.

An abbreviated notation is used throughout for the gaussian representation; for example, for the sulphur dioxide molecule: (244/224242). This notation specifies that the basis on the atom of lower atomic number consists of 2 gaussians for the 1s orbital, four gaussians for the 2s, and 4 gaussians for each of the three 2p orbitals. Similarly for the centre of higher atomic number- where the basis is comprised of 1s, 2s, 3s, 2P, 3p and 3d functions in that order.

Use of the linear combination of gaussian type functions for representation of Slater type orbitals (LCGTF-STO) approximation requires the specification of gaussian orbital exponents and combination coefficients. From among the several possible sources of expansion data available[3,5,33,34], the set of parameters selected for these calculations was taken from Stewart[4]. This work reports expansions, consisting of one to six gaussian functions, for the Slater type orbitals 1s through 5g. This expansion

TABLE I

ZETA VALUES[(a)] USED IN DETERMINATION OF EXPONENTIAL PARAMETERS

ATOM	1S	2S	2p	3S	3p	3d
C	5.6727	1.6083	1.5679			
O	7.6579	2.2458	2.2266			
S	15.5409	5.3144	5.9885	2.1223	1.8273	1.78[(c)] 1.58
H	1.2[(b)]					

(a) All values except 3d taken from Reference 36.

(b) This value was chosen on the basis of previous calculations.

(c) Taken from Reference 37; 1.78 used in H_2S and 1.58 for SO_2.

data was obtained by a least squares fit of gaussian functions to Slater orbitals. Using Stewart's notation, the mathematical representation of the Slater type function is:

$$\phi_{n_s lm} = \left[\frac{(2\zeta)^{2n_s+1}}{(2n_s)!} \right]^{\frac{1}{2}} r^{n_s-1} \exp(-\zeta r)\ Y_{lm}(\theta,\phi)$$

or in terms of a linear combination of gaussians,

$$\chi_{n_g lm} = \left[\frac{\left(\frac{2}{\pi}\right)^{\frac{1}{2}} 2^{2n_g+1}}{(2n_g+1)!!} \right]^{\frac{1}{2}} r^{n_g-1} \quad Y_{lm}(\theta,\phi)$$

$$\times \sum_{k=1}^{N} d_k\, \alpha_k^{(2n_g+1)/4} \quad \exp(-\alpha_k r^2)$$

where N refers to the number of gaussians in the expansion, and d_k, α_k are the sets of expansion coefficients and exponential parameters. The exponential zeta parameters appearing in Slater orbitals may be assigned values according to Slater's rules for atoms[35], or alternatively, optimised within the calculation. Sets of α_k appearing in the literature have been obtained for a gaussian fit to a Slater type function in which zeta is assumed to be unity. Prior to their use in calculations, these values are appropriately rescaled by a factor ζ^2 in the manner required by the scaling theorem as reported by O-Ohata[34].

For the present series of computations the optimised atomic zeta values reported by Raimondi and Clementi[36] have been used; these are listed in Table I.

TABLE II

OPTIMIZED VALUES OF SINGLE AND SPLIT-d ZETA FOR ORBITAL EXPONENTS

Molecule	Single Zeta Value	Split Zeta Value[a]	
		ζ_1	ζ_2
H_2S	1.66	1.66	1.65
CS	1.68	1.63	1.75
SO_2	1.58[b]	1.40	1.63

(a) In H_2S and CS ζ_1 value refers to $d_{x^2-y^2}$, d_{z^2} and ζ_2 to dxy dxz dyz.

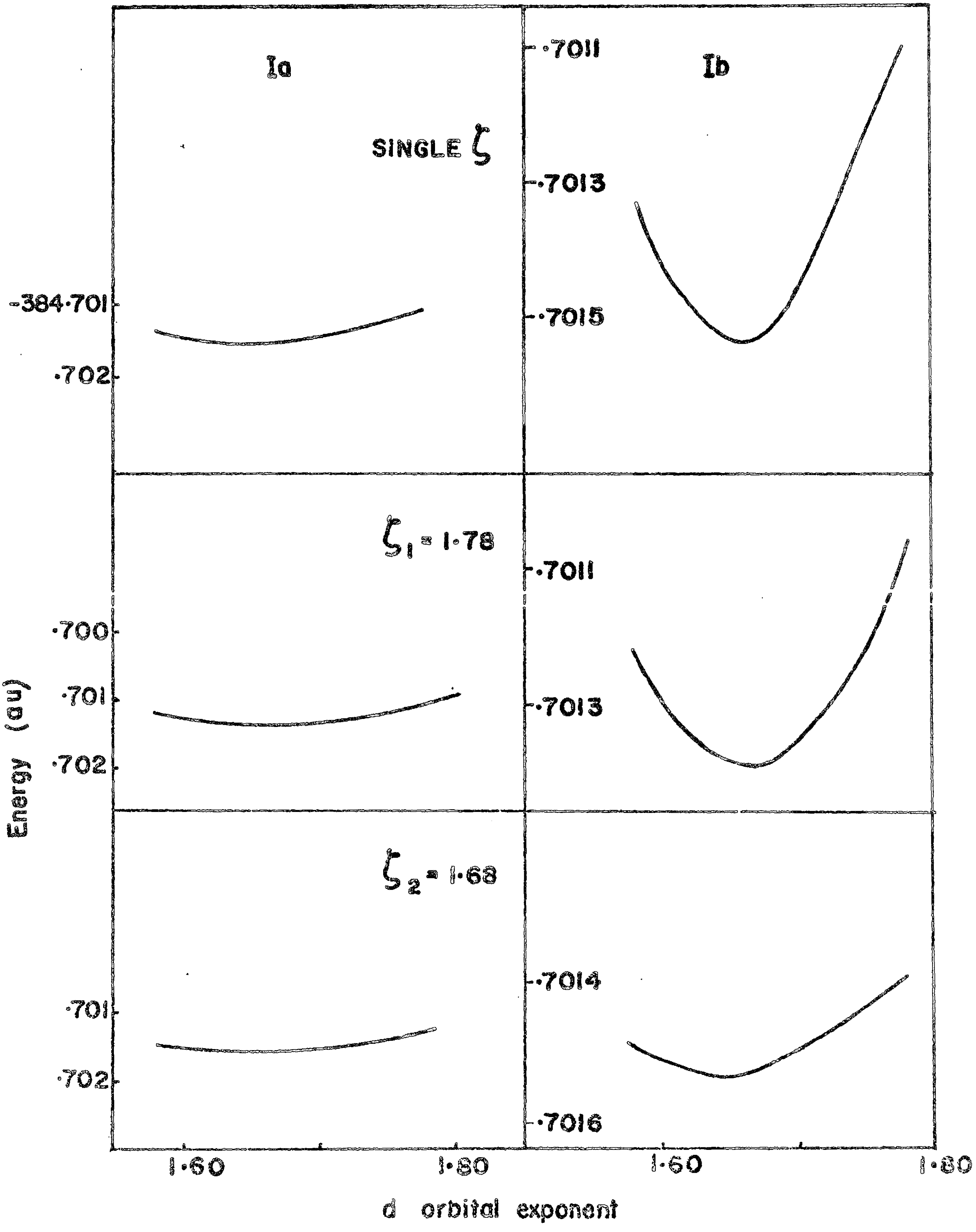
In SO_2 ζ_1 refers to only the dxy exponent, remaining exponents being determined by value of ζ_2.

(b) Not optimized in these calculations but taken from Reference 37.

Figure I

Variation of Molecular Energy as a function of 3d orbital exponent for Hydrogen Sulphide for a single exponent, for ζ_2 with constant ζ_1 and for ζ_1 with constant ζ_2.

I(b) is simply a repetition of I(a) on an expanded scale.


Ia
Ib
SINGLE ζ
ζ_1 = 1·78
ζ_2 = 1·68
-384·701
·702
·700
·701
·702
·701
·702
·7011
·7013
·7015
·7011
·7013
·7014
·7016
Energy (au)
1·60
1·80
1·60
1·80
d orbital exponent

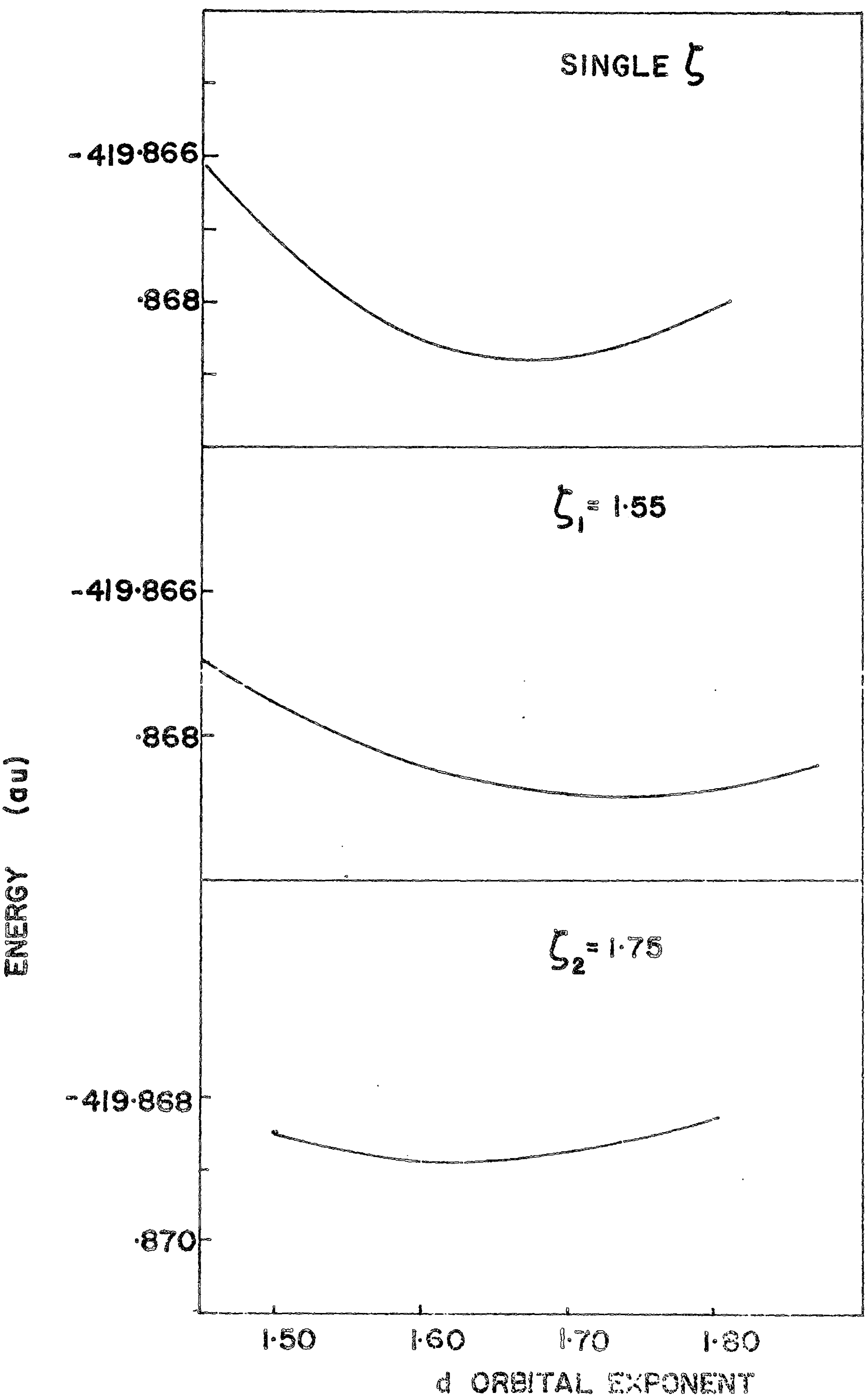
II.2 d ORBITAL EXPONENTS

Prior to the investigation of molecular properties for the series of sulphur compounds in the extended basis set, the sulphur atom d orbital exponents were optimized for each molecular environment. This procedure involved a variation of the single d orbital exponent and also an energy minimization for the split zeta-d exponent. In the latter case, the d orbitals were divided into two groups - one consisting of $d_{x^2-y^2}$ and d_{z^2}, each with exponent ζ_1, and the other of dxy, dxz and dyz for which the exponent was ζ_2. This division conforms with qualitative chemical ideas concerning involvement of d orbitals in bonding. The calculated sets of optimum zeta values are presented for H_2S, CS and SO_2 in Table II.

According to the results of these calculations, for the hydrogen sulphide molecule, the atomic d orbitals centred on the sulphur atom are not greatly perturbed by the bonded hydrogen atoms. This is reflected by the result that the single zeta value is equal to both components of the split zeta exponent. Furthermore, very little variation in energy occurs over a wide range of d orbital exponents ζ_1 and ζ_2 - as is indicated by the plots in figure Ia. However, when the energy scale is expanded, as in figure Ib, for the purpose of comparison of the variation in the two zeta components, it is apparent that response of ζ_2 is more pronounced than that of ζ_1. This may indicate that in hydrogen sulphide, the bonding is much more sensitive to expansion or contraction of the dxy, dxz, dyz set of orbitals. Since in this case, the dyz orbital has the correct spatial orientation to interact appreciably with the hydrogen

Figure 11

Variation of Molecular Energy as a function of 3d orbital exponent for Carbon Monosulphide for a single exponent, for ζ_2 with constant ζ_1 and for ζ_1 with constant ζ_2.


SINGLE ζ
-419·866
·868
ζ1 = 1·55
-419·866
·868
ζ2 = 1·75
-419·868
·870
ENERGY (au)
1·50
1·60
1·70
1·80
d ORBITAL EXPONENT

atoms, this result is not unexpected. As the split zeta component values are identical, it may be presumed that in hydrogen sulphide interaction of one set of d functions is not predominant over that of the other.

The situation for carbon monosulphide and sulphur dioxide differs from that for hydrogen sulphide in that the sulphur atom is bonded to first row atoms in these molecules. This means that included in the basis set are functions with symmetry conducive to more extensive interaction with the sulphur atom d orbitals. It might be expected therefore, that the d orbital exponent values would be appreciably different for these molecules.

For carbon monosulphide, as may be seen upon referring to figure II, the variation in energy with change in the d orbital exponent is again quite gradual. However, the plots are more sharply inflected than those for hydrogen sulphide. The optimum split zeta values are no longer equal; ζ_1 for $d_{x^2-y^2}$ and d_{z^2} has a value of 1.63 and ζ_2 for the remaining participating d functions, dyz and dxz, is 1.75. There is no contribution to molecular bonding from the dxy function because the symmetry of this orbital prohibits interaction with any of the carbon p functions. The optimum single zeta exponent was found to be 1.68, a value which is equal to the weighted average of the split zeta components.

The smaller magnitude of the d_{z^2}, $d_{x^2-y^2}$ exponent indicates that the radial maximum for these functions occurs at a larger distance from the sulphur atom than for the dxz, dyz orbitals. The contraction of the dxz and dyz is greater than that of the remaining d orbitals indicating a greater sensitivity of these orbitals to the electron density at the bonded oxygen atoms.

Interactions which might be operative between the p orbitals of any bonded first row atom and the sulphur atom d orbitals are usually referred to as the synergic effect[39]. The σ contribution to bonding consists of the normal s and p type combinations, but is enhanced by the $p\sigma - d\sigma$ interactions which are possible. In addition to the donation of electronic charge from the carbon to the sulphur, a back donation may occur via the d orbitals, dxz and dyz, on sulphur to vacant p orbitals of appropriate symmetry on carbon. This mechanism is analogous to the simultaneous σ-acceptor, π donor capabilities attributed to transition metals when bonded to π-acid ligands.

The greater degree of contraction found for the dxz and dyz orbitals might be an indication of the removal of electron density from these orbitals compared to an increase in electron density localized in the d_{z^2} orbital.

For the third molecule studied, sulphur dioxide, the division of d orbitals did not conform to that used for the other two molecules. The dxy component was optimised alone as ζ_1 and the other four d orbitals were treated as a single group with exponent ζ_2. This choice was based on the unique role which the dxy orbital plays in sulphur dioxide - being the only atomic orbital with a_2 symmetry. Such a symmetry orbital is capable of participation in π type bonding in the molecule. Furthermore, a grouping of this kind would provide a more economical route to d orbital optimisation than one involving three categories of d functions.

Figure III

Variation of Molecular Energy as a function of 3d orbital exponent for Sulphur Dioxide for ζ_1 with a constant ζ_2 and for ζ_2 with a constant ζ_1.

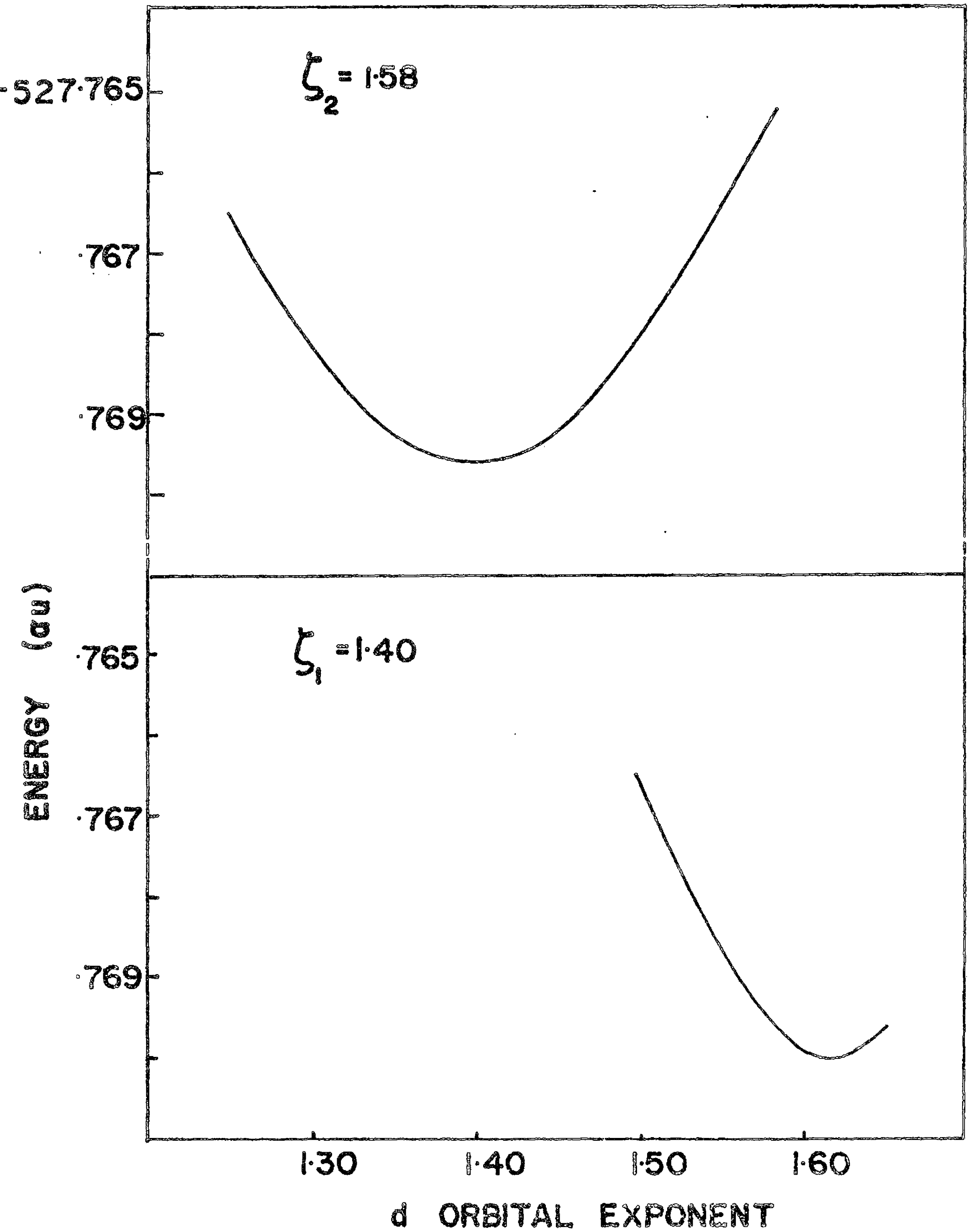

-527·765
·767
·769
ζ₂ = 1·58
ENERGY (au)
·765
·767
·769
ζ₁ = 1·40
1·30
1·40
1·50
1·60
d ORBITAL EXPONENT

TABLE III

COMPARISON OF MOLECULAR ENERGIES AND DIPOLE MOMENTS FOR CALCULATIONS USING OPTIMUM SPLIT ZETA AND SINGLE ZETA d ORBITAL EXPONENTS

Molecule	Energy (a.u)		Dipole Moment (D)	
	Single Zeta	Split Zeta	Single Zeta	Split Zeta
H_2S	-384.7015	-384.7015	0.466	0.466
CS	-419.8687	-419.8689	2.53	2.52
SO_2	-527.7653	-527.7699	1.28	1.26

The single zeta exponent was not optimised in the case of sulphur dioxide, but was assumed to have the value found[37] using a much more extensive basis set. Once again, the weighted average of the optimum split zeta exponents was found to be equal to the single zeta value. However, for sulphur dioxide, the difference between the components of the split zeta exponent was greater than that found for carbon monosulphide. Furthermore, the variation of energy with change in d orbital exponent is much greater than for carbon monosulphide, as indicated by the curves in figure III. This increased sensitivity might be a reflection of increased participation in molecular bonding by the d orbitals. Another interesting feature which emerges upon examination of the results, is the decreased magnitude of the dxy orbital exponent. This could be interpreted as an indication that this particular d orbital is more involved in the molecular bonding than the remaining less diffuse d functions. An explanation of this kind would correlate with the unique quality possessed by the dxy orbital - namely its symmetry - which distinguishes it from the remaining d functions. This symmetry property allows a $p\pi$ - $d\pi$ interaction, so creating an additional contribution to the bonding through π type molecular orbitals in sulphur dioxide.

The merits of the use of split zeta d exponents may be established by a comparison of molecular properties calculated for the double exponent with those obtained for a single exponent. Such a comparison is presented in Table III. Split zeta exponents are expected to lower the energy since additional freedom is introduced into the wave function by their use. However, upon examination of the computed dipole moments,

TABLE IV

EXPERIMENTAL GEOMETRIES FOR H_2S, SO_2, CS WITH MOLECULAR CO-ORDINATES IN ATOMIC UNITS

Molecule	Bond Length Å	Bond Angle	Centre	X	Y	Z
H_2S	1.328	92.2(a)	H_1	0.0	-1.808296	1.740163
			H_2	0.0	+1.808296	1.740163
			S	0.0	0.0	0.0
CS	1.5349(b)		C	0.0	0.0	2.900596
			S	0.0	0.0	0.0
SO_2	1.4321	119.5(c)	O_1	0.0	-2.337823	1.363378
			O_2	0.0	+2.337823	1.363378
			S	0.0	0.0	0.0

(a) Reference 40

(b) Reference 42

(c) Reference 41

it is seen that incorporation of split zeta d exponents does not produce significant improvements over the values obtained using single zeta d functions.

II.3 GEOMETRY:

The investigation of geometry for the three molecules included an optimisation of bond lengths in both of the basis sets considered, but not of bond angles. This neglect of bond angle optimisation was justifiable on the basis of previous investigation by other workers in the group. Their results[37] indicate that the inclusion of d orbitals does not greatly affect the bond angle. The pertinent experimental geometries, together with the cartesian coordinates calculated using these values are presented in Table IV. Results of bond length optimisation are included in Table V for H_2S, Tables VI, VII for CS and Tables VIII, IX for SO_2. In each case the optimum bond length reported for the 'with d' calculations have been obtained using the optimum theoretical d orbital exponents.

For hydrogen sulphide, it was found that the computed optimum bond length was only slightly improved by the addition of d functions to the molecular basis. Without d orbitals, the theoretical H-S bond length was 1.36Å in fair agreement with the experimental value of 1.328Å[40]. When d functions were added, the computed bond length improved to a value of 1.33Å.

Again, as for hydrogen sulphide, the agreement of calculated optimum geometry with experimental observation for carbon monosulphide is improved by the inclusion of d functions in the basis set. The decrease of the C-S bond length from 1.63Å to 1.56Å which was observed

TABLE V

HYDROGEN SULPHIDE RESULTS OF CALCULATIONS COMPARED WITH PREVIOUS WORK

	This Work Without d	This Work with d	Calculation II Without d (a)	Calculation II With d (a)	Calculation III With d (b)	Experimental Values
Gaussian Primitive Set	(4/22424)	(4/224242)	(3/33333)	(3/333333)	(41,1/62,11,11,61,11,1)	
Orbital Energies	-87.7324 -8.4083 -6.1377 -6.1363 -6.1324 -0.9208 -0.5396 -0.4375 -0.3412	-87.7250 -8.3948 -6.1283 -6.1263 -6.1206 -0.9133 -0.5529 -0.4533 -0.3342			-91.9744 -8.9617 -6.6520 -6.6510 -6.6487 -0.9859 -0.5940 -0.5008 -0.3834	
Total Energy (a.u)	-384.6491	-384.7015	-394.463	-394.516	-398.68624	
-V/T	2.022	2.022			2.00019	
Optimized Bond Length Å	1.38	1.33				
d Orbital Exponents		1.66			0.6	
1st Ionizat'n Potent'l (a.u)	0.3412	0.3342	0.356	0.343	0.3833	0.384 (a)
Dipole Moment (D)	1.55	0.469	1.74	0.66	1.3345	0.937 (c)

(a) Reference 43 (b) Reference 17 (c) Reference 38 upon addition of d orbitals is to be expected as a result of the sulphur atom's capacity for participation in pπ - dπ bonding. Agreement of the optimum theoretical bond length of 1.56Å, with the experimental value of 1.5349Å[42] is quite good.

Optimisation of the sulphur-oxygen bond length was also influenced by the addition of d functions. For the minimal basis, an optimum bond length of 1.60Å was obtained and was improved to a value of 1.46Å upon extension of the basis set. This latter result agrees fairly well with experiment at 1.4321Å[41]. Addition of d orbitals increases the bonding between sulphur and oxygen through a dπ - pπ mechanism and a consequent decrease in the sulphur-oxygen bond distance is observed.

II.4 DIPOLE MOMENT

The effects of d orbitals included in the basis set on the calculated dipole moment were also studied. A prerequisite for this study was the compilation of a new version of the dipole moment programme which could be appended to the POLYATOM package. Details of the required integral formulae are given in appendix I and a copy of the programme itself constitutes appendix II of this work.

On the basis of the results obtained in this set of calculations, it may be concluded that the dipole moment is a molecular property which is extremely sensitive both to molecular geometry and the nature of the basis set. To illustrate this sensitivity, it was found in the extended basis hydrogen sulphide calculations that a bond length change of 0.1Å produced a difference of 0.12D in the dipole moment. Dependence of dipole moment on bond length, and also bond angle, is to be expected since

TABLE VI

CARBON MONOSULPHIDE: RESULTS OF CALCULATIONS

	This Work With d	This Work Without d
Gaussian Primitive Set	(244/224242)	(244/22424)
Orbital Energies	-87.7982 -10.7413 -8.4670 -6.2033 -6.1932 -6.1932 -1.0390 -0.6339 -0.4282 -0.4282 -0.4007	-87.7986 -10.7659 -8.4748 -6.2053 -6.1990 -6.1990 -1.0493 -0.6290 -0.4240 -0.4240 -0.4117
Total Energy (a.u)	-419.8689	-419.8099
Optimized Bond Length. (Å)	1.56	1.60
-V/T	2.022	2.022

TABLE VII

COMPARISON OF PRESENT CARBON MONOSULPHIDE CALCULATIONS WITH PREVIOUS WORK

	This Work Without d	This Work With d	Calculation II Without d (a)	Calculation II With d (a)	Experimental Values
Gaussian Primitive Set	(244/22424)	(244/224242)	(333/33333)	(333/333333)	
Total Energy (a.u)	-419.8099	-419.8689	-430.617	-430.679	
d Orbital Exponents		$\zeta_1 = 1.63$ $\zeta_2 = 1.75$		1.60	
1st Ionization Potential (a.u)	0.4117	0.4007	0.425	0.417	0.393(a)
Dipole Moment (D)	1.05	2.52	0.97	2.23	1.97 (b)

(a) Reference 43

(b) Reference 38

geometry determines the charge distribution and hence the polarity in the molecule. However, the effect of incorporation of d functions into the minimal basis set was to produce a large change in the dipole moment. For the experimental equilibrium geometry of hydrogen sulphide, the minimal basis dipole moment was 1.55D and the extended basis value 0.553D. The difference could be an indication of participation by d orbitals in the molecular bonding. This participation is made possible by the ability of these orbitals to alter the charge distribution in the molecule by behaving as polarizing functions.

On comparison of the calculated dipole moment (0.553D) of H_2S with the experimental value[38] of 0.937D it is evident that the addition of d functions produces an improvement, in the correct sense, from the value obtained without d functions (1.55D). Despite the improvement on addition of d orbitals, a discrepancy in dipole moment of approximately forty per cent still remains to be accounted for. To obtain better agreement, further modifications to the basis set seem to be necessary.

In order to explore in more detail the influence of basis set upon dipole moment, a series of calculations in which the primitive composition of the set was varied, was performed. The results of this study for H_2S are presented in Table X and seem on the whole to indicate that the molecular properties are intrinsically dependent on the size of the gaussian set chosen to represent the functions constituting the minimal basis set. According to these calculations, although the molecular wave function and molecular energy both improve upon increased gaussian specification of the s type functions, the dipole moment computed deteriorates. Furthermore, it is evident that the most influential factor in the determination of dipole moment is the nature of the gaussian representation of the p functions in the set. As the number of p type gaussian primitives used for the expansion of Slater p orbitals is augmented, the dipole moment improves, especially if the s type functions remain unaltered. Also, the dipole moment does not seem to be greatly influenced by inclusion of additional d type gaussians in the set. Hence, it would seem that the critical factor in determining the value of dipole moment is the quality of the gaussian expansion used for the representation of the polarizable p type Slater orbitals. This evaluation of the effect of the nature of gaussian primitive set on molecular properties was performed exclusively for H_2S and not repeated for the other two molecules. However, it is reasonable that similar results could be obtained for sulphur dioxide and carbon monosulphide, and in fact be extended to all second row molecule calculations which rely on Stewart's expansions of Slater type orbitals.

Calculations for the equilibrium geometry of carbon monosulphide also indicate that addition of d orbitals to the minimal basis set improves the dipole moment in the desired sense but tends to overcompensate by creating too large a correction. The dipole moment obtained without d orbitals was 1.36D and this value increased to 2.52D upon addition of d orbitals, whereas the experimental dipole moment is quoted as 1.97D[38]. Since the experimental value is almost the mean of the two calculations, a significant improvement obtained by extension of basis set cannot in this case be justifiably claimed. However, the fact that

TABLE VIII

SULPHUR DIOXIDE: COMPARISON OF ENERGIES FOUND IN PRESENT CALCULATION WITH PREVIOUS RESULTS

	This Work Without d	This Work With d	Calculation II Without d (a)	Calculation II With d (a)	Calculation III With d (b)
Gaussian Primitive Set	(244/22424)	(244/224242)	(333/33333)	(333/333333)	(34,21,41,1/62, 11,11,61,11,1)
Orbital Energies (a.u)	-87.9532 $1a_1$ -19.4331 $1b_2$ -19.4327 $2a_1$ -8.6094 $3a_1$ -6.3417 $2b_2$ -6.3366 $4a_1$ -6.3363 $1b_1$ -1.3003 $5a_1$ -1.1999 $3b_2$ -0.7850 $6a_1$ -0.5465 $7a_1$ -0.5250 $4b_2$ -0.5250 $2b_1$ -0.3948 $5b_2$ -0.3481 $8a_1$ -0.3002 $1a_2$ +0.2203 $3b_1$	-88.0647 -19.6136 -19.6118 -8.6772 -6.4204 -6.4095 -6.4091 -1.4447 -1.3364 -0.7838 -0.6513 -0.6265 $2b_1$ -0.6208 $4b_2$ -0.4786 $5b_2$ -0.4614 $1a_2$ -0.4280 $8a_1$ +0.3108 $3b_1$	-90.9994 -20.2615 -20.2614 -8.9846 -6.6609 -6.6538 -6.6537 -1.4533 -1.3244 -0.7910 -0.6046 -0.6019 -0.5572 -0.3963 -0.3319 $8a_1$ -0.3184 $1a_2$	-91.1017 -20.5120 -20.5116 -9.0565 -6.7371 -6.7287 -6.7289 -1.5329 -1.4244 -0.8541 -0.6878 -0.6628 -0.6603 -0.5016 -0.4838 $1a_2$ -0.4437 $8a_1$	-92.1961 $1a_1$ -20.6134 $1b_2$ -20.6134 $2a_1$ -9.1632 $3a_1$ -6.8532 $2b_2$ -6.8519 $1b_1$ -6.8500 $4a_1$ -1.5095 $5a_1$ -1.4038 $3b_2$ -0.8695 $6a_1$ -0.6986 $4b_2$ -0.6959 $7a_1$ -0.6665 $2b_1$ -0.5400 $5b_2$ -0.5161 $1a_2$ -0.4917 $8a_1$ +0.0140 $3b_1$
Total Energy (a.u)	-527.4034	-527.7699	-540.648	-541.008	-547.2089
-V/T	2.019	2.025			2.00026

(a) Reference 16, 43

(b) Reference 15

TABLE IX

MOLECULAR PROPERTIES OF SULPHUR DIOXIDE: COMPARISON OF PRESENT WORK WITH PREVIOUS CALCULATIONS

	This Work Without d	This Work With d	Calc. II Without d (a)	Calc. II With d (a)	Calc. III Without d (b)	Calc. III With d (b)	Experimental Values
Optimized Bond Length (Å)	1.60	1.46					1.4321 (d)
d Orbital Exponents		$\zeta_2 = 1.63$ $\zeta_1 = 1.40$		1.20		S: 0.6 O: 0.8	
1st Ionization Potential (a.u)	0.3002	0.4280	0.318	0.444	0.4928	0.4917	0.454 (a)
Dipole Moment (D)	1.12	1.26	1.24	0.81	2.83	2.28	1.61 (c)

(a) Reference 16, 43

(b) Reference 15

(c) Reference 38

(d) Reference 41

the addition of d orbitals produces an increase in value of dipole moment, in agreement with required change, while in H_2S this process results in a decrease, as desired, seems to indicate the necessity of inclusion of d orbitals in these compounds. It appears that d orbitals are definitely required for an accurate description of bonding in sulphur compounds, and presumably also those involving other second row elements.

An additional calculation was performed for carbon monosulphide with the purpose of investigating the contribution made by the core orbitals to the dipole moment of this molecule. It was found that the sum of the electronic and balancing nuclear components of the dipole moment was only 6.56×10^{-3}D, approximately 0.3% of the total. Consequently, it would appear the dipole moment is determined almost completely by the effectiveness of the valence orbital representation. In these calculations however, the valence representation is affected by improvement to core atomic orbitals. This is a consequence of the non orthogonality of the core and valence functions comprising the basis sets used in these calculations. The relatively small proportion of the dipole moment attributable to the core orbitals is not surprising since the dipole moment is a property dependent on the electron distribution within a molecule. As the core orbitals are quite tightly associated with the nucleus, and not extensively delocalized, their contribution to the polarization within the molecule will be negligible. Therefore, in carbon monosulphide, as most probably in all molecules, the dipole moment is largely determined by the valence electron distribution.

TABLE X

EFFECTS OF VARIATION OF CONTRACTION IN THE GAUSSIAN REPRESENTATION OF THE BASIS SET ON COMPUTED DIPOLE MOMENT FOR HYDROGEN SULPHIDE *

Basis	-V/T	Energy (a.u)	Dipole Moment (D)
(4/224242)	2.02	-384.7015	0.466
(5/335242)	2.00	-392.3561	0.392
(5/335352)	2.00	-394.5211	0.627
(5/335353)	2.00	-394.5229	0.603
(5/225252)	2.02	-384.7022	0.466
(4/224352)	2.02	-386.8755	0.698
(4/224452)	2.02	-387.3098	0.744

* at the experimental equilibrium geometry

Contrary to the trend emerging for the other two molecules studied, the dipole moment of sulphur dioxide deteriorated upon extension of the minimal basis set to include d functions. Theoretical dipole moments calculated for the experimental equilibrium geometry were 1.54D without d and 1.26D with d, compared to an experimental literature value of 1.61D[38]. In this case then, the best computed value was for the basis set in which d orbitals were not included. A possible explanation of this unexpected result is disclosed if the calculation is compared to that for the hydrogen sulphide molecule.

For the series of calculations for H_2S, in which the nature of the gaussian primitive set was varied, it was found that the magnitude of dipole moment was decreased when additional s components were included in the gaussian primitive set. A similar effect was produced by the addition of d orbitals, a modification which also served to improve the quality of the molecular wave function. The improvement was indicated by the decrease in the deviation of theoretical dipole moment value from the experimental value. Although the same improvements in wave function were produced in the case of sulphur dioxide when d orbitals were added, the theoretical value of dipole moment was not improved. The minimal basis dipole moment seemed to agree so well with experiment that the additional d functions produced an effect opposite to the one desired - the deviation from the experimental value being increased. However, this effect does not necessarily imply that d functions are not required for second row atoms. The interpretation attributed to data available from this type of calculation is extremely subjective, in that it depends upon choice of experimental data for comparison. For example, two microwave values for dipole moment quoted in the tables[38] are 1.47D and 1.59D. This difference is fairly important in the comparison with calculated theoretical results. To illustrate this point it only requires comparison of this work with a similar type of calculation recently reported[16], in which three gaussian functions were used for each Slater orbital. In that work, an evaluation of the use of minimal basis as opposed to extended basis (d orbital exponent 1.20) calculations was based on the theoretical values found for various molecular properties including dipole moment. The dipole moments reported are 1.244D without d, 0.806D with d and 1.47D experimental. Although the general trend obtained is analogous to that found in this series of computations, the quoted experimental value is quite difference from that used here (1.61D) but was taken from the same reference[38]. So it would seem that part of the difficulty in evaluating theoretical results is the fairly wide variation of experimental values available for comparison. If the present theoretical results were compared to an experimental value of 1.47D, then the two basis sets would appear almost equally suited for the prediction of dipole moment. Despite the conclusion of the authors in the above reference that the results obtained with the minimal basis calculations might be fortuitous, this pattern has been repeated in the present computation and cannot so readily be dismissed. It is believed that the most likely explanation is the inadequacy of the gaussian representation used in both of the calculations. As discussed in the case of hydrogen sulphide, the present basis set would require extensive modification in order to produce the optimum gaussian representation of the minimal basis which would be appropriate for an evaluation of the participation made by d orbitals in bonding.

II.5 FORCE CONSTANTS:

Although this molecular property could be readily determined on the basis of the data already obtained in the course of these computations, the significance of such a procedure is questionable. There are at least two reasons for such a statement. The first is the aura of uncertainty connected with experimental data available for comparison with theoretical results in the case of all molecules, except diatomics.

To obtain the appropriate experimentally determined values would require an investigation of the mathematical analysis used by the various experimentalists to calculate these constants from spectroscopic data. Once this had been established, then a transformation of the experimental force constants would most probably be necessary to ensure that both experimental and theoretical calculations were referred to the same coordinate system. The main problem for polyatomic molecules is obtaining the correct experimentally derived value of the force constant for comparison with the theoretically computed second derivative.

The second reason for doubting the significance of a comparison between theory and experiment is the fact that there exists a marked dependence of theoretically computed values on the nature of the computational technique used. The mathematical concepts pertaining to three possible computational methods available for calculation of force constants within the ab initio approach are discussed in the literature[46].

The force method, which involves initial analytical differentiation followed by numerical differentiation, is concluded to be superior to the alternative approach requiring two successive direct numerical differentiations. Economically, this latter procedure is less suitable since it requires computation of molecular wave functions for a series of geometries. Another disadvantage is that additional numerical inaccuracy is introduced by this technique. It is also pointed out that ab initio calculations which do not predict accurate bond dissociation energies will naturally not yield accurate results but are found to overestimate bond stretching force constants. This problem is often encountered in ab initio calculations and will partially account for the poor theoretical results obtained in force constant evaluation.

In this work, the force constants of carbon monosulphide, hydrogen sulphide, and sulphur dioxide were computed. However, the method used was comparatively straightforward, since force constant values were determined directly by double differentiation despite the previously mentioned disadvantages of such a procedure. To evaluate this secondary molecular property, it was simply necessary to fit the energy as a function of bond length data to a quadratic equation representing a parabolic curve:

$$E(r) = ar^2 + br + c$$

If $E(r)$ is the energy, r the bond length and a, b, c are constants, then the force constant is given by the second derivative of $E(r)$ with respect to r and in this notation is equal to $2a$.

TABLE XI

FORCE CONSTANTS CALCULATED USING BOTH A QUADRATIC AND CUBIC FIT OF BOND LENGTH DATA FOR H_2S, CS AND SO_2 MOLECULES

Molecule	Force Constants (mdyn/Å)		
	Quadratic	Cubic	Experimental(a)
H_2S minimal basis	4.78	5.32	4.14
H_2S with d	6.78	5.53	
CS minimal basis	12.8	10.8	8.48(b)
CS with d	15.6	11.8	
SO_2 minimal basis	8.61	37.5	9.97
SO_2 with d	13.9	15.4	

(a) Reference 44

(b) Calculated according to formula and data given in Reference 47

As well as the quadratic fit, a cubic fit of the data was also attempted in order to determine whether any improvement in the force constants could be achieved by including the third order term; in this case, the force constants were evaluated for the computed optimum bond length, in accordance with the equation:

$$f = \frac{d^2E(r)}{dr^2} = 6ar_o + 2b$$

However, as a comparison of the results presented in Table XI will indicate, no advantage is gained by use of the cubic fit for the available computational data.

It will be observed that in the calculation of force constants, contrary to the trend obtained for other molecular properties, the inclusion of d functions was found to cause an increase in the discrepancy between experimental and theoretical values. The experimental force constants[44] which are listed in Table XI are not strictly the correct values for comparison with calculations. The reasons for this have been discussed earlier in this section. An additional factor which should be taken into consideration in making such a comparison is the nature of the assumptions made regarding the molecular system in the process of computation of the force constants. In the present calculations, the force constants of the triatomic molecules have been computed for the symmetric stretch of two bond lengths simultaneously. Values tabulated in the literature refer to the stretch of one bond of the molecule only. Consequently, on account of the existing arbitrariness, the agreement of computed force constants with experimental observation cannot be used as an effective criterion in determining the importance of d orbitals.

To complete this section concerned with the effects of d orbitals on the molecular properties of some sulphur compounds it remains to summarize the scope and significance of these ab initio calculations. This is partially accomplished in an extensive presentation of results in Tables V through IX, where the calculations are also compared with similar work by other investigators. Several of the results quoted from other sources are for calculations in which the basis set was much more elaborate than that used in the present work. For example, one series of calculations involved a basis set which had been extended to include p type functions on hydrogen and d functions on oxygen atoms. Although such differences in basis set achieve significant improvement in the molecular energy, it will be noted that molecular properties computed using the present minimal basis set are comparable to those obtained by other workers using their elaborate basis sets. In this sense then, the necessity of a very large basis is dubious and it would appear that minimal basis sets are relevant for calculations of second row molecules.

CHAPTER III

SULPHUR DIOXIDE: A STUDY OF THE MOLECULE, THE RADICAL ANION, AND SOME EXCITED STATES; A COMPARISON WITH OZONE

Since to date much interest has been expressed in the electronic spectrum of sulphur dioxide, it was decided to attempt an extended basis ab initio calculation for the purpose of investigating some of the excited states. It was hoped that such a study would provide a theoretical comparison for experimental results, and at the same time determine whether some of the spectral features could be interpreted. In this chapter are presented results of calculations for the ground state and lowest excited triplet states of sulphur dioxide. Comparable calculations were run for ozone in order to obtain an estimate of the importance of d orbitals in sulphur compounds. The sulphur dioxide radical anion was also considered since this ion might prove to be important in the study of atmospheric pollutants.

III.1 ELECTRONIC SPECTRUM OF SULPHUR DIOXIDE

In order to provide a frame of reference for theoretical results, a brief description of the electronic spectrum of sulphur dioxide will be presented here. The details have been taken from one of the several available sources[48] which provide a fairly extensive description of the electronic spectrum together with numerous references to the original experimental data.

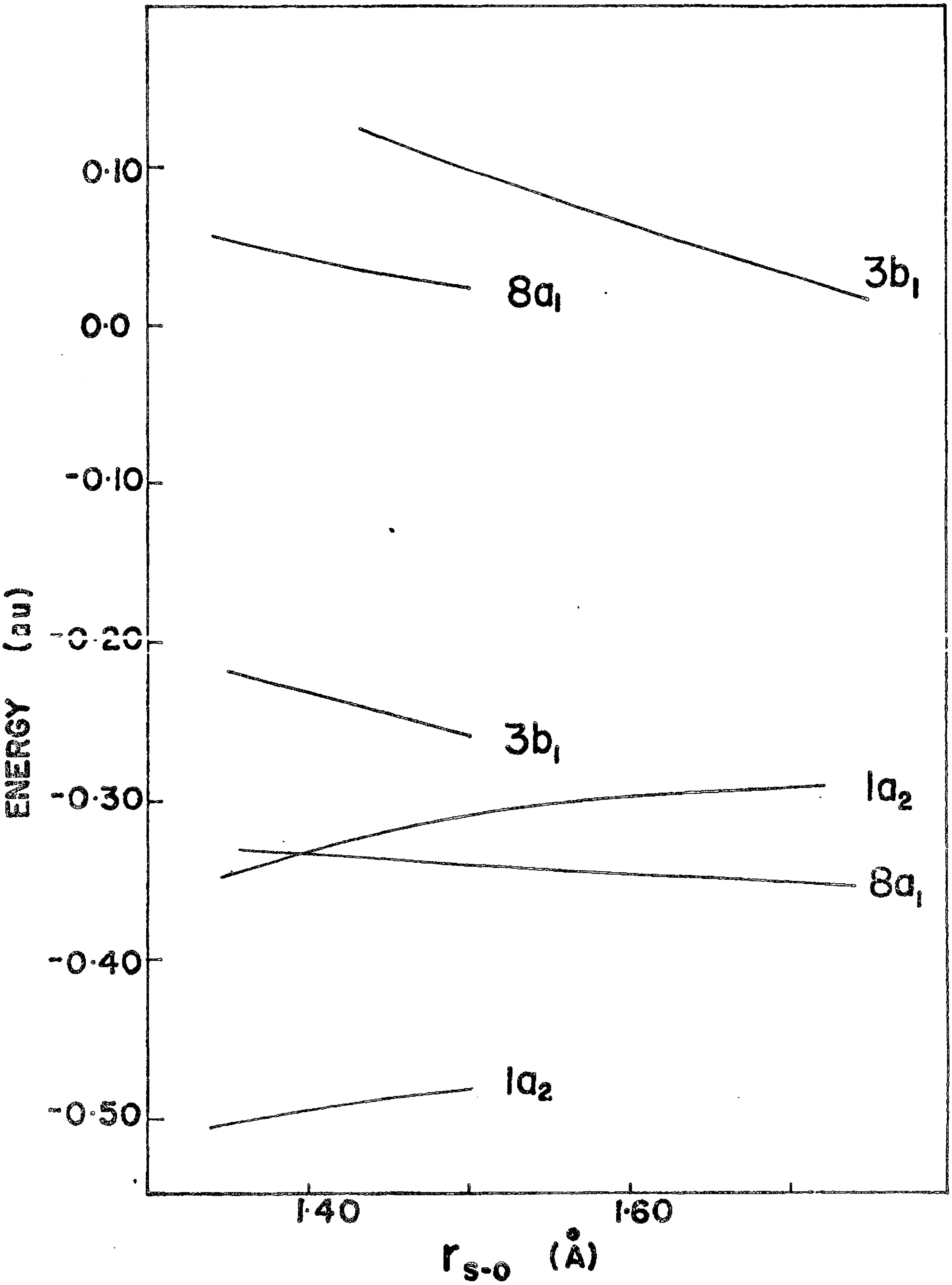
The sulphur dioxide spectrum consists of a series of discrete absorption bands, of which the lowest energy occurs at 3900Å - 3400Å and is also the weakest band. This band, and that immediately adjacent to it, (3400Å - 2600Å) have been shown to correspond to separate transitions. The extensive band structure associated with these absorptions is explained by the Franck-Condon principle[49] to be a result of a change in both bond angle and bond length occurring during excitation. The intensity of some of the bands is greater than that expected on the basis of the Franck-Condon principle. To account for this, Mulliken[50] has suggested that the geometry of the lowest energy excited state is asymmetric. Furthermore it is thought, on the evidence of a strong Zeeman splitting[61], that the upper state for the lowest energy band has a triplet multiplicity and that the transition involved corresponds to $^3B_1$-$^1A_1$. Although such a transition is spin forbidden, it occurs as a result of spin orbit coupling, perhaps borrowing intensity from the neighboring $^1B_1$-$^1A_1$ transition[48].

III.2 GROUND STATE CALCULATIONS FOR SULPHUR DIOXIDE

In Chapter II, the results of an investigation using minimal and extended basis calculations, of several of the ground state properties of sulphur dioxide have been reported. During the minimal basis sulphur-oxygen bond length optimisation procedure a discontinuity in behaviour was encountered. It was found that for the 'free' calculation - one in which the orbital occupancy is determined by the self consistent field procedure rather than being specified by input data - the orbital occupancy for S-O

Figure IV

Energy of the $8a_1$, $1a_2$ and $3b_1$ symmetry orbitals as a function of S-O bond length in Sulphur Dioxide without d orbitals. The curves at short S-O distances are for free occupancy.


0·10
0·0
-0·10
-0·20
-0·30
-0·40
-0·50
ENERGY (au)
8a₁
3b₁
3b₁
1a₂
8a₁
1a₂
1·40
1·60
r_{s-o} (Å)

bond distances shorter than 1.52Å differed from that for longer distances. The occupancy determined for the short bond length calculation was:

$$\ldots\ (7a_1)^2(4b_2)^2(1a_2)^2(5b_2)^2(3b_1)^2$$

compared to that for the longer S-O distances which was:

$$\ldots\ (2b_1)^2(5b_2)^2(8a_1)^2(1a_2)^2$$

For the short S-O bond lengths, the calculation without d functions appeared to converge naturally on an excited state of sulphur dioxide. The results obtained for the calculations without d functions are summarized in figure IV where the variation of orbital energies is presented as a function of bond distance. It will be noted that the rearrangement of orbitals is drastic enough, for the free calculation, to result in the apparent discontinuity caused by the calculation being trapped in a local minimum. Once the orbital occupancy had been specified in accordance with that found by other workers[51] this discontinuity in results was removed.

No such complication occurred for calculations with the extended basis set. The free calculation in this instance yielded an orbital occupancy which agreed with other results[15,51]. However, as seen in the comparison presented in figure V, the ordering of orbitals obtained for the basis set used in this computation differs from that qualitatively suggested by Walsh[51] for non linear 18-electron AB_2 systems. More important, the present ordering is also different from that found by Rothenberg and Schaefer[15] in their fairly detailed and extensive ab initio

Figure V

ORDERING OF MOLECULAR ORBITALS IN SULPHUR DIOXIDE

WALSH:[51]

.... $(a_1)^2\ (b_1)^2\ (b_2)^2\ (a_1)^2\ (a_2)^2\ (b_2)^2\ (a_1)^2/b_1$

ROTHENBERG AND SCHAEFER[15]

$(1a_1)^2\ (1b_2)^2\ (2a_1)^2\ (3a_1)^2\ (2b_2)^2\ (1b_1)^2\ (4a_1)^2\ (5a_1)^2\ (3b_2)^2$

$(6a_1)^2\ (4b_2)^2\ (7a_1)^2\ (2b_1)^2\ (5b_2)^2\ (1a_2)^2\ (8a_1)^2/3b_1$

HILLIER AND SAUNDERS:[16]

$(1a_2)^2\ (1b_2)^2\ (2a_1)^2\ (3a_1)^2\ (2b_2)^2\ (4a_1)^2\ (1b_1)^2\ (5a_1)^2\ (3b_2)^2$

$(6a_1)^2\ (7a_1)^2\ (2b_1)^2\ (4b_2)^2\ (5b_2)^2\ (1a_2)^2\ (8a_1)^2/3b_1$

PRESENT EXTENDED BASIS CALCULATION:

$(1a_1)^2\ (1b_2)^2\ (2a_1)^2\ (3a_1)^2\ (2b_2)^2\ (4a_1)^2\ (1b_1)^2\ (5a_1)^2\ (3b_2)^2$

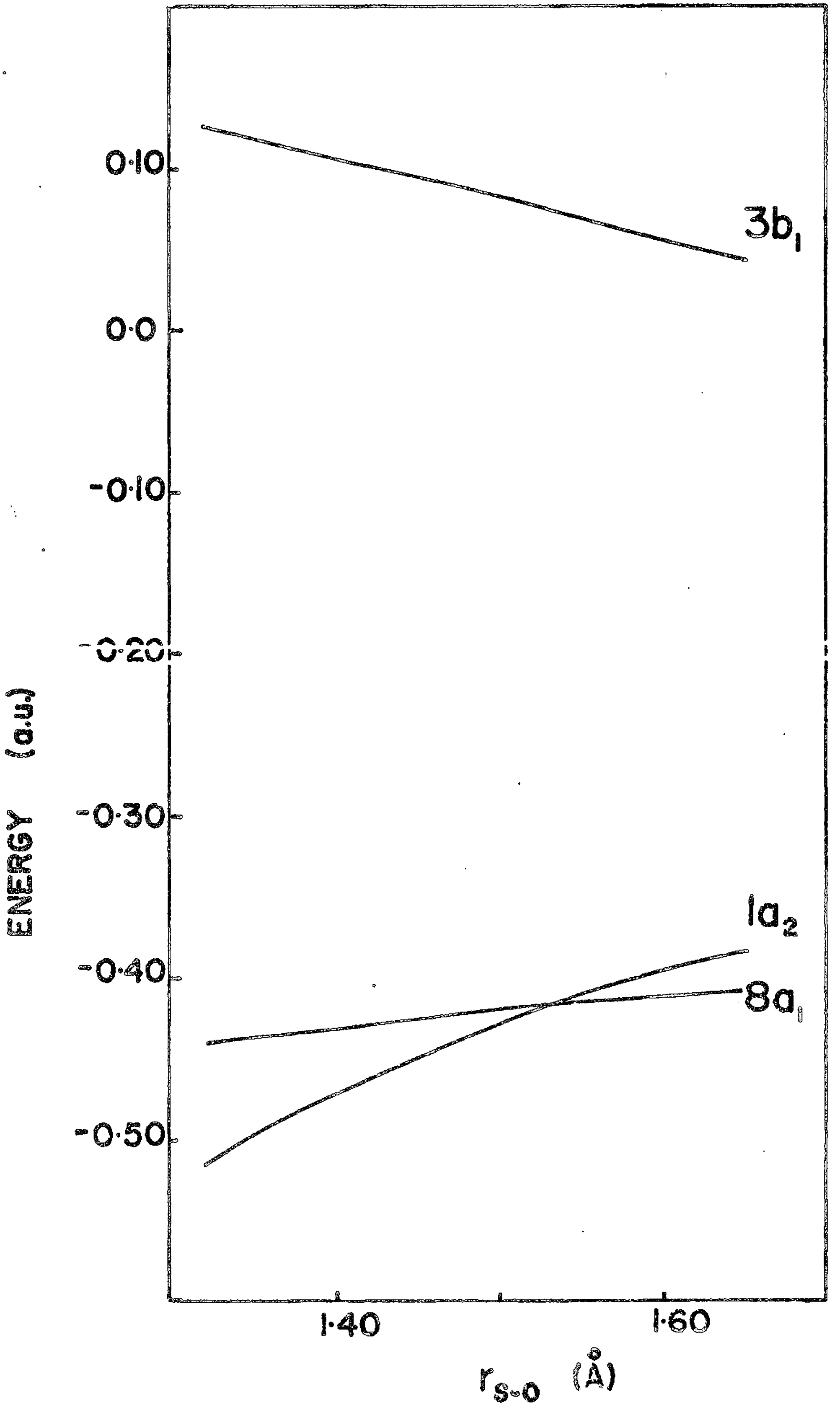
$(6a_1)^2\ (7a_1)^2\ (2b_1)^2\ (4b_2)^2\ (5b_2)^2\ (1a_2)^2\ (8a_1)^2/3b_1$

Figure VI

Energy of $3b_1$, $8a_1$ and $1a_2$ symmetry molecular orbitals

as a function of S-O bond length for the

ground state of Sulphur Dioxide with d orbitals.


0·10
0·0
-0·10
-0·20
-0·30
-0·40
-0·50
ENERGY (a.u.)
3b$_1$
1a$_2$
8a$_1$
1·40
1·60
r$_{S-O}$ (Å)

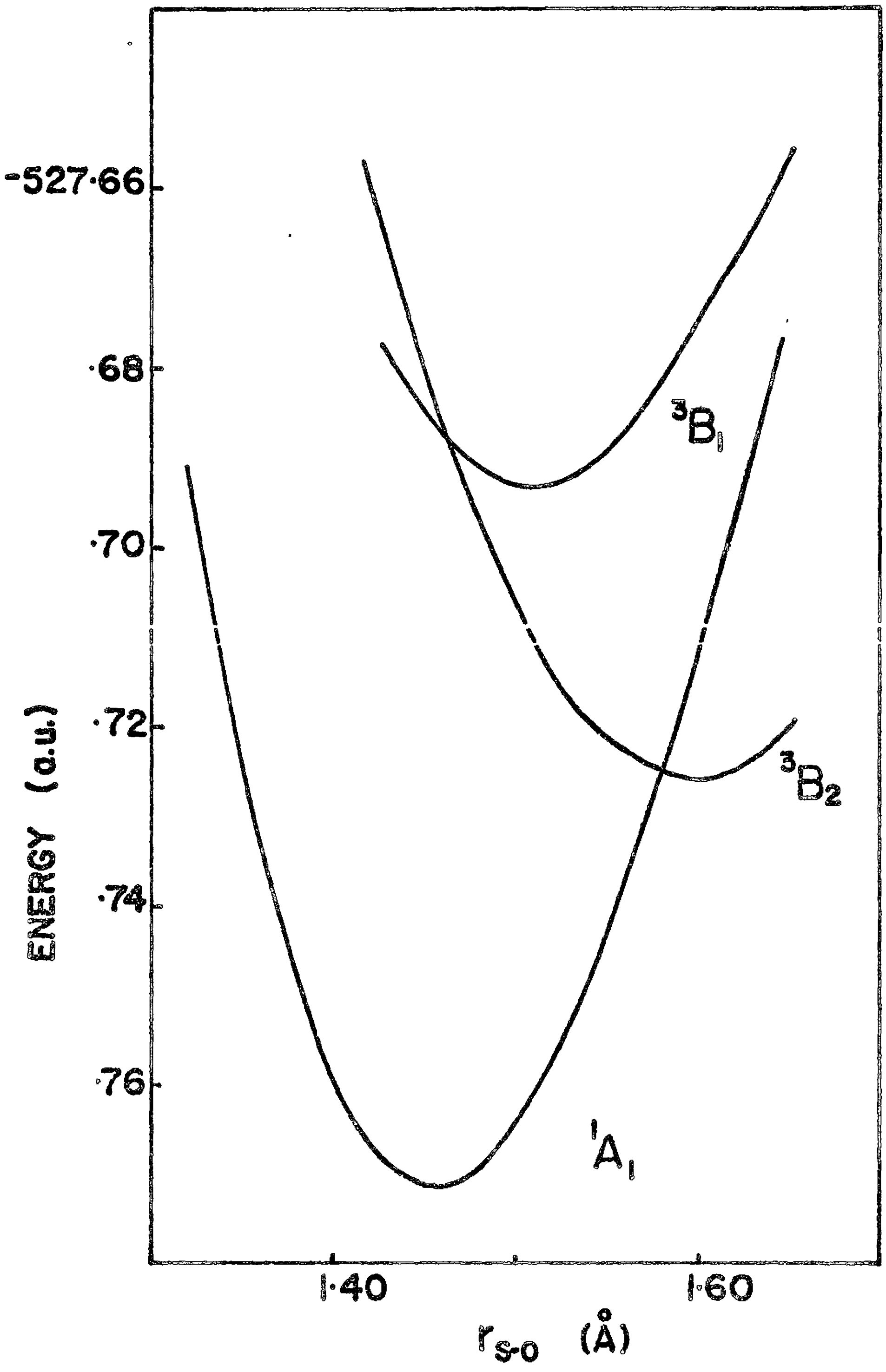
calculations. The difference is only minor since the three molecular orbitals which are out of order have very similar energies, in this calculation -0.6514 a.u. ($7a_1$), -0.6265 ($2b_1$), and -0.6029 ($4b_2$). The energy variation of the two highest occupied and of the lowest vacant molecular orbitals in sulphur dioxide as a function of bond length is presented in figure VI. It is seen that for S-O bond distances greater than 1.53Å, the highest occupied molecular orbital is one of a_2 symmetry, a result also obtained in the minimal basis calculations. However, at both the theoretical and experimental equilibrium S-O bond distances, 1.46Å and 1.4321Å respectively, the orbital of a_2 symmetry is stabilized relative to the a_1. This relative stabilization is understandable if the composition of these symmetry orbitals is considered. The a_1 symmetry orbital consists mainly of p_z components on the three nuclei, whereas the a_2 orbital is composed of p_x functions on the oxygen atoms and dxy function on the sulphur atom. At short internuclear distances, the $d\pi$-$p\pi$ interaction is much more extensive than the $p\sigma$ contribution to bonding through the a_1 symmetry molecular orbital. This explanation also accounts for the more rapid destabilization of the a_2 symmetry orbital.

III.3 EXCITED TRIPLET STATES OF SULPHUR DIOXIDE

Since the results of the sulphur dioxide computation for the basis set which included d functions seemed reliable, it was decided to use this basis for the study of the two lowest energy excited triplet states of sulphur dioxide. The lowest energy triplet studied was the $^3B_1$ state, corresponding to the excitation of an electron from the highest occupied molecular orbital in the ground state calculation - one

Figure VII

Energy of the ground state ($^1A_1$), and the two lowest energy excited triplet states ($^3B_2$, $^3B_1$) of Sulphur Dioxide as a function of S-O bond length for constant OSO bond angle of 119.5°.


-527·66
·68
·70
·72
·74
·76
ENERGY (a.u.)
1·40
1·60
r$_{S-O}$ (Å)
$^3B_1$
$^3B_2$
$^1A_1$

of a_1 symmetry - to the lowest vacant molecular orbital which was of b_1 symmetry:

$$\ldots\ldots (5b_2)^2\ (1a_2)^2\ (8a_1)^1\ (3b_1)^1 \qquad {}^3B_1$$

Also, the ${}^3B_2$ state, resulting from promotion of an electron from the second highest energy occupied molecular orbital, symmetry a_2, to the lowest vacant molecular orbital, was included in this study:

$$\ldots\ldots (5b_2)^2\ (1a_2)^1\ (8a_1)^2\ (3b_1)^1 \qquad {}^3B_2$$

The results described in this work for the excited triplet states are based on calculations performed using PA400 - a version of the unrestricted Hartree-Fock open shell programme included in the POLYATOM compendium.

The theoretical ordering of states found, as well as a comparison of the energy dependence of the excited states on the S-0 bond distance with that observed for the ground state, is presented in figure VII.

An important feature of the dependence of state energies on bond distance, as presented in figure VII, is that at bond lengths close to the theoretical optimum ground state value, the ${}^3B_1$ and ${}^3B_2$ excited states have the same energy. At the experimental equilibrium geometry the ordering of states, in order of increasing energy, is ${}^1A_1$, ${}^3B_1$, ${}^3B_2$ whereas for bond lengths greater than 1.46Å, this becomes ${}^1A_1$, ${}^3B_2$, ${}^3B_1$. In addition, the optimum S-0 bond distance calculated for the ${}^3B_1$ state (1.51Å) is longer than that obtained for the ground state but shorter than the ${}^3B_2$ state bond length (1.60Å). These results are summarized in Table XII.

TABLE XII

RESULTS OF CALCULATIONS FOR EXCITED STATES OF SULPHUR DIOXIDE

State	Nature of Excitation	Theoretical Bond Length (Å)	Minimum Energy (a.u)	Excitation Energy (e.v)	Wave Length (Å)	Experimental Wave Length (Å) (a)
$^1A_1(C_{2v})$	ground	1.46	-527.7717			
$^3B_1(C_{2v})$	$b_1 \leftarrow a_1$	1.51	-527.6940	2.30	5382	3800
$^3B_2(C_{2v})$	$b_1 \leftarrow a_2$	1.60	-527.7260	2.36	5243	2900
$^1A_1(C_s)$	ground	1.46/1.56	-527.7534			
$^3B_1(C_s)$	$b_1 \leftarrow a_1$	1.46/1.56	-527.714	1.57	7898	

(a) Reference 46

Again referring to figure VII, and assuming vertical excitation in accordance with the Franck Condon principle, the excitation energies may be calculated. At the equilibrium internuclear distance of 1.4321Å, these are 2.30 ev for the $^3B_1$ state and 2.34 ev for the $^3B_2$ state. These excitation energies would correspond to spectral bands at 5382Å and 5243Å respectively. Both these values occur at lower energy than any of the bands comprising the sulphur dioxide spectrum[48]. The corresponding experimental results[50] indicate that the two lowest energy transitions in sulphur dioxide occur at 3.3 ev and 4.4 ev for the B_1 and B_2 states respectively, giving rise to spectral bands at 3800Å and 2900Å. Furthermore, experimentalists have concluded that an increase in the S-O bond distance of close to 0.06Å[52,53] occurs in the excitation producing the B_1 state and that this value increases further to 1.53Å[48] in the next excited singlet state. Although the theoretical ordering of states, as well as the geometrical changes involved in the excited states, are in agreement with experimental observation the theoretical values for excitation energies are much too small. Such results are however typical of unrestricted open shell calculations.

In the unrestricted Hartree-Fock method, electron correlations not included in the closed shell ground state calculations are introduced for the excited states with the result that the excited state energies are too low relative to the ground state. Hence the theoretical excitation energies calculated in this manner tend to be too low. In order to characterize with more reliability the excited states of sulphur dioxide, further investigation including configuration interaction and a bond angle optimization would seem to be required.

To complete the present study of the excited states of sulphur dioxide, a few calculations were performed in order to test Mulliken's[50] suggestion that the lowest excited state of B_1 symmetry is asymmetric. These calculations consisted of a computation for a typical asymmetric geometry - the ground state equilibrium bond angle of 119.5° and $r_{SO_1} = 1.46\text{Å}$, $r_{SO_2} = 1.56\text{Å}$. This particular geometry was selected since it was thought to be typically representative of an asymmetric stretch from the optimum configuration calculated for the $^3B_1$ state. The ground state for this configuration was less stable than the symmetric ground state configuration at a bond length of 1.51Å. However, the lowest energy triplet excited state produced by an electronic transition from the highest occupied molecular orbital of a' symmetry to the lowest vacant molecular orbital of a'' symmetry, working in the appropriate C_s symmetry group, has a total energy of -527.714 a.u. Comparing this value with the $^3B_1$ (symmetric) energy of -527.684 a.u., it appears that the lowest energy B_1 excited state of sulphur dioxide is indeed asymmetric.

Except for a comparison of these results with a series of analogous calculations for ozone, which remains to be discussed later in this chapter, this concludes the examination of the triplet excited states of sulphur dioxide.

III.4 SULPHUR DIOXIDE RADICAL ANION - GROUND STATE AND LOWEST ENERGY EXCITED STATES

Recently, electron spin resonance spectra[54,55] of the sulphur dioxide radical anion in both the solid and liquid state have been studied, in the hope of elucidating the electronic structure of this radical anion. A similar theoretical investigation was undertaken in order to provide a comparison for experimental results and so perhaps to aid in the interpretation of future experimental observations. The comparison of ground and excited states for the radical involves two open shell calculations and therefore the theoretically computed excitation energies should correspond more closely to the experimental values than those found for sulphur dioxide.

Since no experimental data was available, the geometry assumed for the radical ion was the equilibrium geometry of sulphur dioxide: OSO angle of 119.5° and S-O bond length of 1.4321A. The integrals required for this series of computations had previously been evaluated in the sulphur dioxide calculations. Just as for the excited states of sulphur dioxide, the extended basis set, in which the split zeta d exponents had been optimized was used in the sulphur dioxide radical calculations.

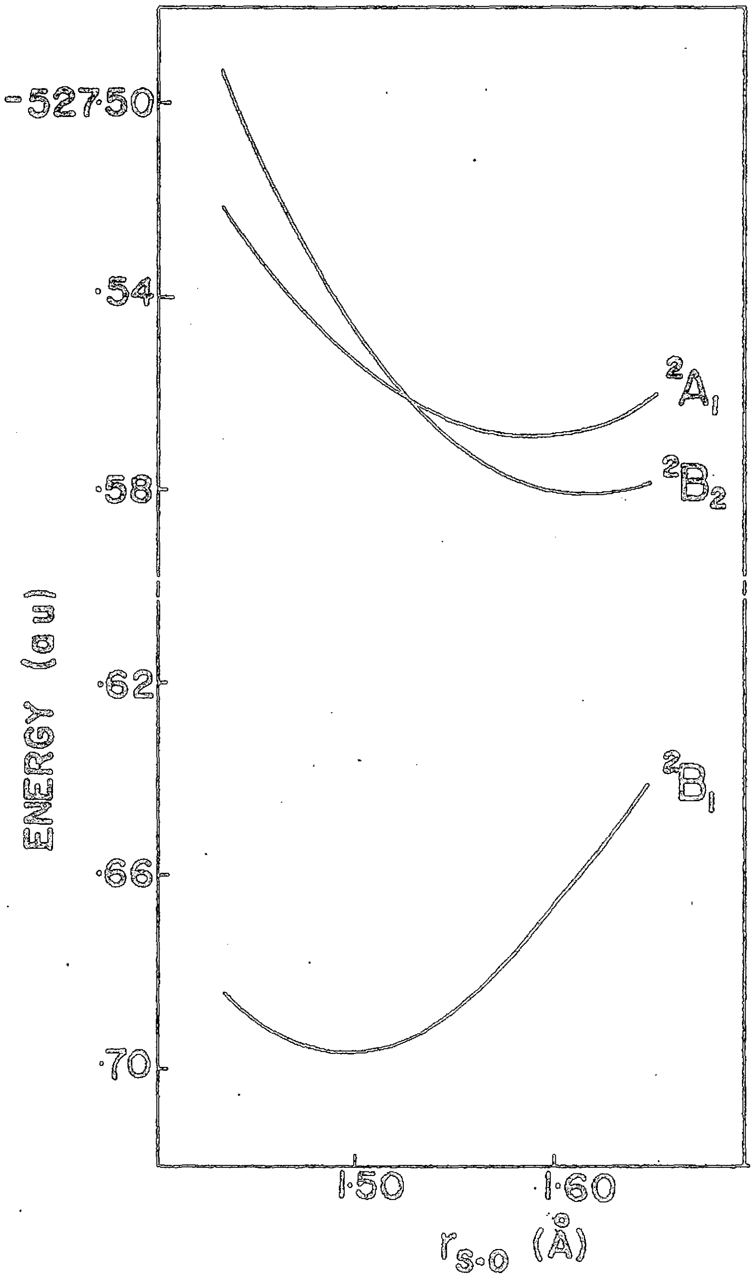
Three states of the sulphur dioxide radical anion were studied to determine the energy dependence on S-O bond length. The $^2B_1$ ground state electronic configuration was the following:

α spin: .... $(4b_2)^1\ (1a_2)^1\ (5b_2)^1\ (8a_1)^1\ (3b_1)^1$

β spin: .... $(4b_2)^1\ (2b_1)^1\ (5b_2)^1\ (1a_2)^1\ (8a_1)^1$

Figure VIII

Energy of the ground state ($^2B_1$) and the two lowest energy excited states ($^2B_2$, $^2A_1$) of the Sulphur Dioxide Radical Anion as a function of S-O bond length.


-527·50
·54
·58
·62
·66
·70
ENERGY (au)
$^2A_1$
$^2B_2$
$^2B_1$
1·50
1·60
$r_{S\text{-}O}$ (Å)

and the two excited states:

$^2A_1$ $(3b_1 \leftarrow 8a_1)$

α spin: .... $(7a_1)^1$ $(4b_2)^1$ $(1a_2)^1$ $(5b_2)^1$ $(3b_1)^1$

β spin: .... $(2b_1)^1$ $(1a_2)^1$ $(5b_2)^1$ $(8a_1)^1$ $(3b_1)^1$

$^2B_2$ $(3b_1 \leftarrow 5b_2)$

α spin: .... $(4b_2)^1$ $(1a_2)^1$ $(7a_1)^1$ $(8a_1)^1$ $(3b_1)^1$

β spin: .... $(2b_2)^1$ $(5b_2)^1$ $(1a_2)^1$ $(8a_1)^1$ $(3b_1)^1$

Not surprisingly, the ordering of the alpha and beta spin molecular orbitals is found to vary considerably depending on the occupancy. The variation in energy as a function of change in S-O bond length is presented in figure VIII. For the radical ion, it was found that the ground state lies well below the lowest excited doublet state, and that the two lowest energy excited doublet states respond quite similarly to change in S-O bond length. An intersection of the energy curves for the $^2B_2$ and $^2A_1$ states occurs at an S-O distance of 1.53Å, the $^2B_2$ state becoming the lower energy excited state of the two at internuclear distances larger than this. For the ground state of the sulphur dioxide radical anion, an optimum S-O distance of 1.50Å was found, with the excited state values being 1.59Å for the $^2A_1$ and 1.62Å for the $^2B_2$ states. These results, in addition to excitation energies and spectral band locations are summarized in Table XIII.

The calculations performed in the course of the study of this radical species are capable of providing useful information for the

TABLE XIII

RESULTS OF CALCULATIONS FOR THE $^2B_1$ GROUND STATE AND $^2B_2$,$^2A_1$ EXCITED STATES OF THE SULPHUR DIOXIDE RADICAL ANION:

State	Optimum Bond Length (Å)	Minimum Energy (a.u)	Excitation Energy (e.v) (a)	Band Location (Å)
$^2B_1$	1.50	-527.698		
$^2A_1$	1.59	-527.570	3.89	3186
$^2B_2$	1.62	-527.581	4.08	3037

(a) Calculated for vertical excitation at the optimum ground state bond distance.

experimental chemist. For instance Green[56] has postulated that the dimerization process leading to the formation of dithionate ion $S_2O_4^=$ in some way involves an excited state of the $SO_2^{\bar{\cdot}}$ species. According to the present results, a minimum activation energy of 3.89 ev would be required for such a process, if the lowest energy excited state were involved. Since this excitation energy is quite high, and the dimerization is known to occur readily, it is unlikely that either of the two doublet states studied here are involved in this process.

III.5 OZONE - GROUND AND EXCITED STATES

The final stage in these calculations consisted of an attempt to evaluate the extent of participation by d orbitals in the bonding of second row atoms. From the experimental point of view, 3d orbitals are thought to play a significant role in the bonding of second row atoms but this does not extend to first row atoms. In theoretical treatments 3d orbitals are included in the basis set of both first and second row atoms for the purpose of expanding the basis set and so increasing the flexibility of the wave function. No special importance is assigned these functions as regards their contribution to bonding.

In order to elucidate the role of 3d orbitals it was decided to perform a series of minimal and extended basis set calculations for ozone, comparable to those previously reported for sulphur dioxide. The extent of d orbital involvement in bonding of first and second row atoms was judged on the basis of three factors: the diffuseness of the 3d functions as determined by the optimum orbital exponent, the contribution made by the 3d orbitals to the bonding molecular orbitals, and the effect of the

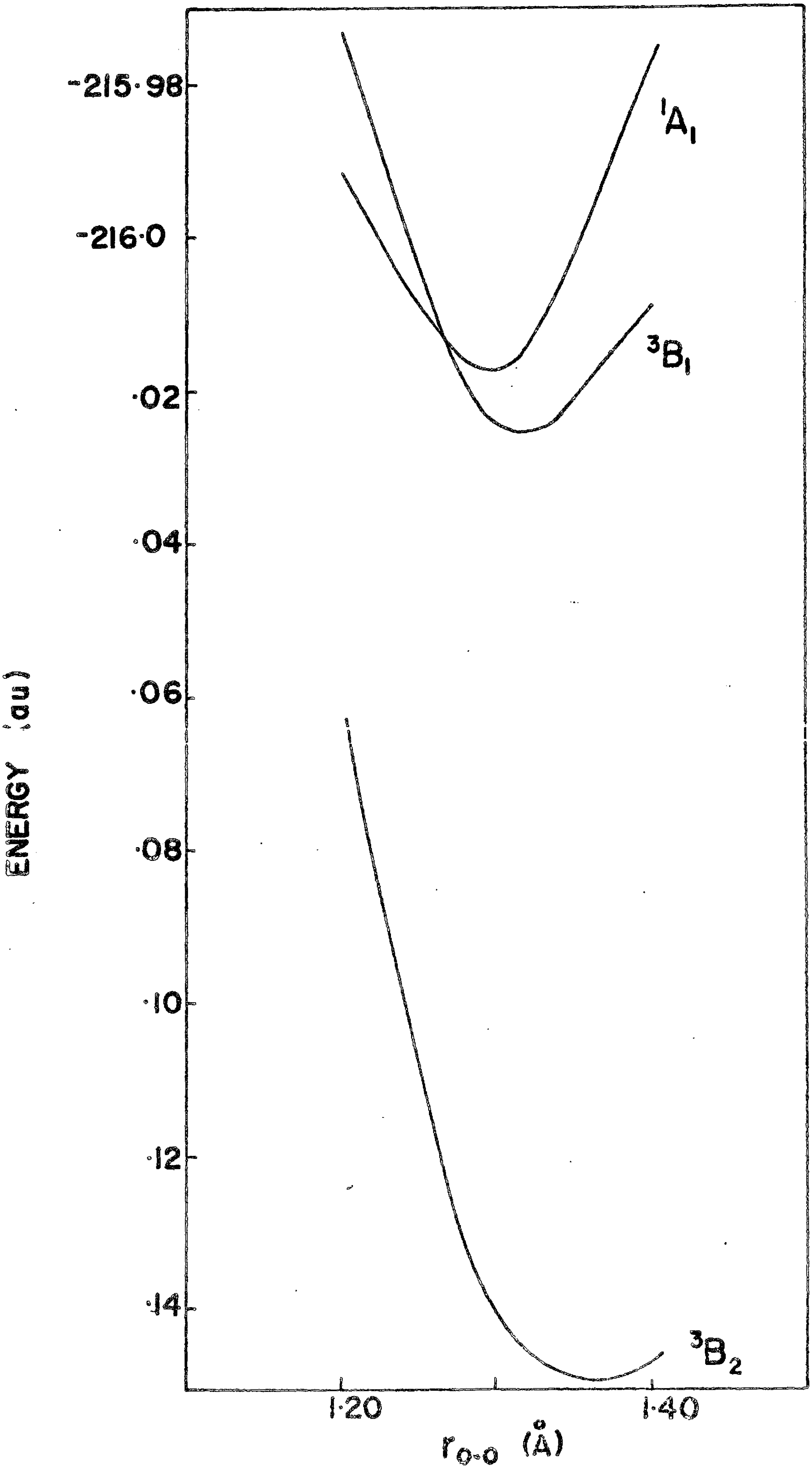
3d orbitals on the molecular properties.

In addition to these ground state calculations for ozone, the lowest energy excited triplet states were also studied. It was thought that such a comparison might prove interesting since the electronic spectra of these two molecules are quite dissimilar despite the fact that their valence shells are isoelectronic. The spectrum of ozone is quite diffuse whereas that of sulphur dioxide consists of sharp discrete bands. Furthermore, ozone shows absorption[57] at very long wave lengths, the lowest energy of these occuring at 10000Å compared with 3900Å for sulphur dioxide. Mulliken[50] assigns the band at wavelength 6000Å to a B_1 state ($2b_1 \leftarrow 4a_1$), with an excitation energy of 2.1 ev. The next excited state is a B_2 state ($2b_1 \leftarrow 1a_2$), (which is assigned to a band at wavelength 2550Å) with an excitation energy of 4.86 ev. On the whole the assignments of the ozone spectrum are tentative and thought to require further study.

In the course of investigation, the ground state equilibrium geometry bond angle of 116.8° was assumed and the O-O bond length, for which the experimental value is 1.278Å, was optimized using the same minimal basis set as reported in Chapter II for the other molecules studied. Initially, only the minimal basis calculations were performed for the study of the ground state and two excited states of ozone, since the d orbitals, because of their high energy relative to the valence orbitals of oxygen are thought not to participate strongly in bonding. Then the one d orbital which was found to be most important in sulphur dioxide - the dxy orbital - was introduced into the basis; the effect

Figure IX

Energy of the ground state ($^1A_1$) and the two lowest energy excited triplet states ($^3B_1$, $^3B_2$) of Ozone as a function of O-O bond length.


-215·98
-216·0
·02
·04
·06
·08
·10
·12
·14
ENERGY (au)
1·20
1·40
r_{O-O} (Å)
$^1A_1$
$^3B_1$
$^3B_2$

of this function was determined by a comparison of the two sets of calculations. Also, the exponent of this single d function was optimized in order to establish and compare the orbital contraction with that found for sulphur dioxide.

The electronic configuration found for the ground state minimal basis ozone calculation was:

$$(1a_1)^2\ (2a_1)^2\ (1b_2)^2\ (3a_1)^2\ (2b_2)^2\ (4a_1)^2\ (5a_1)^2$$
$$(1b_1)^2\ (3b_2)^2\ (4b_2)^2\ (6a_1)^2\ (1a_2)^2/(2b_1)$$

This configuration has a different ordering from that suggested for the ground state by Herzberg[57]:

$$\ldots.\ (5a_1)^2\ (4b_2)^2\ (6a_1)^2\ (1a_2)^2$$

However, in either case, the two lowest energy triplet excited states are the $^3B_2$ $(b_1 \leftarrow a_2)$ and the $^3B_1$ $(b_1 \leftarrow a_1)$ as was also found for the sulphur dioxide minimal basis calculation.

A graphic presentation of the results for bond length optimisation in $^1A_1$, $^3B_1$ and $^3B_2$ states is given in figure IX. Immediately obvious is the unexpected energy ordering of the states; both the $^3B_1$ and $^3B_2$ states are found to be energetically more stable than the $^1A_1$ ground state. This ordering is not so surprising if the electronic spectrum of ozone is considered. The transition producing the lowest energy excited state occurs at 10000Å - an unusually long wave length. The corresponding transition energy is 0.0455 a.u., a value which easily lies within the range of uncertainty in this type of calculation involving a comparison of closed and open shell Hartree-Fock results.

One important result of these excited state calculations, was the optimization of the O-O bond length in the triplet states studied. Although at the experimental internuclear distance the $^1A_1$ and $^3B_1$ states have almost identical energy, the $^3B_2$ state is 0.12 a.u. lower in energy than the $^1A_1$. The O-O bond length increases in going from $^1A_1$ (1.30Å) to $^3B_1$ (1.32Å) and $^3B_2$ (1.36Å). No excitation energies could be determined on the basis of these results.

The theoretical behaviour of the excited states of ozone could be improved by one, or a combination, of the following factors: a configuration interaction calculation, an improvement in basis set, and a complete geometry optimization. As explained in the discussion of results for the sulphur dioxide calculations, it is an inherent property of the unrestricted Hartree-Fock method used in the excited state computations that the computed energies are too low relative to the corresponding closed shell ground state calculation. The ground state energy could be improved by a configuration interaction calculation; this would also serve to improve the ordering of the excited states and their energies relative to the ground state since such a calculation would take into account the interaction between low and higher energy states of the same symmetry. However, a configuration interaction calculation alone would possibly not produce a difference in energies of 0.12 a.u. Further complications could be due to an incomplete geometry optimization. Although such a possibility was not extensively investigated, a brief bond angle optimization procedure indicated that for the minimal basis

TABLE XIV

MINIMAL AND EXTENDED BASIS ENERGIES FOR OZONE - COMPARISON WITH OTHER WORK

	Minimal Basis Calculation		Extended Basis Calculation	Calculation (a) II		Calculation (b) III	
Nature of Basis Set	(244)		(244/244/2442)	Whitten's (c) gaussian lobe functions		Slater orbital basis	
Orbital Energies	-19.8387	$1a_1$	-19.8848	-20.8896	$1a_1$	-20.9597	$1b_2$
	-19.5410	$2a_1$	-19.6344	-20.7255	$1b_2$	-20.6773	$1a_1$
	-19.5410	$1b_2$	-19.6348	-20.7255	$2a_1$	-20.6773	$2a_1$
	-1.6214	$3a_1$	-1.6546	-1.7233	$3a_1$	-1.6677	$3a_1$
	-1.2893	$2b_2$	-1.3297	-1.4263	$2b_2$	-1.3361	$2b_2$
	-0.9416	$4a_1$	-0.9758	-1.1108	$4a_1$	-1.0063	$4a_1$
	-0.7078	$5a_1$	-0.7411	-0.8168	$5a_1$	-0.7115	$5a_1$
	-0.6847	$1b_1$	-0.7099	-0.7808	$3b_2$	-0.6800	$1b_1$
	-0.6603	$3b_2$	-0.7002	-0.7602	$1b_1$	-0.6725	$3b_2$
	-0.4404	$4b_2$	-0.4872	-0.5807	$4b_2$	-0.4410	$4b_2$
	-0.4157	$6a_1$	-0.4569	-0.5657	$6a_1$	-0.4184	$1a_2$
	-0.3458	$1a_2$	-0.4041	-0.4906	$1a_2$	-0.3495	$6a_1$
	+0.0767	$2b_1$	+0.0573	-0.0839	$2b_1$		
Total Energy (a.u)	-216.0161		-216.0834	-224.1618		-223.4790	
-V/T	2.019		2.023			2.005	

(a) Reference 58 (b) Reference 59 (c) Reference 60 set, and an O-O bond distance of 1.278Å, the minimum energy configuration is one in which the bond angle is 117° - a value close to the experimental angle. A final source of discrepancy could be the nature of the basis set, the minimal basis set chosen being inadequate for an accurate molecular orbital description of ozone. This possibility becomes unlikely when the results of this calculation are compared in Tables XIV and XV with those of other workers. The molecular orbital energies and computed molecular properties are similar to those obtained for different types of basis set[58,59]. That the present molecular energy is higher than that for other calculations is due to the comparatively poor 1s representation. Although any one of these factors might not cause vast improvement in the ozone calculations, it seems likely that a combination of these and other less obvious modifications would yield theoretical results in better agreement with experiment.

It was decided to expand these computations designed to assess the role of d functions in sulphur dioxide and ozone by including a third phase. Initially, minimal basis calculations were performed for the two molecules. This was followed by an extended basis calculation in which a single d function had been incorporated into the minimal basis set. Since the results of these two sets of calculations were not conclusive, a third series of calculations involving a comparison of results for an ozone basis including the full set of d functions seemed appropriate. A comparison of the results obtained for the two types of basis set should provide a clear indication of the advantages associated with the use of an expanded basis set.

TABLE XV

COMPARISON OF MOLECULAR PROPERTIES COMPUTED FOR OZONE WITH OTHER RESULTS

	Minimal Basis Calculation	Extended Basis Calculation	Calculation II (a)	Calculation III (b)	Experimental Results
1st Ionization Potential (a.u)	0.3458	0.4041	0.4906	0.3495	0.4704
d Orbital Exponent		1.10			
Dipole Moment (D)	0.516	0.044			0.53 (d)
Optimum Bond Length (Å)	1.30				1.278
Optimum Bond Angle	117°				116.8°

(a) Reference 58

(b) Reference 59

(c) Reference 60

(d) Reference 38

The next step in the sequence of investigations concerning the influence of basis set on results was to determine the effect of d orbitals on the results of molecular calculations for ozone. As explained previously, in sulphur dioxide the dxy orbital because of its symmetry makes a unique contribution, being the d orbital most involved in the bonding. Therefore, to a good approximation, the contribution of d functions could be represented by addition of only this basis function to the minimal basis set of ozone. The results of these calculations for sulphur dioxide and ozone are presented in Table XVI, together with a comparison with full d set calculations.

As part of this investigation, the exponent of the dxy orbital was optimized for both sulphur dioxide and ozone. Optimum values found were 1.10 for O_3 and 1.40 for SO_2, indicating that the d orbital is more diffuse in ozone than in sulphur dioxide.

For the single d calculations, the ratio of 3dxy to $2p_x$ coefficients in the molecular orbital may be considered a measure of the contribution to bonding made by the dxy orbital. This ratio for the lowest a_2 symmetry molecular orbital was found to be 0.35 in ozone, compared with 0.62 in sulphur dioxide. The dxy orbital charge density was in SO_2 0.2723 and in O_3 0.1862. Although these calculations may prove that the d orbital is more involved, by almost 80%, in the molecular bonding of sulphur dioxide than in ozone, at the same time they show that the participation of d orbitals in ozone is not negligible.

TABLE XVI

COMPARISON OF EXTENDED BASIS CALCULATIONS FOR OZONE AND SULPHUR DIOXIDE

	Sulphur Dioxide		Ozone	
	Single dxy	Full d set	Single dxy	Full d set
d Orbital Exponent	1.40	1.40 1.63	1.10	1.10 1.20
Orbital Occupancy	$8a_1$ $1a_2$ $2b_1$ $5b_2$		$6a_1$ $1a_2$ $1b_1$ $4b_2$	
Ordering of Molecular Orbitals	$(5b_2)^2$ $(1a_2)^2$ $(8a_1)^2/3b_1$		$(4b_2)^2$ $(6a_1)^2$ $(1a_2)^2/2b_1$	
Total Molecular Energy (a.u)	-527.5152	-527.7709	-216.0834	-216.1431
Dipole Moment (debyes)	0.76	1.26	0.06	0.11
$1a_2$ M.O. Coefficients 2px 3dxy	 0.5627 0.3597	 0.5832 0.3240	 0.6201 0.2293	 0.6280 0.2119
Density in dxy Orbital	0.2723	0.2436	0.1862	0.1742

As indicated in Table XVI, the expansion of basis from the single d set to the full d set did not greatly alter the results. In both ozone and sulphur dioxide, the best theoretical value of dipole moment was obtained for the minimal basis set. However, the full d set substantially modified the energies of ground and excited states of ozone. At the experimental equilibrium geometry of ozone, the various state energies computed for the full d set were: -216.1431 a.u. for $^1A_1$, -216.1998 a.u. for $^3B_2$, and -216.1301 a.u. for $^3B_1$. Although the $^3B_2$ excited state is still lower in energy than the ground state, the discrepancy is now only 0.05 a.u. as compared with a minimal basis set difference of 0.12 a.u. For a difference of the magnitude of 0.05 a.u., it is quite likely that the improvements suggested previously for these calculations would produce more reasonable results. Thus, d functions in the case of ozone as well as sulphur dioxide seem to improve the theoretical results obtained for the excited state study considerably.

These findings are another point of evidence concerning the validity of the use of a minimal basis set. The ordering of states for ozone seems to be much improved by simple expansion of the basis set to include d functions on the central oxygen atom. It would certainly be of interest to study the effects of other modifications made to the basis set, since it seems quite probable that expansion achieved by inclusion of extra functions other than d should have important consequences.

An additional problem which has to be resolved is whether the d functions are necessary in molecular orbital calculations of ozone since on a qualitative basis, 3d functions are thought to be of special importance only in the bonding of second row atoms. The difference found between the optimum d orbital exponents in the present calculations for oxygen and sulphur was not as large as might be anticipated. This result tends to indicate a surprisingly large participation of d orbitals in bonding of ozone. In addition, a good theoretical bond length was calculated for ozone without the use of d functions, whereas for sulphur dioxide the bond length was considerably improved upon addition of d functions. Yet on the other hand, good theoretical values of dipole moment were calculated for the minimal basis set in both O_3 and SO_2. Since agreement between experimental and theoretical values of dipole moment for both CS and H_2S is poor, the results found for minimal basis sulphur dioxide may be spurious.

Given this variety of theoretical results, it is difficult to assess the involvement of d orbitals in bonding. Furthermore, it seems on the basis of these calculations that the d functions do not play a special role in the bonding of sulphur and other second row atoms. Had this comparative ozone-sulphur dioxide study revealed only a minor contribution by the d orbitals in ozone, then conclusions concerning the use of d orbitals would have been obvious. As they stand, the results for the minimal basis calculations are unfortunately too nebulous to provide indisputable evidence that participation by d orbitals in bonding is a property exclusive to second row atoms.

The fact that the addition of d functions in ozone effects a considerable improvement probably is indicative of the poor quality of basis set. Although these calculations for sulphur dioxide were greatly improved by addition of d functions to the basis set, the analogous calculations for ozone seem to establish the necessity for improved gaussian representation of the minimal basis and even perhaps a necessity for extension of basis set to include higher energy atomic orbitals prior to an investigation of the use of d functions in bonding of first and second row molecules. Thus an optimization of the basis set should have been the first consideration in a study of this nature. Once this had been accomplished, the effects of addition of d orbitals could be established without the ambiguity which has arisen in the present computations.

CHAPTER IV

CONCLUDING SUMMARY

The investigations performed in the course of this work have served to indicate the necessity for further study in this area, rather than establishing conclusively the role of d orbitals in bonding. Although the present calculations have produced numerous interesting results, they constitute merely the initial stage of a potentially illuminating, lengthy and complex study.

One purpose of the work described in this thesis was to ascertain the contribution made by d functions to the bonding in second row atoms. The problem was investigated by observing the effect of addition of d functions to a minimal basis set on certain molecular properties - such as bond lengths, dipole moment and force constants. It was found that theoretical bond lengths improve upon addition of d functions. However, the results of dipole moment and force constant calculations are not so straightforward. Although in the case of carbon monosulphide and hydrogen sulphide the calculated dipole moment values improved upon inclusion of d orbitals, no similar improvement was obtained for sulphur dioxide, perhaps the most interesting molecule in the series studied. It is believed that these results are unreliable since the gaussian expansions used in the calculations have been proven inadequate - especially for p-type functions. A major improvement, and indeed an essential one, in this type of study is the optimisation of basis set prior to further calculation. The results of force constant calculations are not especially meaningful since this property is always difficult to calculate, as it depends on the second derivative of the energy. On the basis of these results alone, it is impossible to arrive at definite conclusions concerning involvement of d orbitals in bonding of second row atoms.

A more interesting and meaningful aspect of this work was the study of the ground and excited states of sulphur dioxide, which led to a theoretical description of the electronic spectrum of this molecule. It was found that d orbitals were required in order to obtain reasonable results. However, once these functions were added, the spectral features observed experimentally were also predicted theoretically. The theoretical ordering of states as well as the variation in geometry among these states, was found to agree well with experimental observation. The low excitation energies calculated did not detract from the importance of these results, as it was realized that such a discrepancy is inherent in a molecular orbital investigation based on the unrestricted Hartree-Fock method.

Another interesting feature of this work, perhaps the most relevant to the study of the role of d functions in the bonding of second row atoms, is the comparative calculation performed for ozone. The results of these calculations seem to indicate that d functions are not especially significant in the bonding of second row molecules, but may be incorporated, with almost equivalent repercussions, in the basis of analogous first row molecules. Indeed, the extent of involvement of d functions in ozone relative to that in sulphur dioxide is surprisingly large. These calculations tend to cast some doubt on Cruickshank's[62] recent conclusions that d orbitals are essential to an accurate theoretical description of bonding in fluorosilanes and fluorogermanes. The fallacy in making such a general conclusion is caused by a complete reliance on success of theoretical reproduction of experimentally determined molecular properties. To obtain a complete assessment of the extent of involvement of d orbitals, a study of this nature should include a parallel evaluation for first row analogues.

Although such an approach was adopted in this work, the scope of the project was much too narrow to allow formulation of general, all-inclusive conclusions. It would seem, on the basis of this restricted study, that the d orbitals do not play a unique role in bonding of second row atoms. However, such a statement remains to be confirmed by much more extensive research which should include a large range of second row molecules and their first row analogues. Also, as mentioned earlier, such a study should be preceded by an optimisation of basis set to be used in the course of the calculations.

Unfortunately, these factors were discovered late in the course of the reported investigations with the consequence that the study has disappointingly been terminated without further exploration in the proposed directions.

APPENDIX I

FORMULATION OF THE EQUATIONS REQUIRED FOR THE DIPOLE MOMENT ROUTINE WHICH MAY BE INCORPORATED INTO POLYATOM PACKAGE

To obtain all the necessary integrals for evaluation of dipole moments, only the following integral need be evaluated:

$$\left\langle \chi_s^A \mid \hat{r}_i \mid \chi_s^B \right\rangle \equiv \iiint_{-\infty}^{\infty} \chi_s^A \, \hat{r}_i \, \chi_s^B \; dxdydz$$

In this notation, $\hat{r}_i$ is the ith component of the dipole moment operator and χ_s^A, χ_s^B are s type functions on centres A and B respectively.

All other integrals for higher order functions may be obtained by simple differentiation of this integrand with respect to the appropriate parameter.

In figure X, a pictorial representation of the situation considered in a typical integration is presented. Referring to this diagram for definition of the variables occurring in the process of integral evaluation, the procedure is as follows:

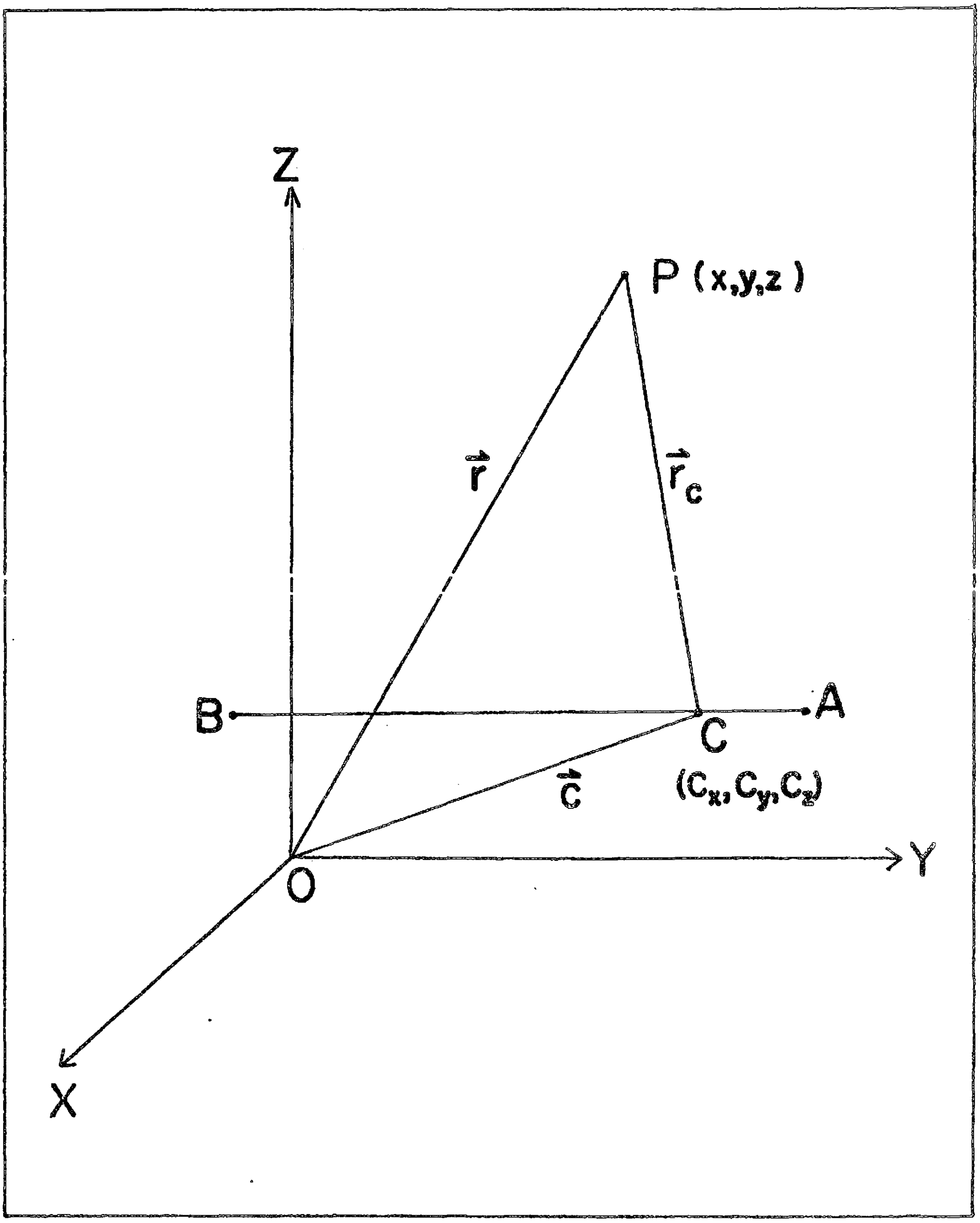
$$\chi_s^A = \exp(-\alpha_A \; r_A^2)$$

$$\chi_s^B = \exp(-\alpha_B \; r_B^2)$$

Expanding the product $(\chi_s^A \; \chi_s^B)$ about the point C:

Figure X

Illustration of reduction of a product of two gaussian functions, centres at A and B to a single gaussian function centred at C.


Z
P (x,y,z)
$\vec{r}$
$\vec{r}_c$
B
A
C
(C_x, C_y, C_z)
$\vec{c}$
Y
O
X

$$\chi_s^A \chi_s^B = \exp\left(-\frac{\alpha_A \alpha_B}{(\alpha_A+\alpha_B)} R_{AB}^2\right) \exp(-\alpha_{AB} r_C^2)$$

where R_{AB} is the distance between points A and B, and

$$r_C^2 = (x - C_x)^2 + (y - C_y)^2 + (z - C_z)^2$$

$$C_x = \frac{\alpha_A A_x + \alpha_B B_x}{\alpha_A + \alpha_B} \quad \text{etc.}$$

$$\alpha_{AB} = (\alpha_A + \alpha_B)$$

Taking the x component of the dipole moment as a specific example, the integral becomes:

$$\left\langle \chi_s^A \mid \hat{x} \mid \chi_s^B \right\rangle = \iiint_{-\infty}^{\infty} \chi_s^A \chi_s^B \, x \, dxdydz$$

Transforming from the origin of the coordinate system, to a local origin at centre C:

$$x = x' + C_x$$

$$y = y' + C_y$$

$$z = z' + C_z$$

$$\left\langle \chi_s^A \mid \hat{x} \mid \chi_s^B \right\rangle$$

$$= \exp\left(-\frac{\alpha_A \alpha_B}{(\alpha_A+\alpha_B)} R_{AB}^2\right) \iiint_{-\infty}^{\infty} \exp[-\alpha_{AB}(x'^2 + y'^2 + z'^2)](C_x + x') \, dx'dy'dz'$$

$$= \exp\left(- \frac{\alpha_A \; \alpha_B}{\alpha_A + \alpha_B} R_{AB}^2\right) \left\{ \iiint_{-\infty}^{\infty} x' \exp[-\alpha_{AB} \; (x'^2 + y'^2 + z'^2)] \; dx'dy'dz' \right.$$

$$\left. + \iiint_{-\infty}^{\infty} C_x \exp[-\alpha_{AB} \; (x'^2 + y'^2 + z'^2)] \; dx'dy'dz' \right\}$$

$$= \frac{\pi^{3/2}}{\alpha_{AB}^{3/2}} \quad C_x \exp\left(- \frac{\alpha_B \; \alpha_A}{\alpha_A + \alpha_B} R_{AB}^2\right)$$

that is:

$$\left\langle \chi_s^A \mid \hat{x} \mid \chi_s^B \right\rangle = - \left(\frac{\pi}{\alpha_A + \alpha_B} \right)^{3/2} \left(\frac{\alpha_A A_x + \alpha_B B_x}{\alpha_A + \alpha_B} \right) \exp\left(- \frac{\alpha_A \; \alpha_B}{\alpha_A + \alpha_B} R_{AB}^2\right)$$

Now χ_s^A may be written:

$$\chi_s^A = \exp \left\{ -\alpha_A [(x - A_x)^2 + (y - A_y)^2 + (z - A_z)^2] \right\}$$

Differentiating with respect to A_x, one obtains the gaussian p function:

$$\frac{\partial}{\partial A_x} (\chi_s^A) \equiv \frac{\partial}{\partial A_x} [\exp(-\alpha_A \; r_A^2)]$$

$$= 2 \; \alpha_A (x - A_x) \exp(-\alpha_A \; r_A^2)$$

$$\frac{\partial}{\partial A_x} (\chi_s^A) = 2 \; \alpha_A \; x_A \; \exp(-\alpha_A \; r_A^2)$$

or:

$$p_x = x_A \exp(-\alpha_A \; r_A^2)$$

$$p_x = (2\,\alpha_A)^{-1} \frac{\partial}{\partial A_x} [\exp(-\alpha_A \cdot r_A^2)]$$

Thus a p_x function may be obtained from an s type function; similarly for p_y and p_z. For the series of d functions, a double differentiation with respect to the appropriate variables is required.

It is now obvious that the dipole moment integrals for p and d type functions may be obtained with relative ease from the s formula by differentiation.

For example, the formula for the x component due to the interaction of an s orbital on centre A and a p_x orbital on centre B is obtained in the following manner:

$$\left\langle \chi_s^A \,|\, \hat{x} \,|\, \chi_{p_x}^B \right\rangle = \frac{1}{2\alpha_B} \frac{\partial}{\partial B_x} \left\langle \chi_s^A \,|\, \hat{x} \,|\, \chi_s^B \right\rangle$$

$$= \frac{1}{2\alpha_B} \frac{\partial}{\partial B_x} \left\{ \left(\frac{\pi}{\alpha_{AB}}\right)^{3/2} \left(\frac{\alpha_A A_x + \alpha_B B_x}{\alpha_A + \alpha_B} \right) \exp\left(- \frac{\alpha_A\,\alpha_B}{(\alpha_A+\alpha_B)} R_{AB}^2\right) \right\}$$

$$= \frac{1}{2\alpha_B} \left(\frac{\pi}{\alpha_{AB}} \right)^{3/2} \exp\left(- \frac{\alpha_A\,\alpha_B\,R_{AB}^2}{\alpha_A+\alpha_B}\right) \left\{ \frac{\alpha_B}{\alpha_A+\alpha_B} - \frac{\alpha_A\,\alpha_B}{\alpha_A+\alpha_B} [-2(B_x - A_x)] \right\}$$

$$= \frac{\pi^{3/2}}{2\alpha_B \cdot \alpha_{AB}^{3/2}} \left[\frac{\alpha_B}{\alpha_A+\alpha_B} + \left(2\,\frac{\alpha_A\,\alpha_B}{\alpha_A+\alpha_B}\right) (B_x - A_x) \right] \exp\left(- \frac{\alpha_A\,\alpha_B}{\alpha_A+\alpha_B} R_{AB}^2\right)$$

In the remaining formulae which are presented below, the same procedure has been followed. The only difference is the introduction of a more efficient notation:

$$C_i = (\alpha_A A_i + \alpha_B B_i)$$

$$S = \left(\frac{\pi}{\alpha_{AB}} \right)^{3/2} \circ \left(\frac{1}{\alpha_A + \alpha_B} \right)$$

$$\alpha_C = \frac{\alpha_A \; \alpha_B}{\alpha_A + \alpha_B}$$

Subscripts (i, j, k, l, q) are used to designate the various components (x, y, or z) and δ_{ij} is the Kronecker delta function.

I $$\left\langle s^{A} \mid \hat{r}_{i} \mid s^{B} \right\rangle = S\, C_{i} \exp(-\alpha_{C}\, R_{AB}^{2})$$

II $$\left\langle p_{j}^{A} \mid \hat{r}_{i} \mid p_{k}^{B} \right\rangle = \tfrac{1}{2} S \exp(-\alpha_{C}\, R_{AB}^{2}) \times \left\{ \frac{\alpha_{C}}{\alpha_{A}} (B_{j} - A_{j})\, \delta_{ik} - \frac{\alpha_{C}}{\alpha_{B}} (B_{k} - A_{k})\, \delta_{ij} + \frac{\alpha_{C}}{\alpha_{A}\, \alpha_{B}}\, C_{i}\, \delta_{jk} - \frac{2\alpha_{C}^{2}}{\alpha_{A}\, \alpha_{B}}\, C_{i}\, (B_{j} - A_{j})\, (B_{k} - A_{k}) \right\}$$

III $$\left\langle s^{A} \mid \hat{r}_{i} \mid p_{j}^{B} \right\rangle = S \exp(-\alpha_{C}\, R_{AB}^{2}) \left\{ \tfrac{1}{2}\, \delta_{ij} - \frac{\alpha_{C}}{\alpha_{B}}\, C_{i}\, (B_{j} - A_{j}) \right\}$$

IV $$\left\langle s^{A} \,\middle|\, \hat{r}_{i} \,\middle|\, d_{jj}^{B} \right\rangle = \frac{S \exp(-\alpha_{C}\, R_{AB}^{2})}{2\alpha_{B}} \left\{ \left[C_{i} - \frac{\alpha_{C}}{\alpha_{B}}\, C_{i} - 2\alpha_{C} (B_{j} - A_{j})\, \delta_{ij} + 2 \frac{\alpha_{C}^{2}}{\alpha_{B}} (B_{j} - A_{j})^{2}\, C_{i} \right] \right\}$$

V $$\left\langle p_{j}^{A} \,\middle|\, \hat{r}_{i} \,\middle|\, d_{kk}^{B} \right\rangle = \frac{S \exp(-\alpha_{C}\, R_{AB}^{2})}{4\alpha_{A}\, \alpha_{B}} \Big[\alpha_{A}\, \delta_{ij} - \frac{\alpha_{A}\, \alpha_{C}}{\alpha_{B}}\, \delta_{ij} + 2\alpha_{C}\, \delta_{ij}\, \delta_{ik} - 4 \frac{\alpha_{C}^{2}}{\alpha_{B}} (B_{k} - A_{k})\, C_{i}\, \delta_{jk} + 2\alpha_{C}^{2} \frac{\alpha_{A}}{\alpha_{B}} (B_{k} - A_{k})^{2}\, \delta_{ij} + 4 \frac{\alpha_{C}^{3}}{\alpha_{B}} (B_{k} - A_{k})^{2} (B_{j} - A_{j})\, C_{i} - 4\alpha_{C}^{2}\, (B_{j} - A_{j}) (B_{k} - A_{k})\, \delta_{ik}$$

$$+ \; 2\alpha_C \, C_i \, (B_j - A_j) \; - \; 2\frac{\alpha_C^2}{\alpha_B} C_i \, (B_j - A_j) \;]$$

VI $$\left\langle s^A \mid \hat{r}_i \mid d^B_{kl} \right\rangle = \frac{S \, \exp(-\alpha_C \, R^2_{AB})}{2\alpha_B} \; [\; -\alpha_C (B_k - A_k) \, \delta_{il}$$

$$- \; \alpha_C \, (B_l - A_l) \, \delta_{ik} \; + \; 2\frac{\alpha_C^2}{\alpha_B} \, C_i \, (B_k - A_k)(B_l - A_l) \;]$$

VII $$\left\langle p^A_j \mid \hat{r}_i \mid d^B_{kl} \right\rangle$$

$$= \frac{S \, \exp(-\alpha_C \, R^2_{AB})}{4\alpha_A \, \alpha_B} \; [\; - \; 2\alpha_C^2 \, (B_j - A_j)(B_k - A_k) \, \delta_{il}$$

$$- \; 2\alpha_C^2 \, (B_j - A_j)(B_l - A_l) \, \delta_{ik} \; + \; 4\frac{\alpha_C^3}{\alpha_B} C_i \, (B_j - A_j)$$

$$\times (B_k - A_k)(B_l - A_l) \; + \; \alpha_C \, \delta_{il} \, \delta_{jk} \; + \; \alpha_C \, \delta_{ik} \, \delta_{lj}$$

$$+ \; 2\alpha_C^2 \, \frac{\alpha_A}{\alpha_B} \, (B_k - A_k)(B_l - A_l) \, \delta_{ij} \; - \; 2\frac{\alpha_C^2}{\alpha_B} C_i \, (B_l - A_l) \, \delta_{jk}$$

$$- \; 2\frac{\alpha_C^2}{\alpha_B} C_i \, (B_k - A_k) \, \delta_{lj} \;]$$

VIII $$\left\langle d^A_{kk} \mid \hat{r}_i \mid d^B_{jj} \right\rangle$$

$$= \frac{S \, \exp(-\alpha_C \, R^2_{AB})}{4\alpha_A^2 \, \alpha_B^2} \; [\; \alpha_A \, \alpha_B \, C_i \; - \; \alpha_A \, \alpha_C \, C_i \; - \; \alpha_B \, \alpha_C \, C_i$$

$$+ \; 2\alpha_C^2 \, C_i \, \delta_{jk} \; - \; \alpha_C^2 \, C_i \; + \; 2 \, \alpha_A \, \alpha_B \, \alpha_C \, (B_k - A_k) \, \delta_{ik}$$

$$- \; 2 \, \alpha_A \, \alpha_B \, \alpha_C \, (B_j - A_j) \, \delta_{ij} \; + \; 2 \, \alpha_B \, \alpha_C^2 \, (B_j - A_j) \, \delta_{ij}$$

$$- \ 2 \alpha_A \alpha_C^2 (B_k - A_k) \delta_{ik} \ - \ 2 \alpha_A \alpha_C^2 (B_j - A_j) \delta_{ik} \delta_{ij}$$

$$+ \ 2 \alpha_B \alpha_C^2 (B_k - A_k) \delta_{jk} \delta_{ij} \ - \ 2 \alpha_A \alpha_C^2 (B_j - A_j) \delta_{ik} \delta_{jk}$$

$$+ \ 2 \alpha_B \alpha_C^2 (B_k - A_k) \delta_{jk} \delta_{ij} \ + \ 2 \alpha_B \alpha_C^2 C_i (B_k - A_k)^2$$

$$+ \ 2 \alpha_A \alpha_C^2 C_i (B_j - A_j)^2 \ - \ 8 \alpha_C^3 C_i (B_j - A_j)(B_k - A_k) \delta_{jk}$$

$$- \ 2 \alpha_C^3 C_i (B_j - A_j)^2 \ - \ 2 \alpha_C^3 C_i (B_k - A_k)^2$$

$$- \ 4 \alpha_C^3 \alpha_B (B_k - A_k)^2 (B_j - A_j) \delta_{ij}$$

$$+ \ 4 \alpha_C^3 \alpha_A (B_j - A_j)^2 (B_k - A_k) \delta_{ik}$$

$$+ \ 4 \alpha_C^4 C_i (B_j - A_j)^2 (B_k - A_k)^2 \ ]$$

IX $\left\langle d_{jl}^{A} \ \middle| \ \hat{r}_i \ \middle| \ d_{kk}^{B} \right\rangle$

$$= \frac{S \exp(-\alpha_C R_{AB}^2)}{8\alpha_A^2 \alpha_B^2} \ [\ 4 \alpha_C^2 \alpha_B (B_j - A_j) \delta_{ik} \delta_{kl}$$

$$+ \ 2 \alpha_C \alpha_B \alpha_A (B_j - A_j) \delta_{il} \ - \ 2 \alpha_C^2 \alpha_A (B_j - A_j) \delta_{il}$$

$$- \ 4 \alpha_C^2 \alpha_A (B_k - A_k) \delta_{ij} \delta_{kl} \ - \ 4 \alpha_C^2 \alpha_A (B_k - A_k) \delta_{il} \delta_{jk}$$

$$+ \ 4 \alpha_C^2 \alpha_B (B_l - A_l) \delta_{ij} \delta_{ik} \ + \ 2 \alpha_A \alpha_B \alpha_C (B_l - A_l) \delta_{ij}$$

$$- \ 2 \alpha_A \alpha_C^2 (B_l - A_l) \delta_{ij} \ - \ 8 \alpha_C^3 (B_k - A_k)(B_l - A_l) C_i \delta_{jk}$$

$$+ \ 4 \alpha_C^2 \alpha_B C_i (B_j - A_j)(B_l - A_l) \ - \ 4 \alpha_C^3 (B_j - A_j)$$

$$\times (B_l - A_l) C_i \ - \ 8 \alpha_C^3 (B_k - A_k)(B_j - A_j) C_i \delta_{lk}$$

$$+ \ 4 \alpha_C^3 \alpha_A (B_k - A_k)^2 (B_l - A_l) \delta_{ij}$$

$$- \ 8 \alpha_C^3 \alpha_B (B_j - A_j)(B_l - A_l)(B_k - A_k) \delta_{ik}$$

$$+ \; 4 \, \alpha_C^3 \, \alpha_A \, (B_k - A_k)^2 \, (B_j - A_j) \, \delta_{il}$$

$$+ \; 8 \, \alpha_C^4 \, (B_j - A_j)(B_l - A_l)(B_k - A_k)^2 \, C_i \;]$$

$$\times \quad \left\langle d_{kl}^A \,\middle|\, \hat{r}_i \,\middle|\, d_{jp}^B \right\rangle$$

$$= \frac{S \, \exp(-\alpha_C \, R_{AB}^2)}{8\alpha_A^2 \, \alpha_B^2} \; [\; 2 \, \alpha_C^2 \, C_i \, \delta_{pl} \, \delta_{jk} \; + \; 2 \, \alpha_C^2 \, C_i \, \delta_{lj} \, \delta_{pk}$$

$$+ \; 2 \, \alpha_C^2 \, \alpha_B \, (B_k - A_k) \, \delta_{lj} \, \delta_{ip} \; + \; 2 \, \alpha_C^2 \, \alpha_B \, (B_l - A_l) \, \delta_{jk} \, \delta_{ip}$$

$$+ \; 2 \, \alpha_C^2 \, \alpha_B \, (B_l - A_l) \, \delta_{ij} \, \delta_{kp} \; + \; 2 \, \alpha_C^2 \, \alpha_B \, (B_k - A_k) \, \delta_{ij} \, \delta_{lp}$$

$$- \; 2 \, \alpha_C^2 \, \alpha_A \, (B_j - A_j) \, \delta_{il} \, \delta_{pk} \; - \; 2 \, \alpha_C^2 \, \alpha_A \, (B_j - A_j) \, \delta_{ik} \, \delta_{pl}$$

$$- \; 2 \, \alpha_C^2 \, \alpha_A \, (B_p - A_p) \, \delta_{il} \, \delta_{jk} \; - \; 2 \, \alpha_C^2 \, \alpha_A \, (B_p - A_p) \, \delta_{ik} \, \delta_{jl}$$

$$- \; 4 \, \alpha_C^3 \, C_i \, (B_j - A_j)(B_l - A_l) \, \delta_{kp} \; - \; 4 \, \alpha_C^3 \, C_i \, (B_j - A_j)$$

$$\times (B_k - A_k) \, \delta_{pl} \; - \; 4 \, \alpha_C^3 \, C_i \, (B_p - A_p)(B_l - A_l) \, \delta_{jk}$$

$$- \; 4 \, \alpha_C^3 \, C_i \, (B_k - A_k)(B_p - A_p) \, \delta_{lj} \; - \; 4 \, \alpha_C^3 \, \alpha_B \, (B_j - A_j)$$

$$\times (B_k - A_k)(B_l - A_l) \, \delta_{ip} \; - \; 4 \, \alpha_C^3 \, \alpha_B \, (B_p - A_p)(B_k - A_k)$$

$$\times (B_l - A_l) \, \delta_{ij} \; + \; 4 \, \alpha_C^3 \, \alpha_A \, (B_p - A_p)(B_j - A_j)(B_l - A_l) \, \delta_{ik}$$

$$+ \; 4 \, \alpha_C^3 \, \alpha_A \, (B_p - A_p)(B_j - A_j)(B_k - A_k) \, \delta_{il}$$

$$+ \; 8 \, \alpha_C^4 \, C_i \, (B_j - A_j)(B_k - A_k)(B_l - A_l)(B_p - A_p) \;]$$

APPENDIX II

```
      PROGRAM DIPOLE(INPUT,OUTPUT,TAPE4)
      COMMON D(40,40),DM(3),NCENTR(120),Y(40,40),VLIST(120,4),OCC(40)
      COMMON/DIP1/PI,IV,ETA(120,5),NTYPE(120),NFIRST(120),NLAST(120),
     1 DI(3,3),X(40,40),NB
C       THIS VERSION OF DIPOLE INCLUDES FORMULAE FOR INTEGRALS WITH D
C         INPUT DATA CONSISTS OF NR, THE NO OF ROWS IN THE COEFFICIENT
C        MATRIX, NC THE NO OF COLUMNS IN SAME...NEXT IS THE OCCUPATION
C        DATA  1.0 FOR DOUBLY OCCUPIED  0.0 FOR VACANT- FOR ALL NR
C        FORMAT(12F5.0)...THEN THE COEFFICIENT MATRIX ELEMENTS Y(I,J)
C        AS PUNCHED IN POLYATOM...THE GAUSSIAN FUNCTION SPECIFICATIONS
C        ARE READ FROM THE PA 300 INTEGRAL TAPE (TAPE4)
      CALL SECOND(T1)
      PRINT 1100, T1
      NBMX = 40
      PI = 3.14159265359
      REWIND4
      READ(4)
      READ(4) NB,((NFIRST(I),NLAST(I),NCENTR(I),NTYPE(I)),I=1,NB)
      READ(4) NG,((ETA(I,J),J=1,5),I=1,NG)
      READ(4) NOC,((VLIST(I,J),J=1,4),I=1,NOC)
      REWIND4
      DO 1005 I=1,NB
      DO 1005 J = 1,NB
      OCC(I) = 0.0
      D(I,J) = 0.0
 1005 Y(I,J) = 0.0
      READ 1006, NR,NC
      READ 1007,(OCC(I),I=1,NR)
      PRINT 1007,(OCC(I),I=1,NR)
      DO 1004 I=1,NR
 1004 READ 1000,(Y(I,J),J=1,NC)
      CALL PRNT(Y,NB,NBMX)
      DO 1010 I=1,NB
      DO 1010 J=1,NB
      DO 1010 K=1,NB
 1010 D(I,J) = D(I,J) + OCC(K)*Y(K,I)*Y(K,J)
      PRINT 100
      CALL PRNT(D,NB,NBMX)
      PRINT 110
      PRINT 120,((I,NFIRST(I),NLAST(I),NTYPE(I)),I=1,NB)
      PRINT 108
      PRINT 200
      DO 205 I=1,NG
  205 PRINT 210,I,(ETA(I,J),J=1,5)
      PRINT 108
      DO 30 I=1,3
      DO 30 J=1,3
      DI(I,J) = 0.0
```

```
      IF(I.NE.J) GO TO 30
      DI(I,I) = 1.0
   30 CONTINUE
C       THE DIPOLE MOMENT INTEGRALS, PRIOR TO MULTIPLICATION BY DENSITY
C       MATRIX ARE STORED IN ARRAY X
      DO 50 IV =1,3
      CALL DINTS
      PRINT 108
      PRINT 110,IV
      CALL PRNT(X,NB,NBMX)
      DM(IV) = 0.0
      DO 60 I=1,NB
      DO 60 J=1,NB
   60 DM(IV) = DM(IV) - 2.0*D(I,J)*X(I,J)
   50 CONTINUE
C       THE NUCLEAR CONTRIBUTIONS TO THE DIPOLE MOMENT ARE NEXT
C       CALCULATED
      RN1 = 0.0
      RN2 = 0.0
      RN3 = 0.0
      DO 160 I=1,NOC
      RN1 = RN1 + VLIST(I,1)*VLIST(I,4)
      RN2 = RN2 + VLIST(I,2)*VLIST(I,4)
  160 RN3 = RN3 + VLIST(I,3)*VLIST(I,4)
      DM1 = RN1 + DM(1)
      DM2 = RN2 + DM(2)
      DM3 = RN3 + DM(3)
      DPM = SQRT(DM1**2 + DM2**2 + DM3**2)*2.5415
      PRINT 204
      PRINT 201, DM(1),DM(2),DM(3)
      PRINT 202, RN1,RN2,RN3
      PRINT 207, DM1,DM2,DM3
      PRINT 203,DPM
      CALL SECOND(T2)
      PRINT 1101, T2
      TT = T2 - T1
      PRINT 1102 , TT
  100 FORMAT(10X,*POLYATOM DENSITY MATRIX*,//)
  108 FORMAT(//)
  110 FORMAT(10X,*DIPOLE MOMENT MATRIX FOR COMPONENT *,I1,//)
  120 FORMAT(13X,I2,8X,I2,7X,I2,6X,I2)
  130 FORMAT(10X,*FUNCTION*,2X,*NFIRST*,3X,*NLAST*,3X,*NTYPE*,//)
  200 FORMAT(10X,*GAUSSIAN*,2X,*ETA(1)*,7X,*ETA(2)*,7X,*ETA(3)*,7X,
     1 *EXPONENTS *,3X,*COEFFICIENTS*,//)
  201 FORMAT(8X,*ELECTRONIC*,2X,3F10.6,/)
  202 FORMAT(8X,*NUCLEAR*,5X,3F10.6,/)
  203 FORMAT(8X,*TOTAL DIPOLE MOMENT*,3X,F10.6,3X,*DEBYES*)
  204 FORMAT(20X,*COMPONENTS OF DIPOLE MOMENT*,/,24X,*X*,9X,
     1 *Y*,9X,*Z*,//)
```

```
 207 FORMAT(8X,*RESULTANT*,3X,3F10.6,//)
 210 FORMAT(10X,I2,3X,5(3X,F10.6))
1000 FORMAT(4E15.8)
1006 FORMAT(3I5)
1007 FORMAT(12F5.0)
1100 FORMAT(/,10X,*TIME AT START OF DIPOLE ROUTINE*,2X,F10.3,2X,*SEC*,
    1 //)
1101 FORMAT(/,10X,*TIME AT END OF DIPOLE ROUTINE*,2X,F10.3,2X,*SEC*,//)
1102 FORMAT(10X,*TOTAL TIVE USED FOR DIPOLE ROUTINE*,2X,F10.3,2X,*SEC*)
     CALL EXIT
     END
     SUBROUTINE DINTS
     COMMON/DIP1/PI,IV,ETA(120,5),NTYPE(120),NFIRST(120),NLAST(120),
    1 D (3,3),X(40,40),NB
C      THIS SUBROUTINE ORGANIZES THE CALLING PARAMETERS NECESSARY FOR
C      THE INTEGRAL PACKAGE AND POSTMULTIPLIES THE DIPOLE MOMENT
C      INTEGRALS BY THE APPROPRIATE NORMALIZED COEFFICIENTS
     DO 100 I=1,NB
     MT = NTYPE(I)
     LL = NLAST(I) - NFIRST(I) + 1
     DO 100 J=I,NB
     ML = NFIRST(I)
     NT = NTYPE(J)
     MM = NLAST(J) - NFIRST(J) + 1
     X(I,J) = 0.0
     DO 110 M=1,LL
     NL = NFIRST(J)
     DO 111 N=1,MM
     DI = DIPI(ML,NL,MT,NT)
     DD = ETA(ML,5)*ETA(NL,5)*DI
     X(I,J) = X(I,J) + DD
 111 NL = NL + 1
 110 ML = ML + 1
     X(J,I) = X(I,J)
 100 CONTINUE
 200 FORMAT(6X,6I6,6X,F15.8,12X,F15.8)
 210 FORMAT(12X,*I*,5X,*J*,5X,*M*,5X,*N*,4X,*ML*,4X,*NL*,10X,*DIPI(ML,N
    1L)*,20X,*DD*,//)
     RETURN
     END
```

```
      FUNCTION DIPI(ML,NL,M,N)
      COMMON/DIP1/PI,I ,ETA(120,5),NTYPE(120),NFIRST(120),NLAST(120),
     1 D (3,3),X(40,40),NB
C       THIS FUNCTION EVALUATES THE DIPOLE MOMENT INTEGRALS
      INTEGER P
      RAB2 = (ETA(ML,1) - ETA(NL,1))**2 + (ETA(ML,2) - ETA(NL,2))**2 +
     1 (ETA(ML,3) - ETA(NL,3))**2
      AC = ETA(ML,4)*ETA(NL,4)/(ETA(ML,4) + ETA(NL,4))
      ER = (EXP(-AC*RAB2))*(PI**1.5)/(ETA(ML,4) + ETA(NL,4))**2.5
      GO TO (1,2,2,2,3,3,3,4,6,5), M
    1 GO TO (11,12,12,12,23,23,23,241,241,242), N
    2 GO TO (14,15,15,15,25,25,25,261,262,263), N
    3 GO TO (31,32,32,32,351,351,351,352,352,352), N
    4 GO TO (41,42,42,42,352,352,352,363,363,363),N
    5 GO TO (51,52,52,52,352,352,352,363,363,363),N
    6 GO TO (41,62,62,62,352,352,352,363,363,363), N
C           (P/R/S).....EQUATION 3 IN FORMULA LIST
   14 AA = ETA(NL,4)
      AB = ETA(ML,4)
      J = M-1
      AJ = ETA(NL,J)
      BJ = ETA(ML,J)
      CI = AA*ETA(NL,I) + AB*ETA(ML,I)
      GO TO 18
C           (S/R/P).....EQUATION 3 IN FORMULA LIST
   12 AA = ETA(ML,4)
      AB = ETA(NL,4)
      J = N-1
      AJ = ETA(ML,J)
      BJ = ETA(NL,J)
      CI = AA*ETA(ML,I) + AB*ETA(NL,I)
   18 DIPI = ER*(D(I,J)/2.0 - AC*CI*(BJ-AJ)/AB)
      RETURN
C           (S/R/S).....EQUATION 1 IN FORMULA LIST
   11 AA = ETA(ML,4)
      AB = ETA(NL,4)
      AI = ETA(ML,I)
      BI = ETA(NL,I)
      DIPI = ER*(AA*AI + AB*BI)
      RETURN
C           (P/R/P).....EQUATION 2 IN FORMULA LIST
   15 AA = ETA(ML,4)
      AB = ETA(NL,4)
      J = M-1
      K = N-1
      AJ = ETA(ML,J)
      AK = ETA(ML,K)
      AI = ETA(ML,I)
      BJ = ETA(NL,J)
```

```
      BK = ETA(NL,K)
      BI = ETA(NL,I)
      CI = (AA*AI + AB*BI)
      DIPI = 0.5*ER*(-AC*(BK-AK)*D(I,J)/AB + AC*(BJ-AJ)*D(I,K)/AA + AC
     1 *CI*D(J,K)/(AA*AB) - 2.0*AC**2*CI*(BJ-AJ)*(BK-AK)/(AA*AB))
      RETURN
C            (S/R/DJJ).....EQUATION 4 IN FORMULA LIST
   23 AA = ETA(ML,4)
      AB = ETA(NL,4)
      J = N - 4
      AJ = ETA(ML,J)
      BJ = ETA(NL,J)
      CI = AA*ETA(ML,I) + AB*ETA(NL,I)
   40 DIPI = 0.5*ER*(CI - CI*AC/AB - 2.0*  AC*(BJ-AJ)*D(I,J) + 2.0*AC
     1 **2*(BJ-AJ)**2*CI/AB)/AB
      RETURN
C            (DJJ/R/S).....EQUATION 4 IN FORMULA LIST
   31 AA = ETA(NL,4)
      AB = ETA(ML,4)
      J = M - 4
      AJ = ETA(NL,J)
      BJ = ETA(ML,J)
      CI = AA*ETA(NL,I) + AB*ETA(ML,I)
      GO TO 40
C            (S/R/DJK).....EQUATION 6 IN FORMULA LIST
  241 J= M
      K = N - 6
      GO TO 24
  242 J = M + 1
      K = N - 7
   24 AA = ETA(ML,4)
      AB = ETA(NL,4)
      AJ = ETA(ML,J)
      BJ = ETA(NL,J)
      AK = ETA(ML,K)
      BK = ETA(NL,K)
      CI = AA*ETA(ML,I) + AB*ETA(NL,I)
  200 DIPI = ER*(-  AC*(BK-AK)*D(I,J) -    AC*(BJ-AJ)*D(I,K) + 2.0*AC
     1 *CI*(BK-AK)*(BJ-AJ)/AB)/(2.0*AB)
      RETURN
C            (DJK/R/S).....EQUATION 6 IN FORMULA LIST
   41 J = N
      K = M - 6
      GO TO 400
   51 J = N + 1
      K = M   - 7
  400 AA = ETA(NL,4)
      AB = ETA(ML,4)
      AJ = ETA(NL,J)
```

```
      BJ = ETA(ML,J)
      AK = ETA(NL,K)
      BK = ETA(ML,K)
      CI = AA*ETA(NL,I) + AB*ETA(ML,I)
      GO TO 200
C          (PJ/R/DKK).....EQUATION 5 IN FORMULA LIST
   25 AA = ETA(ML,4)
      AB = ETA(NL,4)
      J = M - 1
      K = N - 4
      AJ = ETA(ML,J)
      BJ = ETA(NL,J)
      AK = ETA(ML,K)
      BK = ETA(NL,K)
      CI = AA*ETA(ML,I) + AB*ETA(NL,I)
  250 DIPI = 0.25*ER*(AA*D(I,J) - AA*AC*D(I,J)/AB + 2.0*AC*D(I,J)*
     1 D(I,K) - 4.0*  AC**2*(BK-AK)*CI*D(J,K)/AB + 2.0*AC**2*AA*(BK-AK)
     2 **2*D(I,J)/AB + 4.0*  AC**3*(BK-AK)**2*(BJ-AJ)*CI/AB - 4.0*AC**2
     3 *(BJ-AJ)*(BK-AK)*D(I,K) + 2.0*  AC*CI*(BJ-AJ) -2.0*  AC**2*CI*
     4 (BJ-AJ)/AB)/(AA*AB)
      RETURN
C          (PJ/R/DKL).....EQUATION 7 IN FORMULA LIST
  261 K = N - 7
      L = N - 6
      GO TO 260
  262 K = N - 8
      L = N - 6
      GO TO 260
  263 K = N - 8
      L = N - 7
  260 J = M - 1
      AA = ETA(ML,4)
      AB = ETA(NL,4)
      AJ = ETA(ML,J)
      AK = ETA(ML,K)
      AL = ETA(ML,L)
      BJ = ETA(NL,J)
      BK = ETA(NL,K)
      BL = ETA(NL,L)
      CI = ETA(ML,I)*AA + ETA(NL,I)*AB
  600 DIPI = 0.25*ER*(-2.0*AC**2*(BJ-AJ)*(BK-AK)*D(I,L) - 2.0*AC**2*
     1 (BJ-AJ)*(BL-AL)*D(I,K) + 4.0*  AC**3*CI*(BJ-AJ)*(BK-AK)*(BL-AL)/
     2 AB + AC*D(I,L)*D(J,K) + AC*D(I,K)*D(J,L) + 2.0*AC**2*AA*(BK-AK)
     3*(BL-AL)*D(I,J)/AB - 2.0*  AC**2*CI*(BL-AL)*D(J,K)/AB - 2.0*AC**2
     4 *CI*(BK-AK)*D(J,L)/AB)/(AA*AB)
      RETURN
C          (DKK/R/PJ).....EQUATION 5 IN FORMULA LIST
   32 J = N - 1
      K = M - 4
```

```
      AA = ETA(NL,4)
      AB = ETA(ML,4)
      AJ = ETA(NL,J)
      BJ = ETA(ML,J)
      AK = ETA(NL,K)
      BK = ETA(ML,K)
      CI = ETA(ML,I)*AB + ETA(NL,I)*AA
      GO TO 250
C            (DKL/R/PJ).....EQUATION 7 IN FORMULA LIST
   62 J = N - 1
      K = M - 8
      L = M - 6
      GO TO 500
   42 J = N - 1
      K = M - 7
      L = M  - 6
      GO TO 500
   52 J = N - 1
      K = M - 8
      L = M - 7
  500 AA = ETA(NL,4)
      AB = ETA(ML,4)
      AJ = ETA(NL,J)
      BJ = ETA(ML,J)
      AK = ETA(NL,K)
      BK = ETA(ML,K)
      AL = ETA(NL,L)
      BL = ETA(ML,L)
      CI = ETA(NL,I)*AA + ETA(ML,I)*AB
      GO TO 600
C            (DKK/R/DJJ).....EQUATION 8 IN FORMULA LIST
  351 AA = ETA(ML,4)
      AB = ETA(NL,4)
      J = N - 4
      K = M - 4
      AJ = ETA(ML,J)
      BJ = ETA(NL,J)
      AK = ETA(ML,K)
      BK = ETA(NL,K)
      CI = AA*ETA(ML,I) + AB*ETA(NL,I)
      DIPI = ER*(AA*AB*CI - AB*AC*CI - AC*AA*CI + 2.0*AC**2*CI*D(J,K) +
     1 AC**2*CI + 2.0*AA*AB*AC*(BK-AK)*D(I,K) - 2.0*AA*AB*AC*(BJ-AJ)*
     2 D(I,J) + 2.0*AB*AC**2*(BJ-AJ)*D(I,J) - 2.0*AA*AC**2*(BK-AK)*
     3 D(I,K) - 4.0*AA*AC**2*(BJ-AJ)*D(I,K)*D(I,J) + 4.0*AB*AC**2*(BK-AK
     4 )*D(J,K)*D(I,J) - 8.0*AC**3*CI*(BJ-AJ)*(BK-AK)*D(J,K) + 2.0*AB*AC
     5 **2*CI*(BK-AK)**2 + 2.0*AA*AC**2*CI*(BJ-AJ)**2 - 2.0*AC**3*CI*
     6 (BJ-AJ)**2 - 2.0*AC**3*CI*(BK-AK)**2 + 4.0*AA*AC**3*(BJ-AJ)**2*
```

```
     7(BK-AK)*D(I,K) - 4.0*AC**3*AB*(BK-AK)**2*(BJ-AJ)*D(I,J) + 4.0*AC
     8 **4*CI*(BJ-AJ)**2*(BK-AK)**2)/(4.0*AA**2*AB**2)
      RETURN
C             (DJL/R/DKK).....EQUATION 9 IN FORMULA LIST
  352 IF(M.LT.8) GO TO 370
      K = N - 4
      IF(M - 9) 371,372,373
  370 K = M - 4
      IF(N - 9) 371,372,373
  371 J = 1
      L = 2
      GO TO 375
  372 J = 1
      L = 3
      GO TO 375
  373 J = 2
      L = 3
  375 IF(M.LT.8) GO TO 376
      AA = ETA(ML,4)
      AB = ETA(NL,4)
      AJ = ETA(ML,J)
      BJ = ETA(NL,J)
      AK = ETA(ML,K)
      BK = ETA(NL,K)
      AL = ETA(ML,L)
      BL = ETA(NL,L)
      CI = ETA(ML,I)*AA + ETA(NL,I)*AB
      GO TO 91
  376 AA = ETA(NL,4)
      AB = ETA(ML,4)
      AJ = ETA(NL,J)
      BJ = ETA(ML,J)
      AK = ETA(NL,K)
      BK = ETA(ML,K)
      AL = ETA(NL,L)
      BL = ETA(ML,L)
      CI = ETA(ML,I)*AB + ETA(NL,I)*AA
   91 CONTINUE
      DIPI = ER*(4.0*AC**2*AB*D(I,K)*D(K,L)*(BJ-AJ) + 2.0*AC*AB*AA*
     1 (BJ-AJ)*D(I,L) - 2.0*AC**2*AA*(BJ-AJ)*D(I,L) - 4.0*AC**2*AA*(BK
     2 - AK)*D(I,J)*D(K,L) - 4.0*AC**2*AA*(BK-AK)*D(I,L)*D(J,K) + 4.0*
     3 AC**2*AB*(BL-AL)*D(I,J)*D(I,K) + 2.0*AA*AB*AC*(BL-AL)*D(I,J) -
     3 2.0*AA*AC**2*(BL-AL)*D(I,J) -
     4 8.0*AC**3*(BK-AK)*(BL-AL)*CI*D(J,K) + 4.0*AC**3*AB*CI*(BJ-AJ)*
     5 (BL-AL) - 4.0*AC**3*(BJ-AJ)*(BL-AL)*CI - 8.0*AC**3*(BK-AK)*(BJ-AJ
     6 )*CI*D(L,K) + 4.0*AC**3*AA*(BK-AK)**2*(BL-AL)*D(I,J) - 8.0*AC**3
     7*AB*(BJ-AJ)*(BL-AL)*(BK-AK)*D(I,K) + 4.0*AC**3*AA*(BK-AK)**2*(BJ-
     8 AJ)*D(I,L) + 8.0*AC**4*(BJ-AJ)*(BL-AL)*(BK-AK)**2*CI)/(8.0*AA
     9 **2*AB**2)
```

```
      RETURN
C           (DJK/R/DLP).....EQUATION 10 IN FORMULA LIST
  363 IF(M-9) 390,391,392
  390 K = 1
      L = 2
      GO TO 403
  391 K = 1
      L  = 3
      GO TO 403
  392 K = 2
      L = 3
  403 IF(N-9) 393,394,395
  393 J = 1
      P = 2
      GO TO 401
  394 J = 1
      P = 3
      GO TO 401
  395 J = 2
      P = 3
  401 AA  =  ETA(ML,4)
      AB  =  ETA(NL,4)
      CI  =  AA*ETA(ML,I)  +  AB*ETA(NL,I)
      AJ  =  ETA(ML,J)
      BJ  =  ETA(NL,J)
      AK  =  ETA(ML,K)
      BK  =  ETA(NL,K)
      AL  =  ETA(ML,L)
      BL  =  ETA(NL,L)
      AP  =  ETA(ML,P)
      BP  =  ETA(NL,P)
      DIPI  =  FR*(2.0*AC**2*CI*D(P,L)*D(J,K)  +  2.0*AC**2*CI*D(L,J)*D(P,K)
     1  + 2.0*AC**2*AB*(BK-AK)*D(L,J)*D(I,P)  + 2.0*AC**2*AB*(BL-AL)*D(J,K
     2  )*D(I,P)  + 2.0*AC**2*AB*(BL-AL)*D(I,J)*D(K,P)  + 2.0*AC**2*AB*
     3  (BK-AK)*D(I,J)*D(L,P)  - 2.0*AC**2*AA*(BJ-AJ)*D(I,L)*D(P,K)-2.0*AC
     4  **2*AA*(BJ-AJ)*D(I,K)*D(P,L)  - 2.0*AC**2*AA*(BP-AP)*D(I,L)*D(J,K)
     5  + 2.0*AC**2*AA*(BP-AP)*D(I,K)*D(J,L)  - 4.0*AC**3*CI*(BJ-AJ)*(BL-
     6  AL)*D(K,P)  - 4.0*AC**3*CI*(BJ-AJ)*(BK-AK)*D(P,L)  - 4.0*AC**3*CI*
     7  (BP-AP)*(BL-AL)*D(J,K)  - 4.0*AC**3*CI*(BK-AK)*(BP-AP)*D(J,L)  - 4.
     8  0*AC**2*AB*(BJ-AJ)*(BK-AK)*(BL-AL)*D(I,P)  - 4.0*AC**3*AB*(BP-AP)
     9  *(BK-AK)*(BL-AL)*D(I,J)  + 4.0*AC**3*AA*(BP-AP)*(BJ-AJ)*(BL-AL)*
     1  D(I,K)  + 4.0*AC**3*AA*(BP-AP)*(BJ-AJ)*(BK-AK)*D(I,L)  + 8.0*AC**4
     3  *CI*(BJ-AJ)*(BK-AK)*(BL-AL)*(BP-AP))/(8.0*AA**2*AB**2)
      RETURN
      END
      SUBROUTINE PRNT(Y,NB,ND)
      DIMENSION Y(ND,ND)
      M2=0
```

```
      DO 710 M3=1,10
      M1=M2+1
      M2=M2+12
      IF(M2-NB)711,712,712
712   M2=NB
      M3=10
711   PRINT 6005,(J,J=M1,M2)
      PRINT 108
      DO 505 I=1,NB
505   PRINT50,I,(Y(I,J),J=M1,M2)
710   PRINT 107
107   FORMAT(//)
108   FORMAT(/)
   50 FORMAT(1X,I2,1X,12F10.6)
6005  FORMAT(4X,I7,11I10)
      RETURN
      END
```

APPENDIX III

TRANSFORMATION OF AB INITIO MOLECULAR ORBITALS TO CNDO FORMAT

The self consistent field equations which are solved in ab initio molecular orbital studies are generally expressed in matrix notation as:

$$FC = SCE \qquad (I)$$

where F is the Fock matrix, S the overlap matrix, C the matrix of molecular orbital coefficients and E the eigenvalue matrix. The difference between these equations and the semi-empirical analogues is due to the inclusion of atomic overlap in the former case.

In the CNDO approach, the Hartree-Fock equations reduce to:

$$F'C' = C'E \qquad (II)$$

Prior to their use in the process of parametrization of CNDO, the ab initio wave functions must be transformed so that the coefficients correlate with those obtained in the semi-empirical method. This transformation is quite straightforward consisting of a single mathematical manoeuvre - namely left multiplication of equation (I) by $S^{-\frac{1}{2}}$ to give:

$$S^{-\frac{1}{2}}FS^{-\frac{1}{2}}S^{\frac{1}{2}}C = S^{\frac{1}{2}}CE \qquad (III)$$

TABLE XVII

ORBITAL CHARGE DENSITIES FOR CARBON MONOSULPHIDE

Function	Charge Density	
	Without d(a)	With d(b)
C 1S	0.9983	0.9977
2S	0.8554	0.7548
2px	0.2899	0.2701
y	0.2899	0.2701
z	0.6688	0.6614
S 1S	0.9997	0.9992
2S	0.9990	0.9930
3S	0.8664	0.5006
2px	0.9913	0.9912
3px	0.7186	0.7141
2py	0.9913	0.9912
3py	0.7186	0.7141
2pz	0.9884	0.9880
3pz	0.6236	0.6321
3dxx		0.1337
yy		0.1337
zz		0.2052
xy		0.
xz		0.0244
yz		0.0244

(a) $r_{CS} = 1.5349$ Å

(b) $r_{CS} = 1.5349$ Å; $\zeta_1 = 1.63$, $\zeta_2 = 1.75$

TABLE XVIII

ORBITAL CHARGE DENSITIES FOR HYDROGEN SULPHIDE

Function	Charge Densities		
	No $d^{(c)}$	With $d^{(a)}$	With $d^{(b)}$
H 1S	0.4934	0.4247	0.4110
S 1S	0.9995	0.9992	0.9992
2S	0.9980	0.9925	0.9924
3S	0.8460	0.4803	0.4754
2px	1.0	0.9999	0.9999
3	1.0	0.9988	0.9986
2py	0.9836	0.9829	0.9885
3	0.5103	0.5125	0.5251
2pz	0.9888	0.9886	0.9925
3	0.6857	0.6745	0.6898
3dxx		0.1429	0.1405
yy		0.1570	0.1579
zz		0.1514	0.1514
xy		0.	0.
xz		0.0011	0.0013
yz		0.0681	0.0646

(a) r_{SH} = 1.328 Å, <HSH = 92.2°; ζ = 1.66; (4/224242)

(b) r_{S-H} = 1.328 Å, <HSH = 92.2°; ζ = 1.66; (4/224562)

(c) r_{S-H} = 1.328 Å, <HSH = 92.2°.

TABLE XIX

ORBITAL CHARGE DENSITIES FOR SULPHUR DIOXIDE

Functions	Charge Density		
	No d(a)	Single dxy(b)	Fall d Set(c)
O 1S	0.9986	0.9985	0.9977
2S	0.9121	0.9067	0.7987
2px	0.6876	0.5645	0.6111
y	0.7048	0.7326	0.7283
z	0.9040	0.9138	0.8049
S 1S	0.9995	0.9995	0.9991
2S	0.9974	0.9972	0.9918
3S	0.8176	0.8126	0.4722
2px	0.9890	0.9883	0.9857
3 x	0.6356	0.6100	0.5182
2py	0.9842	0.9831	0.9816
3 y	0.4487	0.4186	0.4181
2pz	0.9921	0.9913	0.9896
3 z	0.7208	0.6934	0.6365
3dxx			0.1537
yy			0.2716
zz			0.2440
xy		0.2723	0.2436
yz			0.0301
xz			0.1816

(a) <OSO = 119.5°, r_{SO} = 1.4321 Å.

(b) <OSO = 119.5°, r_{S-O} = 1.4321 Å; ζ_{xy} = 1.40

(c) <OSO = 119.5°, r_{SO} = 1.4321 Å ; ζ_1 = 1.40, ζ_2 = 1.53

TABLE XX

ORBITAL CHARGE DENSITIES FOR OZONE

Functions	Charge Density		
	Single dxy[(a)]	Fall d Set[(b)]	Without d[(c)]
0 1S	0.9987	0.9984	0.9987
2S	0.9405	0.8174	0.9417
2px	0.5801	0.5910	0.6708
y	0.6031	0.5904	0.5925
z	0.8547	0.7880	0.8516
0' 1S	0.9970	0.9954	0.9970
2S	0.8470	0.7975	0.8480
2px	0.6533	0.6263	0.6582
y	0.5582	0.5544	0.5733
z	0.8035	0.7957	0.8122
3dxx		0.0242	
yy		0.1961	
zz		0.1049	
xy	0.1862	0.1742	
xz		0.0171	
yz		0.1425	

(a) r_{0-0} = 1.278 Å, <000 = 116.8°; ζ_{xy} = 1.10

(b) r_{0-0} = 1.278 Å, <000 = 116.8°; ζ_1 = 1.10, ζ_2 = 1.20

(c) r_{0-0} = 1.278 Å, <000 = 116.8°

On comparison of equations (II) and (III), it is seen that the following relationships hold:

$$F' = S^{-\frac{1}{2}}FS^{-\frac{1}{2}} \qquad \text{(IV)}$$

and

$$C' = S^{\frac{1}{2}}C$$

so that the ab initio molecular orbital coefficient matrix need only be premultiplied by the square root of the overlap matrix to effect a transformation to molecular orbital coefficients of the CNDO type.

Such a procedure was applied to the molecular wave functions obtained for the series of molecules studied in this work. The transformed molecular orbitals were then used to calculate the CNDO bond order-charge density matrix. It is a property of these transformed molecular orbitals that the total charge density is equal to the total number of electrons in the system.

The results of bond order calculations, and hence of the molecular orbital transformations, constitute the first stage in the CNDO parametrization. The transformed molecular orbitals are available for future reference if required. In this appendix, a brief summary of the calculations is presented in the form of a tabulation of charge densities for the various molecules studied. It would be one of the objectives of the procedure of parametrizing CNDO for second row to replicate these charge densities, and in fact the bond orders, as closely as possible.

REFERENCES

1. R. F. Stewart and W. J. Hehre, J. Chem. Phys., 52, 5243 (1970).
2. R. Ditchfield, W. J. Hehre and J. A. Pople, J. Chem. Phys., 52, 5001 (1970).
3. A. Veillard, Theor. Chim. Acta., 12, 405 (1968).
4. R. F. Stewart, J. Chem. Phys., 52, 431 (1970).
5. S. Huzinaga, J. Chem. Phys., 42, 1293 (1965).
6. R. S. Mulliken, J. Chem. Phys., 36, 3428 (1962).
7. J. A. Pople, J. Chem. Phys., 51, 2657 (1969).
8. R. Ditchfield, D. P. Miller, and J. A. Pople, J. Chem. Phys., 53, 613 (1970).
9. R. Ditchfield, D. P. Miller, and J. A. Pople, J. Chem. Phys., 53, 932 (1970).
10. J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys., 43, S129 (1965).
11. D. P. Santry and G. A. Segal, J. Chem. Phys., 47, 158 (1967).
12. W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, J. Chem. Phys., 52, 2769 (1970).
13. D. P. Craig and C. Zauli, J. Chem. Phys., 37, 601 (1962).
14. F. P. Boer and W. N. Lipscomb, J. Chem. Phys., 50, 989 (1969).
15. S. Rothenberg and H. F. Schaefer III, J. Chem. Phys., 53, 3014, (1970).
16. I. H. Hillier and V. R. Saunders, Trans. Far. Soc., 66, 1544 (1970).
17. S. Rothenberg, R. H. Young, and H. F. Schaefer III, J. Am. Chem. Soc., 92, 3243 (1970).

18. D. B. Boyd and W. N. Lipscomb, J. Chem. Phys., 46, 910 (1967).

19. R. Gerdil and L. A. C. Lucken, J. Am. Chem. Soc., 87, 213 (1965).

20. A. Mangini, Molecular Structure and Spectroscopy, (Butterworths, London, 1963), p.103.

21. D. T. Clark and D. R. Armstrong, Chem. Comm. 5, 319 (1970).

22. C. C. J. Roothaan, Rev. Mod. Phys., 23, 69 (1951).

23. J. A. Pople and R. K. Nesbet, J. Chem. Phys., 22, 571 (1954).

24. I. G. Csizmadia, J. W. Moskowitz, M. C. Harrison and B. T. Sutcliffe, Theor. Chim. Acta, 6, 191 (1966).

25. H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944), p.162.

26. S. F. Boys, Proc. Roy. Soc., A200, 542 (1950).

27. I. Shavitt, Methods in Computational Physics, (Academic Press Inc., New York, 1963), Vol. 2, p1.

28. H. H. Jaffe, Acc. Chem. Res., 2, 136 (1969).

29. J. A. Pople and G. A. Segal, J. Chem. Phys., 43, S136 (1965).

30. J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory, (McGraw-Hill Inc., New York, 1970).

31. R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, J. Chem. Phys., 17, 1248 (1949).

32. C. E. Moore, Atomic Energy Levels, (National Bureau of Standards, Circular No. 467, 1952).

33. J. L. Whitten, J. Chem. Phys., 39, 349 (1963).

34. K. O-Ohata, H. Taketa and S. Huzinaga, J. Phys. Soc. Jap., 21, 2306 (1966).

35. H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry, (John Wiley and Sons, Inc., New York, 1944), p.162.

36. E. Clementi and D. L. Raimondi, J. Chem. Phys., 38, 2686 (1963).

37. M. Keeton and D. P. Santry, Chem. Phys., Lett., 17, 105 (1970).

38. A. L. McClellan, Tables of Experimental Dipole Moments, (W. H. Freeman and Co., San Francisco, 1963).

39. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, (Interscience, New York, 1966), p.728.

40. H. C. Allen Jr. and E. K. Plyler, J. Chem. Phys., 25, 1132 (1956).

41. D. Kivelson, J. Chem. Phys., 22, 904 (1954).

42. R. C. Mockler and G. R. Bird, Phys. Rev., 98, 1837 (1955).

43. I. H. Hillier and V. R. Saunders, Chem. Phys. Lett., 4, 163 (1969).

44. G. Herzberg, Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules, (Van Nostrand Co. Inc., New York, 1945), p.161.

45. T. Shimanouchi, Physical Chemistry, An Advanced Treatise, Volume IV, Molecular Properties - H. Eyring, D. Henderson and W. Jost, editors (Academic Press, New York, 1970), p.233.

46. P. Pulay, Mol. Phys., 17, 197 (1969).

47. G. Herzberg, Molecular Spectra and Molecular Structure I, Diatomic Molecules, (Van Nostrand Co. Inc., New York, 1950).

48. G. Herzberg, Molecular Spectra and Molecular Structure III, Electronic Spectra and Electronic Structure of Polyatomic Molecules (Van Nostrand Co. Inc., New York, 1966), p. 511, 605.

49. G. Herzberg, Molecular Spectra and Molecular Structure I, Diatomic Molecules (Van Nostrand Co. Inc., New York, 1950), p.213.

50. R. S. Mulliken, Can. J. Chem., 36, 10 (1958).

51. A. D. Walsh, J. Chem. Soc., 2260 (1953).

52. J. C. D. Brand, C. di Lauro and V. T. Jones, J. Am. Chem. Soc., 92, 6095 (1970).

53. A. J. Merer, Disc. Far. Soc., 35, 127 (1963).

54. A. Reuveni and Z. Luz, J. Chem. Phys., 53, 4619 (1970).

55. D. C. McCain, J. Chem. Phys., 53, 1297 (1970).

56. M. Green, J. Chem. Soc., 2819 (1962).

57. G. Herzberg, Molecular Spectra and Molecular Structure III, Electronic Spectra and Electronic Structure of Polyatomic Molecules, (Van Nostran Co. Inc., New York, 1966), p. 510, 604.

58. S. D. Peyerimhoff and R. J. Buenker, J. Chem. Phys., 47, 1953 (1967).

59. C. Petrongolo, E. Scrocco and J. Tomasi, J. Chem. Phys., 48, 407, (1968).

60. J. L. Whitten, J. Chem. Phys., 44, 359 (1966).

61. A. E. Douglas, Can. J. Phys., 36, 147 (1958).

62. A. Breeze, G. A. D. Collins, and D. W. J. Cruickshank, Chem. Comm., 9, 445 (1971).