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AB INITIO SCF-MO CALCULATIONS ON LINEAR
TRIATOMIC MOLECULES

A thesis presented by

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to the

University of St. Andrews
in application for the Degree
of Master of Science



ABSTRACT

Single configuration wave functions for the ground states of several small species have been calculated - $\text{OCC } ^3\Sigma^-$; $\text{CNC } ^2\Pi$; $\text{NCO } ^2\Pi$; $\text{NC } ^2\Sigma^+$; $\text{PC } ^2\Sigma^+$; $\text{OBO } ^2\Pi$; HBO. Extended Slater function basis sets were used in these calculations, allowing the wave functions so calculated to approach the Hartree-Fock limit. One-electron properties have been calculated for the species; and, where possible, compared with the experimental results. Conclusions are drawn that the near Hartree-Fock wave function gives good predictions of one-electron properties. These investigations were continued for species containing second-row atoms - $\text{SCC } ^3\Sigma^-$; $\text{PCC } ^2\Pi$; $\text{SCN } ^2\Pi$; $\text{PC } ^2\Sigma^+$.

The single configuration approximation has been used in the calculation of wave functions for excited states of some of these species - OCC; NCC; NNC; NCO; CNC. Conclusions are drawn that the single configuration wave function is not an adequate model of excited states.

For the ground state species, HBO, a configuration interaction investigation was undertaken.

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CAREER

The author began his University career in 1966 at St. Andrews University. In 1969 he graduated with BSc Ordinary Degree, following this in 1971, with 2nd Class Honours in Chemistry.

In October of 1971, he matriculated as a Research Student in the Department of Chemistry at St. Andrews University, pursuing research in Theoretical Chemistry. This led to the presentation of this thesis for Master of Science.

During this work, from 1971 to 1974, the author was supported by a grant from the Purdie Fund.

Declaration:

I hereby certify that I am the sole composer of this thesis, that it is a record of my own work and that it has not been previously presented for a higher degree.

This research was carried out in the Chemistry laboratory of St. Salvator's College, in the University of St. Andrews, under the supervision of Dr. C. Thomson.

Certificate:

I certify that B.J. Wishart BSc has spent nine terms at research work in the Chemistry laboratory of St. Salvator's College in the University of St. Andrews under my direction, that he has fulfilled the conditions of Ordinance Number 16 (St. Andrews) and that he is qualified to submit the accompanying thesis in application for the degree of Master of Science.

Research Supervisor.

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" ... events and not particles constitute the true objective reality."

J. Jeans

INTRODUCTION

Quantum chemistry is an area of chemistry that has been receiving increasing attention, particularly in calculations of ab initio quality. This is largely owing to the availability - through the generosity of the originators - of computer programmes capable of performing calculations on species consisting of several atoms. Such calculations have not always been taken to the limit of which the ab initio methods are capable. For a single configuration wave function, the limiting function that can be found is the Hartree-Fock function. Even for closed shell systems, which are simpler, such functions do not make up the bulk of the ab initio results found in the literature. This is shown in the recent book by Schaefer¹², which, as he indicates, is intended as a state-of-the-art survey. In the work presented as this thesis, attempts have been made to obtain near Hartree-Fock wave functions for several linear triatomic species.

Bibliographies of ab initio calculations have been published, by Krauss⁷² - updated by Allen¹⁴ - and by Richards et al¹¹. As these general compilations exist, and as pertinent references are included in each section, a general extension of these bibliographies has not been attempted.

The existing corpus of work on atomic systems has led to the establishment of basis sets that give Hartree-Fock atomic wave functions. By extrapolation from these, basis sets that should give Hartree-Fock molecular wave functions, for ground state systems, have been established. For open shell species, and excited states are usually in this class, it is not clear if these bases will give

wave functions of this accuracy. In fact, for excited states, consideration of a wave function as a single determinant, analagous to the Hartree-Fock limit is not always valid.

As is made clear in the book by Schaefer ¹², there has been growing use of wave functions in the prediction of molecular properties. The use of near Hartree-Fock functions in the calculation of these is not yet, however, common. Prediction of properties related to the detail of the description of the electronic distribution, such as the electric multipole moments, from less than Hartree-Fock wave functions is open to criticism. In the calculation of molecular properties for those species discussed in this thesis, estimation of the basis set quality required for the prediction of these properties was attempted.

An introductory chapter is included, deriving Hartree-Fock theory, which forms the basis of the computer programmes used. The Hartree-Fock wave function being only a single determinant function, some configuration interaction calculation has been attempted.

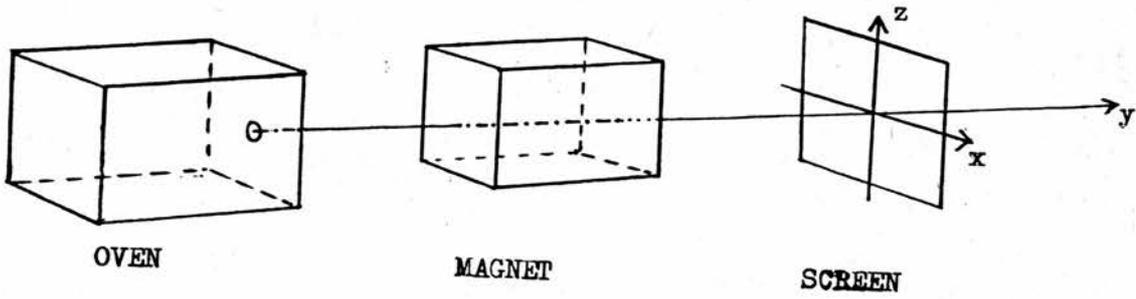
Note on units: in the formal theory presented, atomic units are used throughout. In the discussion of the results, atomic units are also used, with some reference to C.G.S. units. Conversion factors are given in Appendix I.

CHAPTER 1THEORETICAL BACKGROUNDIntroduction

In 1921, O. Stern postulated an experiment to determine whether, in a magnetic field, an atom possessing a magnetic moment would be deflected in a manner consistent with classical or with quantum predictions¹¹⁶. Also in 1921, Stern, together with W. Gerlach, performed this experiment for silver atoms^{117,118}.

Apparatus was set up as following: an oven, generating a flux of atomic silver, was followed by a wedge-shaped electromagnet, then by a screen - Figure 1. The effect is of a highly polarized magnetic field - in the z-direction. The experiment resulted in the following; without the field, a distribution of silver atoms along the x-axis, either side of the centre line - Figure 2a. On applying the field, the classical theory predicts a distribution about the z-axis - Figure 2b; but, if there is a quantum effect, there should be obtained a distribution avoiding the line of the y-axis - Figure 2c. The result found was that as in Figure 2c; that is, the interaction of an atom possessing a magnetic moment, with a magnetic field is consistent with an assumption that the system is governed by the rules of quantum mechanics. That the pattern closes on the x-axis at each end is caused by the decay of the field gradient away from the y-axis. Knowing the applied field, the magnetic moment of the species can be derived from the maximum displacement - as Stern and Gerlach do in their paper subsequent to the above⁴⁷.

Figure 1



Detail of magnet: (hatched areas are pole pieces)

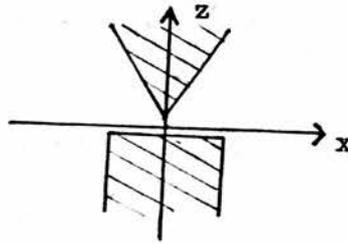
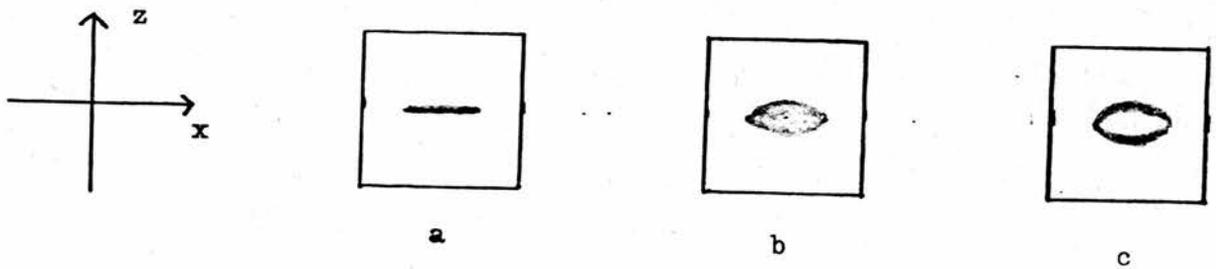


Figure 2



McWeeny, in his book 'Spins in Chemistry'⁷, to whom this beginning is indebted, suggests an extension of the experiment. In this, a second magnet is introduced after the atomic beam has passed the first. With one of the two beams cut off, and the second magnet with field parallel to that of the first, the beam remains the same; but, if the second magnet has field perpendicular to this, the beam is again split in two.

The most important conclusion to be drawn is that, in performing the experiment, the quantity that is being measured is determined by the experiment. From the extension outlined above, a particle with a definite z-component, m_z , as observed in the experiment, is found to have x-components, $+\lambda_1, -\lambda_2$, with an equal chance of being in either. The particle is in a state, $m_z = +\lambda_1$; or, an equally valid description is that the particle is in a state with $m_x = +\lambda_1$, or, $m_x = -\lambda_2$, with an equal probability of either. There is, thus, an indefiniteness in the description of the system, and the state of the particle is describable only in terms of the probability with which the various possible results are observed.

The incoming atomic beam will be in a particular state, which can be represented by a vector, ψ , which is chosen for convenience as a unit vector. This is observed to be resolved into two possible states, λ_1 and λ_2 , with probabilities p_1 and p_2 respectively. If two further unit vectors, α and β , are defined as being orthonormal - λ_1 and λ_2 being representable in terms of these - ψ can be expressed as a linear combination of these - the experiment establishing dependence. In Figure 3, the two coefficients, c_1 and c_2 , indicate the probability of finding the state represented by ψ in state λ_1 or state λ_2 . They can be related to the probabilities p_1 and p_2 as:

Figure 3

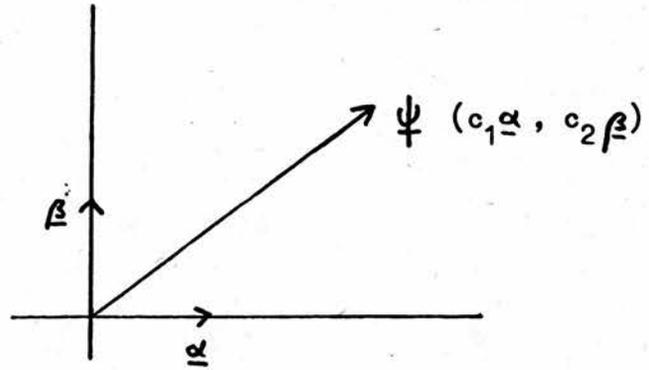
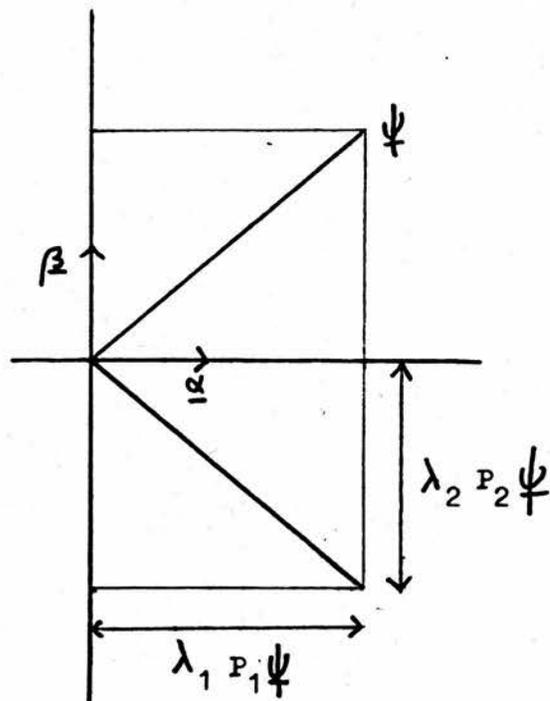


Figure 4



$$\lambda_1 = \frac{1}{2}; \quad \lambda_2 = -\frac{1}{2}$$

$p_1 = c_1^2$; $p_2 = c_2^2$. As Ψ is defined as a unit vector, $c_1^2 + c_2^2 = 1$. By vector addition, $\Psi = c_1\alpha + c_2\beta$. The projection of the state, Ψ , along the α -axis, is c_1 . If this statement is written in algebraic form, with the symbol P_1 indicating the selection from the stream of α -type nuclei , as: $P_1\Psi = c_1\alpha$, the scalar product, $\Psi \cdot P_1\Psi$, can be formed:

$$\begin{aligned} \Psi \cdot P_1\Psi &= (c_1\alpha + c_2\beta) \cdot c_1\alpha \\ &= c_1^2 (\alpha \cdot \alpha) \\ &= c_1^2 \\ &= p_1 \end{aligned}$$

Similar equations hold for the selection along the β -axis. The average value of the property observed in the magnetic-selection experiment is the sum, $p_1\lambda_1 + p_2\lambda_2$. That is, the average value over a large number of observations of the property interacting with the z direction of the magnetic field can be written:

$$p_1\lambda_1 + p_2\lambda_2 = \Psi \cdot (\lambda_1 P_1 + \lambda_2 P_2) \Psi .$$

The quantity in the parentheses is an operator associated with the observed property.

To confirm that this is a valid description of the experimental situation, consider the experiment postulated on page 5. Here, $p_1 = p_2 = \frac{1}{2}$, with the components above and below the y-axis. As the probabilities are the same, the state functions are orthogonal, and the expectation value for the property is zero; that is, an equal probability of being in either state is equivalent to an average of zero (Figure 4).

The state, Ψ , of the atom stream, in which the magnetic state is unknown, is describable as the superposition of states in which that state is known - the two states, α and β .

From the above, an expression of the form, $H\psi = E\psi$, where H is an operator representing the total energy, can be induced. The equation, $\psi \cdot P\psi = p$, where P is an operator corresponding to the property, p , has been obtained. Multiplying from the left gives:

$$\psi \cdot \psi \cdot P\psi = \psi p.$$

As ψ has been chosen as a unit vector, this is equivalent to the form:

$$P\psi = p\psi.$$

Having produced the Schrödinger equation¹¹⁰ by little more than sleight of hand it requires to be pointed out that the Schrödinger theory requires the orbital angular momentum, \underline{L} , to be zero (m_l also = 0), and the observed property derives in fact from some other intrinsic property of the electronic system; a property such that its projections on the directed field are $\pm \lambda$. This property is usually given the symbol, \underline{S} , and referred to as the electronic 'spin'.

In his first paper¹¹⁰, Schrodinger introduced his equation in a non-relativistic, time-independent form. At this point, the equation is taken as an axiom of non-relativistic quantum mechanics. Other axiomatic statements are required: ii) that there exists a function that contains encoded within itself all the measurable properties of the system; iii) forms for operators are required - the P in the above equations; iv) the existence of electronic spin, with only two possible states. Axiom ii) has been introduced in discussing the Stern-Gerlach experiment. For axiom iii), classical expressions can be transformed into quantum mechanical operators by, for example: a property dependent on coordinate alone has the

same expression for the quantum mechanical operator; linear momentum in one direction is given by the operator, $\frac{\hbar}{i} \frac{\partial}{\partial x}$.

Part of axiom iii) is that a value for a property is given by the expectation value,

$$\langle p \rangle = \frac{\langle \psi | P | \psi \rangle}{\langle \psi | \psi \rangle},$$

which form is consistent with the Stern-Gerlach experiment. For the fourth axiom, the Stern-Gerlach experiment again gives justification.

" Schrodinger Wave Equation

A general reference for this section is the text by Pilar⁸, in particular, Chapters 2 and 10.

To describe real systems, the Schrodinger wave equation must involve a wave function which is dependent on variables of both space and time. In one dimensional form, the Schrodinger equation is:

$$\hat{H} \Psi(x,t) = -\frac{\hbar}{i} \frac{\partial}{\partial t} \Psi(x,t).$$

The total energy operator, \hat{H} , is separable into kinetic and potential terms, $\hat{T} + \hat{V}$. The kinetic energy operator is, in one-particle form, $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$, and this will allow separation of the wave function into space- and time-dependent functions; and, if it can be taken that the potential energy operator is time-independent, the wave equation can be separated into the two equations:

$$\hat{H} \psi(x) = W \psi(x); \text{ and, the time-dependent equation,}$$

$$-\frac{\hbar}{i} \frac{d}{dt} \phi(t) = W \phi(t)$$

- where w is a constant. As that function which is a derivative of itself is defined as the exponential function, the solution of this

time-dependent equation is $\phi(t) = \exp(-i\omega t/\hbar)$. The wave function, $\Psi(x,t)$ can be expressed as a linear combination of the stationary state solutions:

$$\Psi(x,t) = \sum_n a_n(t) \psi_n(x) \exp(-i\omega t/\hbar) \quad \dots\dots 1$$

where $a_n(t)$ are expansion coefficients.

This equation indicates that the motion of a single particle can be represented by a wave packet - that is, a combination of waves localizing the particle. As more frequencies are added to give a closer boundary to the particle's position - that is, reducing Δx - the wavelength, λ , of the system becomes more uncertain; and, p_x , which is equal to h/λ , becomes more uncertain - the uncertainty principle. To be useful, the space dependent equation must be soluble for atomic and molecular systems. In even the non-relativistic framework, the Schrodinger wave equation admits of no analytic solution except for the H-atom and analogous one electron problems - a suitable presentation is given in Eyring, Walter, and Kimball⁴ - and this requires the assumption of the independence of the nuclear and electronic wave functions. For molecular systems, this is the Born-Oppenheimer approximation - which is given as Appendix II.

Via solutions of the form of equation 1 above, the time dependent wave equation is used to describe the interaction of matter and radiation. For atoms and molecules in free space, solution of the Schrodinger wave equation depends on approximate methods. These are principally the linear variation method, and perturbation theory. For the former, with the wave equation written as follows, $\hat{H} \psi = E \psi$, in general, solution of this is not known in any known coordinate system. Considering the equation,

$E' = \frac{\langle \psi' | \hat{H} | \psi' \rangle}{\langle \psi' | \psi' \rangle}$, where ψ' is a function in the system coordinates, with E' an approximation to the real energy, it has been shown that this is an upper bound to the real energy by Eckart⁴⁰; thus, if, by altering the function, ψ' , an energy is obtained with a lower value than the previous, then this new function gives a closer approach to the real system. If this wave function, relabelled as ψ_k , is expanded over some basis set of finite size,

$$\sum_i \phi_{ik},$$

the wave function becomes

$$\psi_k = \sum_n \phi_{ik} c_{ik}.$$

In this, c_k are the expansion coefficients; and, the energy can be written as

$$E = \frac{C_k^\dagger H C_k}{C_k^\dagger S C_k}, \quad \text{where: } C_k \text{ is the}$$

coefficient matrix; H the matrix, $\phi^\dagger H \phi$; S the matrix, $\phi^\dagger \phi$; and, E remains a scalar throughout. If a first order variation is now applied to this, there obtains the equation,

$$\delta E = \delta \frac{C_k^\dagger H C_k}{C_k^\dagger S C_k}.$$

From the result obtained by Eckart noted above, if this variation is minimised, then the energy obtained is the closest approach to the real situation that can be obtained with this function. This gives the equation,

$$0 = \frac{(\delta C_k^\dagger H C_k - E \delta C_k^\dagger S C_k)}{C_k^\dagger S C_k} + \text{complex conjugate.}$$

The theorem is satisfied if the equation

$$\delta C_k^\dagger (H C_k - E S C_k) = 0$$

is satisfied, that is, if $(H - ES) C_k = 0$. These are the secular

equations. They have non-trivial solutions if $\det(H - ES) = 0$.

The essence of perturbation theory is to take an already known system as a first approximation to an unknown, and, to this are added extra functions to improve the model¹. The Schrodinger wave equation can now be written in the form,

$$(\hat{H}_0 + \hat{H}_1 + \dots) (\psi_0 + \psi_1 + \dots) = (E_0 + E_1 + \dots) (\psi_0 + \psi_1 + \dots).$$

Solution of this can be achieved by the use of Rayleigh-Schrodinger theory⁸.

In 1929, Hylleraas⁶³ performed a single determinant, non-relativistic calculation on the helium atom, with the coordinates of the electrons expressed in elliptic coordinates. He also invented a form of variation-perturbation theory for calculating the energy of helium⁶⁴. This method has been extended into a more general one by Knight and Scherr^{70,71}. Knight et al have extended this work further, treating, in Rayleigh-Schrodinger formalism, H_2O ⁶⁹; to ten electron hydrides⁸⁵. Using an extended method of the Hylleraas type, Pekeris⁹⁸ obtained the exact ground state energy for helium - the wave function into 1078 terms, expressed in perimetric coordinates, by adding calculated relativistic correction terms to the non-relativistic solution thus obtained.

In fact:

' in so far as quantum mechanics is correct, chemical questions are problems in applied mathematics '

- preface to Eyring, Walter and Kimball⁴.

In the introduction of the variation method above, the Schrodinger wave equation was reduced, to enable solution to take place, to the set of equations known as the Secular Equations,

$$(H - ES) C_k = 0,$$

and solution of this is achieved by setting $\det(H - ES) = 0$. Approximations may be made on the elements of the matrices involved. This gives rise to the 'semi-empirical' methods, otherwise the methods are 'ab initio'.

Given the correct operator, \hat{H} , for the energy, we have that:

' in principle, an exact wave function for a many-electron system can be obtained by diagonalising the matrix of the many-particle Hamiltonian over some complete system of basic functions. '

- from the introduction to a paper by Nesbet⁹², basing this on the work of Boys²³. This exact wave function is a set of Slater determinants.

Apart from the Hylleraas result for helium noted above⁶³, a convergent method obtaining a solution for the hydrogen molecule was established by James and Coolidge in 1933⁶⁵. The helium atom problem is reviewed by Hylleraas⁶², and in the comprehensive survey of the one- and two-electron problems by Bethe and Salpeter².

To facilitate convergence of the diagonalisation problem noted above, Boys²³ suggested the use of linear combinations of functions grouped on the various centres of electronic charge concerned. The lowest energy terms of the expansion correspond to complete systems of functions on these centres. In his presentation, Boys uses as the complete class of functions the set of Gaussian functions, as all the integral terms can be easily evaluated. He points out that the class of functions of the type:

$$x^l y^m z^n \exp(-ar_i),$$

would be the most rapidly convergent - that is, use the smallest number of functions for a molecular description to a given accuracy.

The class of these functions is complete, as the spherical harmonics are complete with respect to angular variation; and, with $n = 1, 2, \dots$, the term, $\exp(-nkr)$ is complete with respect to radial variation.

The Hartree-Fock method, using a single determinant, is a special case - a simplified version thereof - of the above scheme. The method of configuration interaction - q.v. - approaches the method.

In presenting his variational selection method, Boys states that it is not possible to rigorously prove the theorem:

' Difficulties of rigorous justification are well known in this field, in which theorems are required, appropriate to many dimensions, concerning the solutions of equations with singularities in space which are not bounded. The requisite theorems may not be true for any mathematical function but are very probably true for the functions permissible for wave functions. '

Hartree-Fock Equations

The method of solution of the Schrödinger molecular problem is usually in the single configuration approximation, using the Hartree-Fock self-consistent field method. Hartree suggested in 1928⁵⁶ the expansion of the molecular wave function in terms of one-electron functions, orbitals. These functions are used to define operators for establishing the molecular problem. Solution is then obtained, and the resulting wave function used to establish a new operator. The process is repeated until further alteration of the wave function produces no further change in the energy.

The wave function does not, however, satisfy the anti-symmetry principle for electrons; and, the method was extended by Fock in 1930⁴⁴, and independently by Slater in the same year¹¹², producing a form concurring with the principle. If a system of two electrons is described by Hartree type functions, u_1 and u_2 , the system wave function is of the form,

$$\psi = u_1(1) u_2(2).$$

Applying the antisymmetry principle constraint to the function, the alternative function,

$$\psi = u_1(2) u_2(1),$$

must be an equivalent representation of the system; so, the system is described by the antisymmetric combination of these two functions,

$$\psi = u_1(1) u_2(2) - u_1(2) u_2(1).$$

In general, the antisymmetric wave function has the form,

$$\psi = \det u_i(j).$$

In the Hartree-Fock method, the wave function is expressed as a function of two-electron, spatial orbitals - each occupied by two electrons - of opposite spin. For a molecular system of $2N$ electrons - a closed shell system being simpler to describe - the wave function is expressed as a single determinant of N doubly-occupied spatial orbitals. The total electronic energy can be expressed as the expectation value of the operator, $\hat{H} = \hat{T} + \hat{V}$, where: T is the kinetic energy of the electrons, $-\frac{1}{2}\nabla_i^2$; and, V is the potential energy, inclusive of two parts: the Coulombic attraction of each electron by the positive nucleus, $-\frac{Z}{r_i}$; and, electrostatic interactions between the electrons, $\frac{1}{r_{ij}}$. The first two of these parts of H depend on the coordinates of only one electron at a time, and they can be abbreviated as the one electron

operator, \hat{h} . The total energy operator has become:

$$\hat{H} = \sum_{i=1}^{2N} \hat{h}_i + \sum_{i < j} \frac{1}{r_{ij}}.$$

This operator will be used in an expression to form,

$$\hat{H} \psi = E \psi.$$

Given that the function, ψ , is a combination of orthonormal spatial functions, the one electron part of the total energy operator can be written as:

$$\sum_{i=1}^{2N} \langle \hat{h}_i \rangle = 2 \sum_{i=1}^N \epsilon_i^{(0)},$$

where $\epsilon_i^{(0)}$ is defined as:

$$\langle \phi_i | \hat{h} | \phi_i \rangle.$$

For the two electron part, there result Coulomb integrals, which after integration over the spin variable are of the form,

$$J_{ij} = \sum_{i,j=1}^N \langle \phi_i^{(a)} \phi_j^{(b)} | \frac{1}{r_{ab}} | \phi_i^{(a)} \phi_j^{(b)} \rangle.$$

There are four terms with $i \neq j$, ϕ_i^α or ϕ_i^β with ϕ_j^α or ϕ_j^β .

There are, thus, the following Coulomb terms:

$$\sum_{i=1}^N J_{ii} + 4 \sum_{i < j} J_{ij}.$$

For the two electron permutations of terms, the two electron integrals are of the form,

$$\langle \phi_i^{(a)} \phi_j^{(b)} | \frac{1}{r_{ab}} | \phi_j^{(a)} \phi_i^{(b)} \rangle = K_{ij},$$

which are called exchange integrals. From spin orthogonality,

when $b = a+1$, K_{ij} are zero. Of the four $a \times b$ combinations, only two give non zero K_{ij} .

The total energy can be written:

$$\langle \hat{H} \rangle = 2 \sum_i^N \epsilon_i^{(0)} + \sum_{i < j}^N (4J_{ij} - 2K_{ij}) + \sum_i^N J_{ii}.$$

The form of this can be simplified by noting that:

$$J_{ij} = J_{ji}; K_{ij} = K_{ji}; J_{ii} = K_{ii},$$

giving the total energy as:

$$\langle \hat{H} \rangle = 2 \sum_{i=j}^N \epsilon_i^{(0)} + \sum_{i,j}^N (2J_{ij} - K_{ij}).$$

Having obtained the energy in this format, the presentation of the Hartree-Fock method can proceed. For a solution in the variational formalism, the set of orbitals which gives the minimum value for this energy is required, subject to the restriction that the set is orthonormal. The following functional is now considered:

$$A = 2 \sum_{i=1}^N \epsilon_i^{(0)} + \sum_{i,j}^N (2J_{ij} - K_{ij}) - \sum_{i,j}^N \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}),$$

where the λ_{ij} are Lagrangian multipliers. For optimal energy it is required that the variation in A, δA , is zero for small variations, $\delta \phi_i$, of the orbitals. Two operators, Coulomb and exchange are now defined:

$$\hat{J}_i(a) \phi_j(a) = \langle \phi_i(b) | \frac{1}{r_{ab}} | \phi_i(b) \rangle \phi_j(a),$$

$$\hat{K}_i(a) \phi_j(a) = \langle \phi_i(b) | \frac{1}{r_{ab}} | \phi_j(b) \rangle \phi_i(a).$$

The first order variation in the functional can now be written as:

$$\begin{aligned} \delta A = & 2 \sum_i (\langle \delta \phi_i | \hat{h}_a | \phi_i \rangle + \langle \phi_i | \hat{h}_a | \delta \phi_i \rangle) \\ & + \sum_{i,j} (\langle \delta \phi_i | 2\hat{J}_j - \hat{K}_j | \phi_i \rangle + \langle \phi_i | 2\hat{J}_j - \hat{K}_j | \delta \phi_i \rangle) \\ & + \sum_{i,j} (\langle \delta \phi_j | 2\hat{J}_i - \hat{K}_i | \phi_j \rangle + \langle \phi_j | 2\hat{J}_i - \hat{K}_i | \delta \phi_j \rangle) \end{aligned}$$

$$-\sum_{i,j} (\lambda_{ij} \langle \delta\phi_i | \phi_j \rangle + \lambda_{ij} \langle \phi_i | \delta\phi_j \rangle).$$

The first and second double summations are symmetric in their indices, and lead to the same final sums, enabling the equations to be written as:

$$\begin{aligned} \delta A = & 2 \sum_i \left[\langle \delta\phi_i | \hat{h}_a + \sum_j (2\hat{J}_j - \hat{K}_j) | \phi_i \rangle \right. \\ & \left. + 2 \sum_i \left[\langle \phi_i | \hat{h}_a + \sum_j (2\hat{J}_j - \hat{K}_j) | \delta\phi_i \rangle \right] \right. \\ & \left. - \sum_{i,j} (\lambda_{ij} \langle \delta\phi_i | \phi_j \rangle + \lambda_{ij} \langle \phi_i | \delta\phi_j \rangle) \right]. \end{aligned}$$

As the operators, \hat{h} , \hat{J} , \hat{K} , are Hermitian, the first and second summations are the adjoints of each other. For the last term in the equation, summation indices can be interchanged, and as $\langle \phi_j | \delta\phi_i \rangle$ and $\langle \delta\phi_i | \phi_j \rangle$ are adjoints of each other, the functional can be written:

$$\begin{aligned} \delta A = & 2 \sum_i \left[\lambda \delta\phi_i | \hat{h}_a + \sum_j (2\hat{J}_j - \hat{K}_j) | \phi_i \rangle \right. \\ & \left. - \sum_j \lambda_{ij} \langle \delta\phi_i | \phi_j \rangle \right] \\ & + 2 \sum_i \left[\langle \dots \dots \rangle^* - \sum_j \lambda_{ji} \langle \dots \dots \rangle^* \right]. \end{aligned}$$

The vanishing of δA for an arbitrary variation, $\delta\phi_i$, is now satisfied by the conditions,

$$\begin{aligned} \left[\hat{h}_a + \sum_j (2\hat{J}_j - \hat{K}_j) \right] \phi_i &= \sum_j \phi_j \lambda_{ij}, \\ \left[\dots \dots \right] \phi_i^* &= \sum_j \phi_j^* \lambda_{ji}. \end{aligned}$$

The term in the brackets is the Hartree-Fock operator, \hat{F} , and with the difference,

$$\sum_j \phi_j (\lambda_{ij} - \lambda_{ji}^*) = 0,$$

and ϕ_j linearly independent,

$$\lambda_{ij} = \lambda_{ji}^*,$$

the equations are complex conjugates and equivalent. These, the Hartree-Fock equations, can now be written in matrix form:

$$\hat{F} \phi = \phi \lambda.$$

(\hat{F} and λ are $N \times N$ matrices, ϕ $N \times 1$),

The operator, \hat{F} , is mono-electronic - the summation over the Coulomb and exchange operators represents a one electron approximation to the behaviour of each electron in the field of the others.

To obtain solution of the Hartree-Fock equations, the suggestion of Boys²³ that has been noted above is used: the wave function, ϕ , expressed as part of a set of complete functions. These functions are the atom-centred basis functions. The sets used in this thesis are discussed in a separate chapter.

The wave function, as this linear combination of one electron functions, is invariant to a unitary transformation of the functions. This property is used to give a more suitable set of energy values, by use of the transformation,

$$U^\dagger \lambda U = \epsilon_{ij} \delta_{ij};$$

that is, a diagonal matrix. The Hartree-Fock problem becomes

$$\hat{F} \phi' = \phi' \epsilon_{ij} \delta_{ij}.$$

As the operator is also invariant under the transformation, it can be defined from this new set of orbitals, and the Hartree-Fock orbitals obtained by solution will now be an orthonormal set.

Correlation Error

As determined by experiment, the energy of a system is lower than the energy predicted for that system by a Hartree-Fock wave function. The Schrodinger wave equation does not include terms modelling relativistic effects, and there must be a contribution to the energy from this source. Inner shell electrons have greatest kinetic energy, and the relativistic contribution to the energy must be greatest for these, becoming more important the more core electrons there are; for example: in the magnesium atom, the relativistic energy of a 1s electron is approximately 0.20 hartree, 0.03 hartree for a 2s electron⁸. In comparison of states, as the inner shells are largely unchanged from one electronic state to another, the relativistic contribution can be ignored. This lack of a relativistic term is not the only inadequacy of the Hartree-Fock operator, however.

In a non-relativistic framework, the energy operator can be split into kinetic and potential terms. The Born-Oppenheimer approximation enables the separation of the kinetic energy term into parts for the nuclei and parts for the electrons. This part of the total energy operator is satisfied in the Hartree-Fock operator; however, the potential term used is not a satisfactory analogue of the real situation. There are Coulombic interactions between the nuclei - each considered at a point - and each electron, and also between one electron and every other; and, exchange interaction between electrons of the same spin. The interactions are incompletely approximated by the use of a potential field of each electron in the average field of the rest. There are instantaneous interactions which are not covered by this formulation. The experimental energy can be partitioned:

$$E_{\text{exptl.}} = E_{\text{Hartree-Fock}} + E_{\text{relativistic}} + E_{\text{correlation}}$$

This last term, which derives from inadequacy of the Hartree-Fock model of the distribution, can be accommodated by adding terms to extend the description. The terms necessary will give a different set of coefficients in the wave function, differing most for the outer orbitals. The particular selection driven by the variation method, the molecular wave function is expanded as a linear combination of the Hartree-Fock function for that state plus terms describing excited configurations of that system:

$$\psi_{\text{molecule}} = c_0 \psi_{\text{H-F}} + c_1 \psi_1 + c_2 \psi_2 + \dots,$$

where the c_i are the combination coefficients.

The correlation energy has been the subject of attempts at algebraic definition, so that a general method of ab initio computation could be determined. Much of this work has been done by Sinanoğlu¹¹¹.

Recently, Clementi has produced a 'semi-empirical' approach to the correlation problem. Starting from a reference wave function which is a limited configuration interaction function, the addition of an electron-density dependent function is used to model the correlation energy contribution; and, some success is reported³⁰.

Configuration Interaction

In the preceding section, it was noted that the Hartree-Fock energy was at a level higher than the actual energy of a system. The method of Configuration Interaction was mentioned as a means of producing a better approximation to the real energy. It must be borne in mind, however, that no matter how exact the sum of the Hartree-Fock and correlation energies are, there remains the relativistic contribution to the total energy.

In a preceding section, reference was made to the postulation by Boys²³ of a variational procedure over a complete set of determinants of orbitals. The paper by Nesbet⁹² concerns itself with the method of configuration interaction, indicating that a totally anti-symmetric N-particle wave function is produced by constructing all possible Slater determinants of order N from some complete system of single-particle functions.

In the configuration interaction calculation, the variation theorem is used to optimise the expansion coefficient matrix, C, with respect to the total energy, in the equations,

$$\hat{H} \psi = E \psi,$$

where $\psi = C \sum_i \psi_i,$

and ψ_i are formed as different electronic configurations from the set of orbitals produced in a single configuration SCF calculation.

In principle, the CI method is exact. As the 'basis set' of one electron functions approaches completeness, and all configurations which can be constructed from these orbitals are included, the exact solution of the Schrodinger wave equation is approached.

The use of configuration interaction for diatomic molecules is quite well documented - as in the book by Schaefer¹². Calculations vary in the number of configurations used in the expansions - a balance has to be reached between the accuracy of the calculation and the length of time required to carry out the calculation.

Conclusion

The Configuration Interaction wave function consists of a linear combination of electronic configurations of the system,

$$\psi = c \sum_i \psi'_i,$$

where ψ is the Configuration Interaction wave function, C is the combination coefficient matrix, and the ψ'_i are the various electronic configurations, containing the total number of electrons in the system. The total perturbation function is also essentially a linear combination of configuration functions. Trivially, if the total energy obtained from these two functions is the non-relativistic limit, then the two functions will be identical. This is sufficient to show equivalence of the methods.

Kleiner⁶⁷ has started with the Configuration Interaction matrix and shown that energy expressions derived from the partitioned Configuration Interaction matrix are identical to formulae derived from Rayleigh-Schrodinger perturbation theory.

Use of perturbation theory can be made to indicate the importance of errors in the wave function. The n 'th order perturbation equation is:

$$(\hat{H}_0 - E_0) \psi_n = -\hat{H}_1 \psi_{(n-1)} + \sum_{j=0}^{n-1} E_{(n-j)} \psi_j \quad \dots\dots 2$$

Multiplying from the left by ψ_0 and integrating annihilates the left hand side; and, with the ψ_j orthogonal, the n 'th order perturbation energy is:

$$E_n = \langle \psi_0 | \hat{H}_1 | \psi_{(n-1)} \rangle \quad \dots\dots 3$$

It would appear that if there were a first order error in the wave function, there would result a second order error in the energy. The situation is, however, more favourable than this. From this equation, 3, the third order energy is:

$$E_3 = \langle \psi_0 | \hat{H}_1 | \psi_2 \rangle.$$

As E_3 is real, ψ_0 and ψ_2 can be interchanged, and, with $n = 1$ in

equation 2, the term $\hat{H}_1 \psi_0$ can be replaced, giving:

$$E_3 = - \langle \psi_2 | \hat{H}_0 - E_0 | \psi_1 \rangle$$

Interchanging ψ_2 and ψ_1 and substituting for $(\hat{H}_0 - E_0)\psi_2$ from 2, with $n = 2$ gives:

$$E_3 = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle - E_1 \langle \psi_1 | \psi_1 \rangle.$$

This indicates that, for a wave function with an error of order greater than n , the energy value produced is correct to order $2n + 1$. For example, a wave function correct to first order - that is, errors of second and higher orders - will give an energy correct to third order; and, if correct to second order, the error in the energy is only sixth order.

The Hamiltonian energy operator is

$$-\frac{1}{2} \nabla^2 - \frac{Z_a}{r_i} + \frac{1}{r_{ij}} + \frac{Z}{r_a},$$

where i and j are electrons, and a are atomic nuclei, the last term being the nuclear repulsion. The molecular wave function is obtained by optimizing the wave function with respect to the expectation value of this operator.

For electric multipoles, the operators are of r^n form - the dipole depends on the expectation value of \hat{r} , the quadrupole on r^2 . There is no a priori reason that a wave function optimised for the energy should give values for these other properties to the same order. Indeed, for the multipoles, as each can be considered a perturbation of the previous, a wave function giving one to one order will give a higher to lower.

CHAPTER 2NOTES ON PROPERTIESIntroduction

As was shown in the previous chapter, from consideration of the Stern-Gerlach experiment, a value for any type of property can be evaluated from an expression of the form:

$$a = \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle},$$

where a is the value for that particular property, \hat{A} is an operator associated with that type of property, and ψ is the system wave function. As an expectation value, the total energy requires values for the two electron Coulomb and exchange integrals, and is known as a 'two electron property'. If only one electron integrals are required, then the property is a 'one electron property'. Given the form of an operator, \hat{A} , then the appropriate property can be evaluated from the known wave function.

It must be pointed out that the wave functions produced for this thesis have been established by optimization of expansion coefficients with respect to the total energy. Although a first order error in the wave function does not lead to a first order error in the energy, this may not be so for other expectation values. This first order error in the wave function may be averaged over the coordinates in such a way that even though the energy is predicted to one degree of accuracy, there may be a mismodelling of the detail of the electronic distribution.

Because of Brillouin's theorem²⁴, properties associated with one electron operators should have errors in the second order only^{60,92}. For Restricted Hartree-Fock - abbreviated as RHF -

wave functions, Brillouin's theorem holds for closed shells. As the wave functions calculated for this thesis only approach the Hartree-Fock limit, the theorem will not hold exactly, even for the closed shell species, HBO.

Huo⁶⁰ has shown for carbon monoxide, including open shell excited states, that properties from Unrestricted Hartree-Fock wave functions differ from those from RHF wave functions. The UHF function satisfies Brillouin's theorem even for open shell systems, and can be represented by configuration interaction from a RHF function, by addition of single excitations. Brillouin's theorem implies that the most important excitations in a configuration interaction expansion are double: but, single excitations, which couple with the double, are known to give major changes in the one electron properties^{50,54}.

A property particularly sensitive to this error is the dipole moment⁶⁰. Green has investigated this effect for carbon monosulphide, CS^{51,52}, and has shown that such configuration interaction calculations give a superior approach to the experimental value than the RHF wave function.

In analysing the wave functions obtained, some estimate of the electron density on each centre is useful. This is often performed by use of the Mulliken population analysis⁸⁶. Explicitly, the populations are obtained from the following equations: with c the coefficients determined by the self-consistent field procedure, the net atomic population of an atom, I, is

$$\sum_i n_i c_{Ii}^2,$$

where i are molecular orbitals, and n the occupation of that orbital.

The electron density between two nuclei from molecular orbital, i , is given by the overlap population,

$$2n_i c_{Ii} c_{Ji} \langle \phi_I | \phi_J \rangle .$$

The gross population on an atom is obtained by dividing this population equally between atoms I and J, and adding the net population; that is, on atom I:

$$n_i (c_{Ii}^2 + c_{Ii} c_{Ji} \langle \phi_I | \phi_J \rangle) .$$

The equal division of the overlap population is quite arbitrary; but, the resulting population densities are a not unreasonable description of the molecular system.

Apart from the possible error noted above, for comparison with experiment, further sources of deviation exist. Assuming that the state being investigated is the same as that for which the calculations have been performed, the chief source of error is the assumption that the energy surface minimum is unaffected by the presence of bond vibration. For the actual molecular system, experiment measures vibrationally averaged properties.

Properties Evaluated

As the species investigated for this thesis were linear triatomic molecules, the equations from which properties were obtained were designed to apply to such species.

The total molecular energy is evaluated for various geometries of the system, and estimations of the vibrational force constants should be possible. The total equilibrium energy can be expressed as a polynomial series of the form:

$$E(R) = E_0 + aR + bR^2 + cR^3 + \dots ,$$

where R is a function of the variation of bond length. If this is

the equation of the theoretically-derived curve, then the coefficient of the quadratic term will predict the usual bond vibration force constants.

As the energy against bond lengths curves are, in the region of the minimum, closely approximated by a quadratic equation, the curves were fitted by a least-squares procedure to a polynomial of degree two, by use of a FORTRAN programme written by the author. The gradient of this curve was taken, and the coefficient of the term linear in the bond length used to give the force constant. This is a similar procedure to that of Pincelli and Cadioli⁹⁹.

The potential energy at any specific point can be expanded as a Taylor series:

$$V = V_0 + \left(\frac{\partial V}{\partial R_1}\right)_0 r_1 + \left(\frac{\partial V}{\partial R_2}\right)_0 r_2 + \left(\frac{\partial^2 V}{\partial R_1^2}\right)_0 r_1^2 + \left(\frac{\partial^2 V}{\partial R_2^2}\right)_0 r_2^2 + \left(\frac{\partial^2 V}{\partial R_1 \partial R_2}\right)_0 r_1 r_2 + \dots$$

Force constants are defined as the second derivatives, higher terms being anharmonicities. In the calculations discussed, one bond length is held constant while the other is varied. The terms calculated for the force constants will then not contain contributions from the cross term. It should be true, therefore, that the force constant evaluated from each curve is a good approximation to the theoretical force constant for that bond.

A real system exists in space, and operators, in Cartesian form:

$$x^n; y^n; z^n;$$

could be applied to the electron distribution. Expectation values for such operators may be derived from the calculated wave functions.

Molecular properties observable by experiment are given in the text by Davies³, on the electric and magnetic properties of molecular systems.

The principal computer programme used - ALCHEMY - contains a subroutine package enabling the derivation of expectation values of such operators by explicit integration of the expression:

$$\frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle},$$

where \hat{A} is the property operator. The equation that the programme, in fact, uses as the operator is:

$$r_k^n \sin^i \theta_k \cos^j \theta_k (1-x^2)^{m/2} \left(\frac{d^m}{dx^m} \right) \left(\frac{1}{2^{l-1} l!} \right) \left(\frac{d^l}{dx^l} \right) (x^2-1)^l e^{im\phi},$$

where $x = \cos \theta_k$.

The parameter k is an accounting index - indicating the particular nuclear centre for which the expectation value is being evaluated. With appropriate choice of the parameters, n , i , j , l , m , the desired operators can be established; for example: with n and j equal to one, the rest to zero, the expectation value computed is that of the operator, z .

The calculation of the experimental observables from these expectation values has been indicated in papers by McLean and Yoshimine^{77,78}. The application of the equations to the triatomic systems discussed in this thesis is summarised in the following paragraphs.

The species under discussion are linear molecules. With the molecular axis as the z -axis of the Cartesian reference frame, the symmetry of the species precludes an observable value for the x and

y operators, but allows measurement of z . The existence of this can be demonstrated by measurement of the molecular dipole moment.

The dipole moment is given by the formula:

$$\mu = \langle \psi | \sum_i \underline{r}_i | \psi \rangle - \sum_k Z_k \underline{R}_k,$$

where \underline{r}_i are the position vectors of the electrons, and \underline{R}_k of the nuclei. In this expression, the origin for the position vectors is the centre of mass of the system.

The output from the programme is in the form of expectation values with origins at the appropriate nuclear centres. For each nuclear result, it is necessary, therefore, to transform the results to centre-of-mass coordinates and to calculate the molecular property for each centre. For an uncharged molecule, the expectation value of z is invariant to this change of origin. For each nucleus, the formula is:

$$\mu_a = \sum_{k \neq a} Z_k \underline{R}_{ak} - \langle z_a \rangle,$$

where: a is the particular nucleus; k the nuclei; Z_k is the nuclear charge; \underline{R}_{ak} is the distance of the nuclei from a ; $\langle z_a \rangle$ is the expectation value for the z operator for that nucleus.

For charged species - ions - the formula must be in centre-of-mass coordinates. This form is:

$$\mu_a = \sum_k Z_k \underline{R}_{ck} - \langle z_a \rangle - \frac{NR}{\underline{R}_{ca}},$$

where: \underline{R}_{ck} is the distance of each nucleus from the centre of mass; N is the total number of electrons in the molecular system; \underline{R}_{ca} is the distance of each nucleus from the centre of mass.

The quadratic operator, z^2 , gives rise to the second of the electric multipole moments - the quadrupole moment.

This is a second rank traceless tensor,

$$\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0.$$

For an axially symmetric molecule, this reduces to:

$$\Theta_{xx} = \Theta_{yy} = -\frac{1}{2} \Theta_{zz},$$

which is the observable moment, Θ . This is given a value by the expression:

$$\Theta = \sum_k Z_k z_{ck}^2 - \frac{1}{2} \sum_i \langle \psi | 3z_i^2 - r_i^2 | \psi \rangle,$$

where: z_i and r_i refer to the electrons. Now,

$$r_i^2 = x_i^2 + y_i^2 + z_i^2;$$

and, the operator expression in the programme can be set to evaluate the term, $e^2 = x_i^2 + y_i^2$. This value is invariant to change of origin, taking the same value over the whole molecule. The expression for the quadrupole moment can be reexpressed as:

$$\Theta = \sum_k Z_k z_{ck}^2 + \frac{\langle e^2 \rangle}{2} - \langle z^2 \rangle.$$

As the quadrupole moment is not invariant to change of origin, the nuclear coordinates must be reexpressed in this form. For the masses of the nuclei, isotopic masses are taken, in atomic units. The position of the centre of mass from a nuclear centre is given by:

$$z_{ca} = \frac{\sum_{k \neq a} M_k z_{ak}}{\sum_k M_k}$$

where M_k is the isotopic mass.

The programme produces the value, $\langle z^2 \rangle$, with each nucleus in turn as origin. This must be transformed into an expectation value with respect to the centre of mass. If the distance from a nuclear centre to the centre of mass is d_{ck} , then, an expression for the expectation value of z with respect to the centre of mass,

in terms of the value evaluated with the nucleus as centre is:

$$z_{ck} = z_k + d_{ck}.$$

This gives:

$$z_{ck}^2 = z_k^2 + 2d_{ck} z_k + d_{ck}^2.$$

This gives, by summing over all electrons, the operator:

$$\langle z_{ck}^2 \rangle = \langle z_k^2 \rangle + 2d_{ck} \langle z_k \rangle + Nd_{ck}^2.$$

The value for this operator is then found from the results with each nucleus as centre, and is the same for each. The molecular quadrupole moment is, thus, found.

The other two properties usually evaluated in this work, the field gradient and the electrostatic force on each nucleus are evaluated at the particular nuclear centres; and do not, therefore, require to be transformed to centre-of-mass coordinates.

The field gradient is another second rank tensor, and, as for the quadrupole moment,

$$q_{xx} = q_{yy} = -\frac{1}{2} q_{zz},$$

and the value observed for a linear molecule is q_{zz} . The expression for this is:

$$q_{zz} = \langle \psi | \frac{(3 \cos^2 \theta_i - 1)}{r_i^3} | \psi \rangle,$$

for electrons, i .

Reexpressing this in terms of the Cartesian coordinates, this gives an operator of the form:

$$q_a = 2 \sum_{k \neq a} \frac{z_k}{z_{ak}^3} - \langle 3z^2 - r^2 / r^5 \rangle.$$

The property can be measured in an experiment determining the quadrupole coupling constant for each nucleus. This can be done

only if that nucleus possesses a nuclear electric quadrupole moment. The quadrupole coupling constant with a particular nucleus is given by the expression, $e q Q$, where e is the electronic charge, q is the field gradient, and Q the nuclear moment.

In the absence of experimental data, the properties so far discussed can give indication of the quality of a wave function only by trends from one basis to another. For the last property to be discussed, there exists a theorem which enables an independent check of the quality of the wave function to be made. The electrostatic force on a nucleus is given by the expression:

$$F_a = Z_a \left(\sum_{k \neq a} \frac{Z_k}{z_{ak}^2} + \left\langle \frac{Z}{r^3} \right\rangle \right).$$

The theorem is due to Feynman⁴³, and gives that the sum of the forces on the nuclei will be zero for an exact wave function. An independent criterion for the quality of a wave function is thus achieved.

CHAPTER 3COMPUTER PROGRAMMES AND BASIS SETSIntroduction

This ab initio study used Slater type basis functions. Gaussian function programmes are readily available; and, being efficient in use of computer time, have contributed the bulk of the ab initio results in the literature. As this study was intended to cover molecular properties as well as the more usual geometry and total energy investigations, the use of the exponential functions as basis functions was preferred.

One programme that handles such basis sets is the programme POLYCAL¹¹⁹. This programme produces wave functions for multicentre molecular systems from basis sets of s, p, and d type atomic functions. Wave functions are produced as single or as multiple configuration functions, enabling configuration interaction to be studied. The formalism used in establishing the SCF programme is that of Nesbet^{91,95}. For open shell systems, the adaptation of the Fock operator is performed by an approximate technique, producing an adapted, combined operator that models the open shell interactions. A version of this programme was implemented by Dr. Thomson on the IBM 360/44 of the University of St. Andrews, in a form allowing the computation of integrals over s and p functions only - the routines allowing the computation of integrals over the highest order functions requiring more core than is available on this machine. The configuration interaction capability of the programme was also included.

There exists another programme designed to perform ab initio calculations with a Slater type function atomic basis set. This is the programme ALCHEMY⁷⁵. This programme is not so readily

available as the other, as it is still being developed by the originators. A version of this programme was obtained by Dr. C. Thomson in the summer of 1971 at the San José Research Laboratory of the IBM Corporation, where it was produced. The following brief description refers to this version. The originators have under development a version which can implement configuration interaction calculations; but, this is, to an even greater extent, in the development stage.

This programme is capable of producing integrals for multicentre systems in the linear symmetries of $C_{\infty v}$ and $D_{\infty h}$ only. The atomic functions, however, can take values of l from 0 to 10. The SCF routines are similar to those in the IBMOL5 programme of Clementi³¹. This uses the closed¹⁰⁵ and open¹⁰⁶ shell formalisms of Roothaan, as implemented by Bagus et al; and, described for an earlier programme¹⁹. Advantage is taken in the programme of the fact that, with z as the molecular axis, in Cartesian space, functions np_x and np_y on atomic centres are degenerate, giving rise to two, degenerate π symmetry molecular orbitals. Only one orbital is included in the calculation of the SCF wave function, and it is given a possible occupancy of four. The SCF routines are suitably altered, and the establishment of the open shell operator is increased in complexity.

There follows a summary of the open shell formalism of Roothaan.

Open Shell Formalism

If an ab initio wave function is established for a set of completely filled shells, then the electronic state and multiplicity are defined. With unpaired electrons in the system, there

may result several possible electronic states from the same orbital occupancies; and, it may not be possible to describe a particular electronic state in terms of a single determinant.

For example, two, unpaired electrons can give an electronic state that is either a singlet or a triplet. Writing the wave function as a set of molecular orbitals, ϕ_n , with orbitals k and l each singly occupied, gives the determinantal wave function as:

$$|\phi_1 \bar{\phi}_1 \dots \phi_k \bar{\phi}_l \dots \phi_N \bar{\phi}_N|.$$

There is an alternative, and equivalent, expression:

$$|\phi_1 \bar{\phi}_1 \dots \bar{\phi}_k \phi_l \dots \phi_N \bar{\phi}_N|.$$

The wave function describing the system must be a combination of these two. If the second determinant is added with a positive sign, the wave function describes a triplet electronic state, if with a negative sign, a singlet.

If there is only one unpaired electron, then there is only one way of writing the determinant; and, a system with a single electron gives a single determinantal wave function.

If the Hartree-Fock equations are solved for a closed shell system, the total energy can be written as:

$$2 \sum_{i=1}^N \epsilon_i^{(0)} + \sum_{i,j}^N (2J_{ij} - K_{ij}) \dots\dots 4$$

where, ϵ_i are the orbital energies, and J and K are the two electron integral contributions to the total energy.

If an electron is promoted to a previously unoccupied orbital, then the electronic system will be of the type considered above. The total energy expression contains terms of the types as in equation 4. All the terms in equation 4 for interactions between closed shells are included. For an orbital, m , that is partially

occupied - an open shell - the first term in equation 4 does not include $2\epsilon_m^{(0)}$, but $1\epsilon_m^{(0)}$. There exist extra two electron integrals between the unpaired electrons and the rest. The particular choice of these J_{ik} , J_{il} , K_{ik} , K_{il} , depends on the required electronic state - as in, either triplet or singlet.

Integral terms exist from mutual interaction of the unpaired electrons. Again, these are dependent on the electronic state, and their choice is governed by considering the possible permutations of subscripts. With an orthonormal basis, and with the orthogonality of the spin function, many combinations of subscripts lead to zero energy terms. The particular terms depend on the number of open shells; and, formulae for determining them are available in the literature^{8,10}. The open shell Hartree-Fock operator is, then, the closed shell operator with these correction terms - appropriate to the particular electronic state. The total energy expression is:

$$2 \sum_{i=1}^N \epsilon_i^{(0)} + \epsilon_m^{(0)} = \sum_{i,j}^N (2J_{ij} - K_{ij}) + j_m J_m + k_m K_m \dots\dots 5$$

By adding these terms, the open shell wave function can be obtained in single determinant form.

In order to define which electronic state is being calculated, the extra terms of equation 5 must be supplied; that is, which extra J and K terms are required in the Hartree-Fock operator. These are usually defined by specifying the combination coefficients, the vector coupling coefficients, j_m , k_m . The form these coefficients take depends on the particular form of the operator, as coded in that programme. With the programmes as they are supplied, information is usually given on how to calculate these coefficients for particular L,S systems. The precise form that these vector

coupling coefficients take in the ALCHEMY programme are given in an unpublished paper by P.S. Bagus¹⁷.

Implementation

The use of the ALCHEMY programme was essential, as this work forms an extension of work performed by Dr. Thomson at San José, for species for which this programme was used; but, chiefly, because the species studied are almost all open shell species, and the Nesbet SCF procedure used in the POLYCAL programme uses an approximate operator for solution of the open shell SCF problem. This operator differs by a few K terms from the exact Hartree-Fock operator¹⁰; but, as the difference between electronic states may frequently be only a few K terms - as in the difference between the singlet and the triplet states of a particular electronic configuration - this approximation would render conclusions drawn from such wave functions open to question. The SCF procedure used in the ALCHEMY SCF routines does not use approximations in the solution of the Roothaan open shell SCF system.

As this programme was too large to fit on the St. Andrews University Computing Laboratory's 360/44, it was decided to implement it on the 360/195 of the Rutherford Laboratory, on which machine Dr. Thomson has a time allocation. This had the advantage that the same version that had been in use in the 360/195 at the San José Research Laboratory of the IBM Corporation could be used - eliminating the possibility of errors in reprogramming. Access to the faster machine would allow accurate calculations to be performed, as the 360/44 available in St. Andrews is too slow for the massive number computation such calculations require.

The implementation of the programme on the Rutherford machine was made by the staff of the ATLAS laboratory, and was checked out with data from results obtained at San José, and has been used for the bulk of the results produced in this work. The use of this computer, at a distance of several hundred miles from St. Andrews required the use of Her Majesty's postal services. This occasions delay between transmitting data and the resulting output. It was felt that the availability of a version of the programme on the 360/44 at St. Andrews would be of some assistance in the execution of the work; not only for the checking of data; but also, to enable some use of the various options available to computation in both the integral and SCF sections of the programme. Perhaps the chief reason for doing this was to obtain some understanding of how the programme goes about its task.

It was pointed out above that the San José version of the programme was too large for the St. Andrews University machine - requiring almost four times as much core as was available. Fortunately this machine was due for an update, and the core size was doubled in August 1972, when the University Computing Department and its computer were moved to a new Departmental building.

Further attempts at implementing the programme were then carried out on the updated 360/44 by myself. Slight modifications had to be made to some of the coding to enable compilation to take place with the version of the IBM FORTRAN H compiler at St. Andrews, and to make the programme compatible with the system's allocation of data set numbers. Alterations had to be made to the programme before a module small enough to be loaded could be obtained.

Because of the nature of the overlay of the programme, it

was decided to divide the programme into two sections: an integral programme; and, a separate SCF programme. A few new routines had to be derived, and an amount of reprogramming was performed to enable this to be achieved. The resulting two programmes were loaded and checked by reference to results obtained with the 360/195 of the Rutherford laboratory. This set of programmes was fast enough to perform minimum basis set calculations in less than half an hour.

In dividing the programme in this way, various facilities of the programme have been omitted. In particular, the varying of a single basis function to give a minimum total energy by repeated complete SCF calculations had to be omitted. This is not an unreasonable omission when the amount of time each such calculation requires is approximately half the time for a complete integral and SCF calculation.

Basis Sets

It was noted in the preceding section that, if the set of expansion functions were complete, then, in non-relativistic terms, the resulting wave function would be exact. For creation of molecular wave functions, a set of expansion functions must be chosen, and the closer this set is to being complete, the nearer will this function approach the exact solution. However, this can be achieved for the Schrödinger problem only by use of configuration interaction. For a single-configuration wave function only the number of one electron functions can be used to approximate to the exact function.

For atoms, the Hartree-Fock equations are capable of numeric solution, and the total energies and the orbital energies have been

obtained by, for example, Froese-Fischer⁴⁶. The incomplete sets of functions normally used in ab initio calculations are compared to these results, and, for each atom, the exponents are optimized with respect to the total energy. Such basis sets are available in the literature, for example, Clementi²⁸, and Huzinaga⁶¹.

In the analytic solution of the hydrogen atom, the wave function obtained is an exponential function. This suggests the use of such functions, with varying exponents, for expansion functions for other atoms, and for molecular systems.

In the paper of Boys²³ noted in the previous chapter, the use of Gaussian functions was proposed, as their mathematical form allows more amenable solution for the multicentre integrals. The use of Gaussian functions and the efficient computer programmes that have been developed for handling them has produced most of the ab initio studies in the present literature. The use of such basis sets has, however, indicated their intrinsic inadequacies. As Boys introduced them in order to allow evaluation of the necessary integrals to be simplified this is perhaps not too surprising. In fact, that the wave functions produced using them have produced useful results is indicative of the care with which the available basis sets have been established.

A set of Gaussian functions does not produce a derivative that behaves at the nucleus in the same way as does that for an exponential function basis set. Molecular properties that are dependent on the detail of the electronic distribution may not be modelled as effectively as the total energy by the final wave function. In a paper presented at the ATLAS laboratory sponsored conference in 1974, van Niessen⁹⁷ indicates that, for a Gaussian basis, to obtain

a close approach to the Hartree-Fock limit, a prohibitively large number of functions is required, compared with the accuracy that can be obtained with a reasonable number of Slater functions.

The exponential functions are usually known as Slater functions, after J.C. Slater, who proposed rules for their estimation¹¹³. Their quality is indicated by the names under which the various sets are known: 'minimal' basis sets have a single Slater function for each one electron function used; 'double zeta' have two functions - this basis is referred to in the Discussion chapter as a 'DZ' basis; and there are basis sets known as 'best atom' sets, which have been optimised to be close to the numeric Hartree-Fock results - 'BA' in the Discussion.

The double zeta functions are available from the compilation by Clementi²⁸. The best atom functions are available from the compilation of molecular wave functions for a group of linear molecules by McLean and Yoshimine⁷⁴, and they give energies to within 0.001 of an atomic unit of the accuracy of the numerical Hartree-Fock results.

The larger the number of functions in a basis set, the larger the number of expansion coefficients, allowing the variational procedure to achieve a lower energy. In addition, with more than one function representing a one electron function - that is, with more than one Slater function representing one atomic orbital - the exponents are chosen to differ. The extension of the atomic orbitals about the nuclei differ. The larger the exponent, the nearer the centre of the distribution represented is to the atomic centre. This allows a better description of molecular orbitals, as the radius of the atomic orbital electron distribution in the

molecule will be different from that in the atom - a contraction is intuitively reasonable - and, having more than one function will allow of this being modelled - by alteration in the values of the linear combination coefficients. In using such expanded basis sets, care has to be taken to ensure that the bases used on the different atomic centres are balanced - that is, an equivalent expansion of atomic orbitals is used for each centre^{87,79}. Imbalance manifests itself in errors in values of clearly defined physical quantities such as the dipole moment, or, in unreasonable values for arbitrary quantities such as the charge on an atom. This question of balance of basis set is independent of the question of the adequacy of the basis set as an approach to the Hartree-Fock limit.

It was noted that: the atomic orbitals combined into the molecular orbitals have different sizes from those in the atoms; and, using several functions for each orbital enables this to be modelled to some degree. In molecular combinations, the atomic orbitals are likely to be altered in shape by the presence of another system. Inclusion of higher l value functions; that is, functions with l values unnecessary for descriptions of ground states of atoms, will help to model this polarisation effect. Such functions are called polarisation functions⁹⁴. Reasonable choices of the values for these functions can usually be made from optimised small molecule calculations^{12,39,74,104,107}. A double zeta basis set with added polarisation functions is referred to as a 'DL+P' basis. Best atom basis sets with polarisation functions are referred to as 'BA+P' bases.

CHAPTER 4RESULTS AND DISCUSSIONSection I: Introduction

For a given amount of computer time, either accurate, near Hartree-Fock, wave functions can be obtained for small systems, or less accurate functions for larger systems. There are many small molecular systems which have great importance to certain areas of chemistry. In organic chemistry, the small molecular systems known as carbenes undergo vigorous reaction with substrate. The electronic configuration of many such reactive intermediates is not known, and as experimentalists have great difficulty in detecting and investigating such reactive intermediates, before they have combined with some substrate, theoretical investigation of such systems has some value. An ab initio wave function is, in principle, as easy to obtain for such a system as for a stable system. Such short-lived, reactive intermediates have been made the subject of this work. Attempt has been made to study excited states of some of these species, for similar reasons. Also, it is not clear what level of accuracy is attainable for such species. It was hoped that the level of accuracy could be extended to give predictions for the values of one electron properties for some of these species, and that these predictions would be in agreement with experiment.

In this chapter, the results of the ab initio calculations that I have done are recorded. Some data from calculations performed by other workers, in particular, that of my supervisor, Dr. C. Thomson, will also be included. It is hoped that the origin of the results is not confused.

The species discussed in each section are:

- II) OCC ground state, $^3\Sigma^-$; excited states, $^1\Delta$, $^3\Pi$, $^1\Pi$,
 $^1\Sigma^-$; SCC ground state.
- III) NCC $^2\Delta$; CNC ground; excited states, $^2\Delta$, $^2\Sigma$; PCC ground
state.
- IV) NCN ground state, $^3\Sigma^-$; NCN excited state, $^3\Pi$; NNC excited
state, $^3\Pi$.
- V) NCO ground state, $^2\Pi$; excited state, $^2\Sigma^-$; SCN ground
state, $^2\Pi$.
- VI) NC ground state; PC ground state.
- VII) OBO ground state, $^2\Pi$.
- VIII) HBO ground state.

The first and last sections are discussed at length, and contain generalisations which would be applicable to more species, but, to avoid tedious repetition, are given in only these sections. The other sections are confined largely to reporting the results obtained.

Section II: The Carbene, OCC

Introduction

The geometry of the carbene, OCC, had been investigated by Dr. Thomson using wave functions based on DZ and DZ+P basis sets. This was extended to BA+P, and the resulting conclusions published¹²⁵. The investigation was prompted by a paper by Milligan and Jacox⁸², reporting IR spectra of a species they interpreted as linear OCC, after photolysis of matrix-isolated cyanogen azide in the presence of carbon monoxide, and after vacuum photolysis of matrix-isolated carbon suboxide. Following the suggestion of Bayes²¹ of the presence of triplet and singlet multiplicity species, Baker et al²⁰ showed that the addition of the carbene to alkenes was consistent with this. The lower multiplicity was obtained with radiation below 280nm and the higher with radiation above 300nm - this implies that the triplet is more stable than the singlet. Baker indicated that the singlet state is more reactive to the unsaturated bond than the triplet. Ab initio wave functions for the excited states, using bases of the same accuracy as for the ground state, are reported in this section.

As usual in ab initio calculations, the geometry giving optimum energy changes with adjustment of the basis set. For the ground state, these optimum geometries and the energies are given, for the bases used, in TABLE II.1. At the optimum geometry for the BA+P basis, SCF wave functions for the single anion and single cation were produced, enabling estimation of the ionisation potentials to be made. By this means, use of Koopman's theorem, which is not applicable to open shell systems, is avoided. As

TABLE II.1

Optimum Energies for OCC Ground State, with
Energies for the Excited States

Ground State

Basis	R(O-C)	R(C-C)	Total Energy	Virial Coefficient
DZ	2.205	2.645	-150.36987	-2.00045
DZ+P	2.1	2.645	-150.50568	-2.00079
BA+P	2.121	2.58	-150.51632	-2.00000

Energies for the Excited States at the same Geometry as the
Ground State

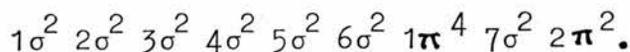
State	R(O-C)	R(C-C)	Total Energy	Virial Coefficient
$^1\Delta$	2.121	2.58	-150.47899	-1.99989
$^3\Pi$	2.121	2.58	-150.44746	-2.00171
$^1\Pi$	2.121	2.58	-150.37137	-2.00180
$^1\Sigma^+$	2.121	2.58	-150.28967	-1.99939

calculation of the SCF wave function for the single ions at the same geometry as the optimized ground state takes only the time for the SCF calculations, as the same integrals as calculated for the ground state can be used, and as this time is a small fraction of the total time taken to optimize the ground state geometry, the extra effort involved is small. The ionization values are approximate for two reasons: the inadequacy of the basis set used - and the Hartree-Fock model itself; and the fact that the geometry of the ionised state is not the same as that of the ground state. The ionization values obtained are; $OCC \rightarrow OCC^+$ 0.3976 hartree; $OCC \rightarrow OCC^-$ -0.0183 hartree. The orbital energies would give a value of 0.4689 hartree for the former potential, indicating that an estimation based on analogy with Koopman's theorem is in error. The difference between the total molecular energy and the sum of the atomic energies with the same basis gives the contribution to the dissociation energy for a wave function with that quality basis. With the Best Atom basis set, the atomic energy of oxygen in the 3P state is -74.80938 hartree, that of carbon, also in 3P state, is -37.68802 hartree; thus the sum of the atomic energies is -150.18542 hartree. The difference between this and the total molecular energy of -150.51632 hartree is 0.33000 hartree. The Hartree-Fock contribution to the dissociation energy would be expected to be approximately 0.005 hartree larger⁷⁶, as the BA basis is about 0.0002 hartree short of the Hartree-Fock limit for atoms⁷⁶. For excited states, however, this assumption cannot be made.

The excited states differ from the ground state in occupation of the highest energy orbitals; therefore, for an adequate

description of them, sufficient functions must be included to model these orbitals, and it is difficult to devise an empirical rule for estimating the sufficiency of those functions that are chosen. The highest energy orbitals are the most diffuse in the molecule, and are the most difficult to model. Mulliken has pointed out that induced configuration mixing takes place for molecular systems⁸⁷. From these two considerations, of diffuseness and induced configuration mixing, the use of a basis extended by functions with values of the quantum numbers n and l not included in the ground states of the constituent atoms is suggested. Although the single configuration wave function may give reasonable predictions for the properties of a ground state, excited states are not necessarily describable in terms of a single determinant of one electron functions. There arise a number of possible choices of quantum numbers for each of the electronic configurations that contain an incompletely filled shell.

Single configuration wave functions were, however, obtained for the excited states considered, and the optimum energies and geometries are given in TABLE II.2. The required excitation energy from the triplet state of the ground electronic configuration to the singlet excited state is only 0.03733 hartree. The electronic configuration for the ground state is:



The electronic states that correspond to this configuration are $^3\Sigma^-$ and $^1\Sigma^+$, $^1\Delta$. By excitation of one electron from the 7σ orbital to the 2π orbital, symmetry states of $^3\Pi$, and $^1\Pi$ occur.

The total energy as function of the total bond lengths for the ground state and excited states of $^1\Delta$ and $^3\Pi$ are plotted

TABLE II.2Total Energies and Bond Lengths for Excited States

State	Bond Length		Total Energy	Virial Coefficient
	OC	CC		
1Δ	2.1279	2.5704	-150.47910	-1.99994
3π	2.1685	2.3188	-150.45950	-1.99922
1π	2.1993	2.3188	-150.39220	-1.99984
$1 \Sigma^+$	2.1279	2.604	-150.28988	-1.99974

as GRAPH II.1. Some explanation of the variables plotted is required. The total energy obtained for each species is plotted against the sum of the two bond lengths for that species. As the energy values are obtained from calculations in which each bond is varied in turn - that is, the one bond length is held constant while the other is varied - each curve is dependent on only one variable. To enable the two energy curves for each species to be drawn on the same graph, to each value of the varied bond length has been added the constant length of the other bond. Each species has a pair of curves - when one bond length had been optimized, it was held at that value and the other varied to minimum energy; thus, the one curve lies below the other. Plotting the species on the same graph enables the closeness in energy of the electronic states to be appreciated. The relative positions of the curves with respect to the ordinate have meaning; their relative positioning with respect to the abscissa, however, does not.

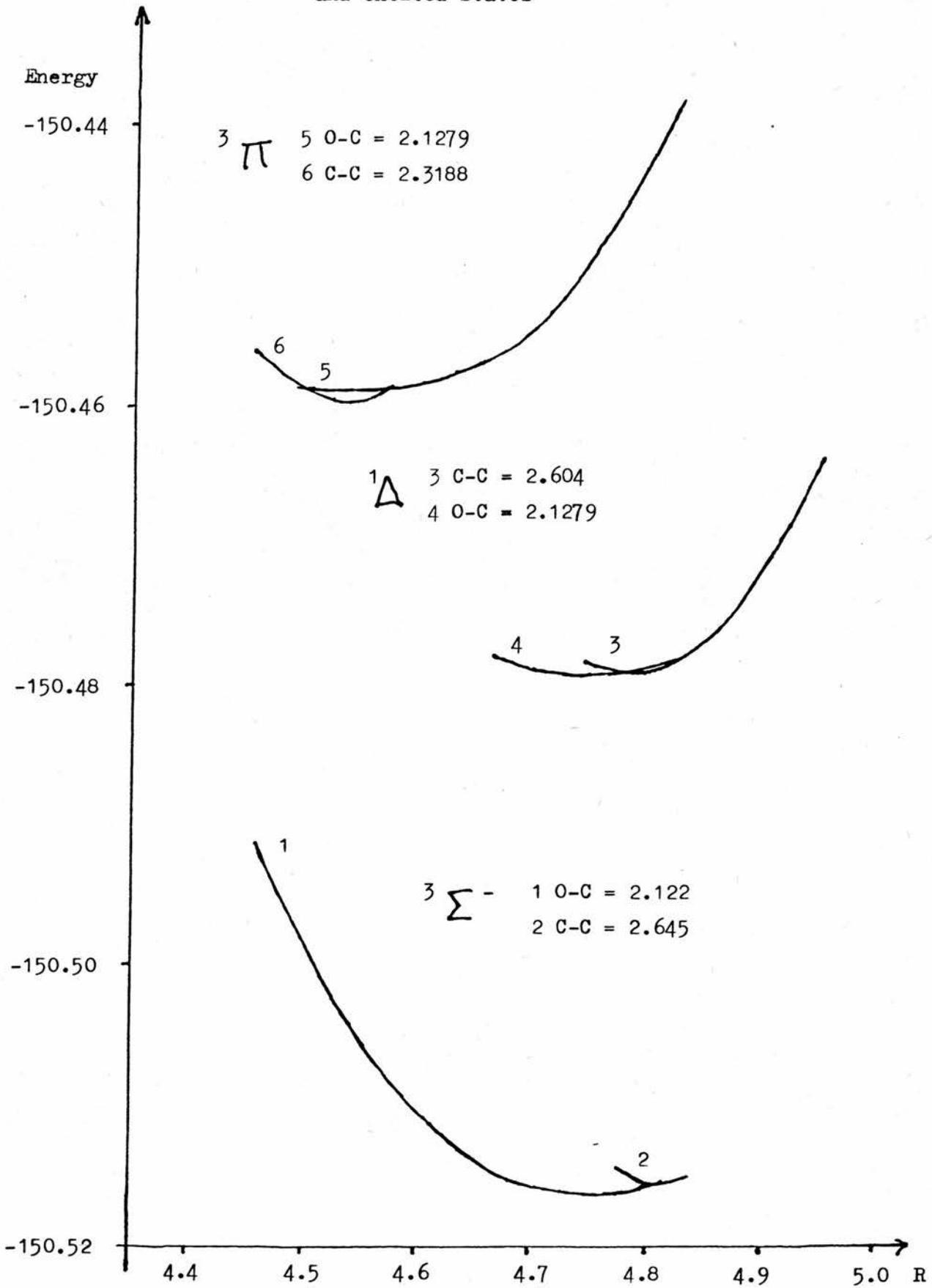
This graph shows that the first state that derives from an excited electronic configuration lies at an energy close to the higher of the two states of the ground configuration - at an energy 0.01960 hartree higher. From the ground state, the state, $^1\Delta$, is at an energy 0.03722 hartree higher.

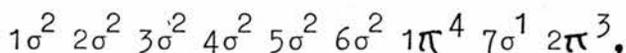
The order of energies of the states is in accordance with Hund's rules; that is, for the one electronic configuration,

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 7\sigma^2 2\pi^2,$$

for the ground state, the state with the highest multiplicity is lowest in energy - the $^3\Sigma^-$. The other states, $^1\Delta$, $^1\Sigma^+$, are in the predicted order - the higher L value at lower energy. For the excited configuration,

GRAPH II.1 Total energy against geometry for OCC ground and excited states





the states, $^3\Pi$, $^1\Pi$, are in order of higher multiplicity at lower energy. This is the expected ordering, as the singlet state has extra K terms in the energy expression over the triplet state.

That the ground state configuration gives states in the order as predicted by Hund's rules is in agreement with the work of Raftery et al.¹⁰². They consider the relative ordering of degenerate electronic states obtainable in open shell linear molecules, by noting which particular two electron integrals are obtained from the particular open shell that is present. For a system including a π^2 open shell, they show that Hund's rules should be followed.

The excitation energy has been noted as being small. At 0.057 hartree, it compares with a value of 0.253 for NCO (D7+P basis), and 0.0209 for CNC (D7+P basis).

Bonding

The bonding in the species is describable in terms of the Mulliken population analysis. The results of this for the ground state and the two monoions - at the optimum bond lengths of the ground state - are given in TABLE II.3. For ground state and ions, the $1\sigma^2$, $2\sigma^2$, $3\sigma^2$ orbitals are 'core' orbitals - that is, orbitals localised almost entirely as $1s^2$ on each atomic centre - on oxygen, the central carbon atom, and the terminal carbon atom in order of increasing energy. The other orbitals describe the bonding in the system - they have electron density on more than one centre. The fourth σ orbital can be considered as corresponding to an oxygen to carbon σ bond of predominantly s character on oxygen, sp on carbon. Similarly, the fifth σ orbital can be described as a carbon

TABLE II.3Gross Population Analysis

The total population on each centre is given for the orbitals shown for the ground state of OCC, and the two ions.

Orbital	O	Centre C	C
$2\pi^2$	0.1768	0.5351	1.2881
$7\sigma^2$	0.0157	0.1537	1.8306
$1\pi^4$	2.6910	1.1298	0.1793
$6\sigma^2$	1.7291	0.2107	0.0602
$5\sigma^2$	0.0672	1.1048	0.8280
$4\sigma^2$	1.4582	0.5311	0.0107
$3\sigma^2$	0.0	0.0008	1.9992
$2\sigma^2$	0.0007	1.9995	-0.0002
$1\sigma^2$	1.9993	0.0007	0.0
Σ	8.1380	5.6661	6.1959
OCC ⁺			
$2\pi^1$	0.0942	0.2044	1.7014
$7\sigma^2$	0.0165	0.1245	1.8590
$1\pi^4$	2.4920	1.2864	0.2216
$6\sigma^2$	1.7700	0.1929	0.0371
$5\sigma^2$	0.0391	1.0915	0.8694
$4\sigma^2$	1.4710	0.5192	0.0098
Σ	7.8826	5.4203	5.6971

TABLE II.3 Continued.

Orbital	O	Centre C	C
$0\sigma^-$			
$2\pi^3$	0.2807	0.9547	1.7646
$7\sigma^2$	0.0155	0.1830	1.8015
$1\pi^4$	2.8385	0.9919	0.1696
$6\sigma^2$	1.6779	0.2260	0.0961
$5\sigma^2$	0.1024	1.0937	0.8039
$4\sigma^2$	1.4490	0.5377	0.0133
Σ	8.3640	5.9878	6.6482

to carbon σ bond, predominantly sp on the central, s on the terminal carbon atom. The two highest σ orbitals, the sixth and seventh, correspond to sp lone pairs on the oxygen atom and the terminal carbon atom. The first π symmetry orbital corresponds to a π bond, predominantly between oxygen and the central carbon atom, with a density bias towards oxygen. The second π orbital corresponds to a π bond between the carbon centres, with a less marked density bias, to the terminal carbon atom.

This general bonding pattern, of 'core' orbitals, two σ bonds between the two pairs of atomic centres, with lone pairs, and a pair of π bonds similar to the σ bonding orbitals - though more diffuse - is repeated in all the triatomic species discussed.

Population analyses for the single anion and cation were carried out after the SCF results, from which the effect on the population of removing, or adding, one electron from the second π orbital can be obtained. It is pointed out that the following analysis is not intended to be a description of the equilibrium ions. For the cation, the σ orbitals are practically unaltered, the loss of electron population in 2π being accompanied by a drift of charge towards the terminal carbon atom, which occurs also, though in a lesser extent, in 1π . The net effect is to localize the positive charge on the central carbon atom. In the anion, the σ orbitals are again almost unperturbed, the extra electron in 2π accommodated by accumulation of electron population on the terminal carbon atom, and further polarization of 1π . The net charge accumulation here is on the terminal carbon atom.

The population analysis is often used to obtain a prediction for the dipole moment. As the ALCHEMY programme solves the

expectation value problem explicitly, it will be merely noted in which direction the population analysis predicts the dipole moment to be directed. For the ground state, however, although the population results show that a dipole moment should exist, the direction is not clear. There is indicated negative charge excess on the two terminal atoms, positive on the central atom; but, the amount of negative charge on the terminal atoms is very similar for each, and no conclusion can be drawn as to the direction of the dipole moment.

Turning to the excited state of this configuration, the $^1\Delta$ state, the population analysis is summarised in TABLE II.4. As would be expected, the bonding is very similar to the lower energy state. Apart from the 2π orbital, there is great numerical correspondence between the two states. The 2π does show a small alteration in the form of the bonding - the charge density gradient towards the terminal carbon is not so great. The total population densities on the atomic centres suggests that the dipole moment in this state might not be as large as that in the ground state. The direction is, again, indeterminate.

Properties

As indicated above, the ALCHEMY programme is equipped to solve the expectation value problem for several one electron operators. The way this is done has been indicated in Chapter 2. The various possible operators, and the related properties have been indicated in that chapter also. The expectation values for the usual properties are given in TABLE II.5, and the properties calculated therefrom in TABLE II.6. For the excited states, only the dipole

TABLE II.4Summary of Population Analysis for OCC¹ State, BA+P Basis

Orbital	O	Centre C	C
$2\pi^2$	0.219	0.573	1.208
$7\sigma^2$	0.016	0.149	1.835
$1\pi^4$	2.653	1.142	0.205
$6\sigma^2$	1.729	0.216	0.059
$5\sigma^2$	0.064	1.091	0.846
$4\sigma^2$	1.462	0.527	0.011
Σ	8.142	5.695	6.163

TABLE II.5Expectation Values of Quoted Operators for OCC

Operator	0	Centre C	C
Ground State			
$1/r$	26.3283	20.6671	18.7191
z	41.4454	-0.97460	-52.5746
z^2	178.914	93.0755	231.233
r^2	202.692	116.853	255.010
p^2	23.7774	23.7774	23.7774
z/r^3	1.61589	-0.87573	-1.26289
$(3z^2 - r^2)/r^5$	0.72398	1.58626	0.06949
$^1\Delta$			
z	41.3825	-1.17548	-52.5835
z/r^3	1.6072	-0.85727	-1.27066
$^3\Pi$			
z	39.2073	-4.1627	-50.5387
z/r^3	1.5857	-0.597	-1.48783
$^1\Pi$			
z	39.4833	-4.50267	-50.8787
z/r^3	1.5462	-0.54359	-1.4854
$^+1\Sigma^+$			
z	41.5837	-0.974334	-53.0543
z/r^3	1.60184	-0.876785	-1.24617

TABLE II.6

Properties of OCC Species

		Value (A.U.)	Value (C.G.S.)
Ground State			
Dipole Moment		-0.5314	-1.305 D
Quadrupole Moment		-4.3415	-5.8469 barn
Field Gradients	O	2.5575	
	C	0.7914	
	C	0.7833	
g Values	g_s	0.5041	
	g_r	0.1292	
Force on nucleii	O	0.0855	
	C	0.0071	
	C	0.0005	
	Σ	0.0931	
Force Constants			
	Bond O-C	1.2916	$2.0108 \times 10^6 \text{ dyn cm}^{-1}$
	Bond C-C	0.61076	$9.5083 \times 10^5 \text{ dyn cm}^{-1}$
Properties for $^1\Delta$:			
Dipole Moment		-0.4253	-1.0809 D
Forces on nucleii	O	0.0823	
	C	0.0084	
	C	-0.0008	
	Σ	0.0898	

TABLE II.6 Continued.

		Value (A.U.)	Value (C.G.S.)
Properties for $^3\Pi$:			
Dipole Moment		0.7275	1.8490 D
Force on nucleii	\checkmark O	0.0946	
	C	-0.0696	
	C	0.1523	
	Σ	0.1773	
Properties for $^1\Pi$:			
Dipole Moment		0.8211	2.0869 D
Force on nucleii	O	0.0945	
	C	-0.0333	
	C	0.1674	
	Σ	0.2286	
Properties for $^1\Sigma^+$:			
Dipole Moment		-0.4249	-1.0799 D
Force on nucleii	O	0.0710	
	C	0.0310	
	C	-0.0250	
	Σ	0.0770	

moment and the forces on the nuclei are calculated. For the excited states, values for properties calculated with a single configuration wave function are not going to have the same accuracy as those from a ground state calculation. The main reason for leaving out calculation of the other properties for the excited states is that it is highly unlikely that experiments will be performed to measure them. The information would be both of uncertain accuracy and of little practical use. Force constants calculated as indicated in the prior chapter are included for the ground state, with the other properties, in Table II.6. The expectation values are given for the optimum geometry for each species.

In the discussion of the results obtained for the species HBO - Section VIII of this chapter - the relative accuracy of the various basis sets used is obtained. It is seen there that the various basis sets show a gradation towards the near Hartree-Fock results - those with the BA+P basis. For that species, there are available experimental values for the force constants for the bond vibrations. These being the force constants that have been calculated with the theoretical results, comparison is possible. The indication is that the near Hartree-Fock wave function produces force constants close to experimental values. This supports the assumption that the energy surface of a Hartree-Fock function parallels that of the real species. It is, thus, reasonable to assume that the molecular properties calculated for the species considered in this thesis, with the BA+P basis set will be close to experimentally-measurable quantities.

It was noted in the discussion of the bonding that the population

analysis indicated negative charge excess on both terminal atoms, of similar magnitude. The dipole moment should thus be small. Explicit calculation of the expectation value gives a moment of 1.31 Debye. It is determined as being directed from the terminal carbon to the oxygen atom. The population analysis indicated, if anything, a dipole in the other direction. For the excited state of the ground configuration, the dipole moment is calculated as 1.08 Debye, in the same direction; but, with a value reduced in comparison with the ground state, as was suggested by the population results.

In the chapter discussing molecular, one-electron properties in general, Chapter 2, the work of Green^{51,52} on the closed-shell species, CS, was noted. For that species, he obtained a value for the dipole which he showed to be of the order of 10^{-1} Debye of the experimental value. The species, OCC ground state, in common with most of the species considered in this thesis, has an open shell electronic configuration. The programme used to calculate the molecular wave function produces a function of Restricted Hartree-Fock form. Brillouin's theorem²⁴, does not hold for the wave function. It cannot, therefore, be said that the dipole calculated from the BA+P wave function predicts an experimental value to the order of 10^{-1} D. Agreement is necessarily poorer. Added to this source of deviation from the experimental value is the effect of single excitation configuration, as are noted in the section on HBO, which couple with the Brillouin-allowed double excitations. This deviation is common to functions that satisfy Brillouin's theorem as well as to those that do not.

For open shells systems, an Unrestricted Hartree-Fock^{95,96}

function satisfies Brillouin's theorem, and a value for the dipole calculated with a function of this type would give a better approximation to the experimental moment. The Unrestricted Hartree-Fock function can be represented by a Restricted Hartree-Fock function plus singly-excited promotions in a configuration interaction expansion⁶⁰. Such a calculation should give a dipole moment close to experiment. Thus, for this species, OCC, as for the other open shell species of this thesis, it can be said that the dipole is predicted to the correct order of magnitude, but not much better than that.

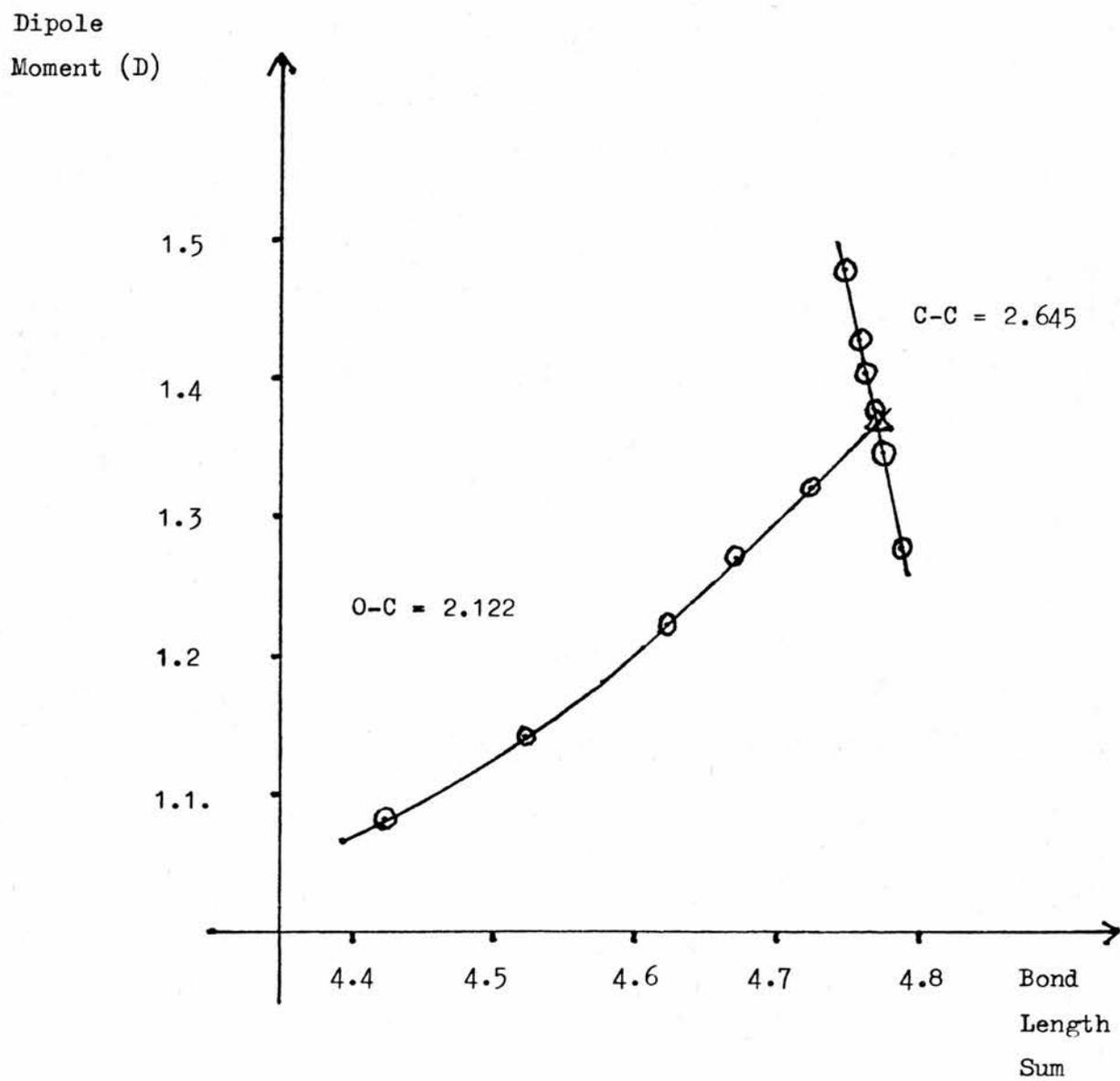
The value calculated for the quadrupole moment is 5.85 barn. The sum of the electrostatic forces on the nuclei is 0.09, which is not far from zero, indicating that the wave function with the BA+P basis, at the geometry obtained, is close to the Hartree-Fock limit.

For the ground state, the dipole moment was calculated at various geometries. These values are given in TABLE II.7. They are used to plot the graph given as GRAPH II.2. As for Graph II.1, the coordinates of the abscissa require elucidation. The bond length held constant is added to the bond length under variation, and the combined term is plotted as the abscissa. This enables the two curves to be plotted on the same graph, and the value that is common to both curves is at one point in the network. The first observation from these curves is that there is no minimisation of the value of the dipole moment at the optimum geometry obtained with respect to the total energy - which occurs at a value of 4.7 on the abscissa. This is expected: the geometry is being altered to obtain the lowest energy, driven by the variation theorem.

TABLE II.7Dipole Moment of the Ground State, at the given Geometries

Bond Lengths		Sum	Dipole Moment	
O-C	C-C		Atomic Units	Debye
2.1	2.645	4.745	-0.5813	-1.4774
2.11	2.645	4.755	-0.5616	-1.4274
2.115	2.645	4.76	-0.5518	-1.4024
2.12	2.645	4.765	-0.5419	-1.3773
2.126	2.645	4.771	-0.5301	-1.3473
2.14	2.645	4.785	-0.5025	-1.2771
2.122	2.645	4.767	-0.5380	-1.3673
2.122	2.6	4.722	-0.5195	-1.3204
2.122	2.55	4.672	-0.4998	-1.2703
2.122	2.5	4.622	-0.4813	-1.2233
2.122	2.4	4.522	-0.4494	-1.1422
2.122	2.3	4.422	-0.4263	-1.0835

GRAPH II.2 OCC Ground State.
Variation Dipole Moment with Bond Length



This search has, because of the variation theorem, real meaning. As no similar variation theorem exists for the property, a search for a minimum value is of no use. For molecular properties, it is only presumed that a wave function that produces an optimum energy will give predictions of the molecular properties that are close to the actual values.

What is required is not only a wave function that is flexible enough to produce an energy surface parallel to the surface of the real species, but also a function that is flexible enough to model well the electron distribution over the molecule. Suitable basis sets are being approached with the near Hartree-Fock sets - in this thesis, the BA+P basis set.

The other point that is noticed from the curves is that the one has a much greater gradient than the other. Noting that this is the curve for the variation of the carbon to carbon bond length, reference is made to the population analysis - Table II.3. The core orbitals are going to retain the same distribution as the bonds are altered. There are two σ bonds, each containing two electrons, between the two terminal atoms and the central atom. They each contain two electrons, and are unlikely to affect the total electron distribution. The two lone pairs are strongly localized on the two terminal atoms, and the LCAO approach cannot give a change to the electron distribution if this remains so over the altered bond lengths. There is no reason to expect the lone pairs to become bonding orbitals; therefore the sensitivity of the dipole moment to the carbon to carbon bond length is not explained by the σ molecular orbitals. Considering the π system, the two bonds have density over the whole molecule; so, both are going to alter

as the bond lengths are altered. The result of the analysis is that the dipole moment is more sensitive to the variation of the carbon to carbon bond length. The π bond that has greater density between these two centres, is the second of the two π molecular orbitals. This is the open shell. The value of the dipole calculated for this open shell species is, thus, dependent on the description of the open shell.

The value of the dipole moment is very sensitive to that bond length that most affects the open shell. The optimum value of this bond length should, then, be chosen with care. A method of plotting the values obtained on a graph, and guessing the minimum of the curve, is not sufficiently accurate. A statistical approach would give a better estimated value. The results obtained in this work have been obtained by use of a curve-fitting routine, implemented on a digital computer; so, this condition begins to be fulfilled. However, to obtain the bond lengths accurately, with statistical help, a large number of values for each bond length is needed. Large numbers of calculations for each bond that most affects the open shell for each of the species studied would require even more computer time; so, the molecular properties calculated for the species must remain open to some improvement, even within the single-configuration approximation.

For the excited states, only dipole moments and the forces on the nuclei were calculated from the expectation values. They are given in Tables II.6 and II.5 respectively. The forces on the nuclei for the states of the ground electronic configuration are:

0.09 for the ground state, ${}^3\Sigma^-$;
 0.09 for the state, ${}^1\Delta$;
 0.08 for the state, ${}^1\Sigma^+$;

These values show that the wave functions obtained for these states, for this configuration, are close to the optimum for the single configuration model. Clearly, the ${}^1\Delta$ state is the singlet state reported by Bayes²¹.

The two Π states, which derive from the excited configuration, are at a greater divergence from optimum - at 0.18 for ${}^3\Pi$, and 0.23 for ${}^1\Pi$. The carbon to carbon bond length was taken to be the same for these two species, as they optimized to values that were very close, the value for ${}^3\Pi$ being used while the oxygen to carbon bond length was optimized for both species. It is the oxygen to carbon bond length that it is more important to optimize for the molecular energy, and obtaining the relative energies for the excited states is more useful than obtaining properties.

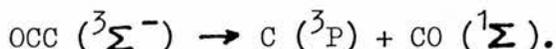
The conclusion is drawn that, for states from an excited electronic configuration, the approach to a limiting single configuration wave function with a BA+P basis is not as close as for the ground state and configuration.

If the virial coefficient is taken as a measure of the accuracy of these wave functions, then the values for these states of OCC, given in Tables II.1 and II.2, show that all the wave functions are close to satisfying the theorem. The ${}^n\Pi$ states are a little less close to optimum, but not far from it; but, for the ground state, the theorem is satisfied exactly to six significant places. However, for excited states, the virial theorem is not so closely defined,

and the use of the coefficient as an index of wave function accuracy is not as useful.

As there are more than one state degenerate in each electronic configuration, the use of a single configuration wave function is not entirely adequate. As the principal extra components in a configuration interaction expansion are configurations in which an electron has been promoted out of a high-lying valence orbital, configuration interaction is more relevant to open-shell excited states. The process of configuration interaction improves the modelling of the diffuseness of the valence orbitals, and, as it is these orbitals which largely determine the electronic properties - dipoles, quadrupoles, and general chemical activity - it would be preferred to make predictions of properties for these species from results of such calculations.

The ground state of the species would be expected to decompose according to the following equation:

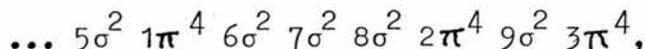


With the near Hartree-Fock results for the atom and for carbon monoxide given in the tables of McLean and Yoshimine⁷⁴, and the result for the carbene obtained in this work, the endothermicity of this reaction can be obtained. The sum of the energies of the carbon atom and carbon monoxide is -150.47712 hartree. As the carbene has an energy of -150.51632 hartree, it is stable with respect to this decomposition. The amount of energy by which it is stable is 0.03920 hartree.

The Second Row Carbene, SCC

For the linear triatomics containing only elements of the first row of the Periodic Table, experimental evidence exists for the order of occupied molecular orbitals. Theoretical calculations have also given the same ordering of orbitals. A sufficient background exists to enable the electronic configurations of these species to be assumed when ab initio calculations are mounted. For the analogues of these species, that include elements of the second row of the Periodic Table, there is neither experimental data nor the same corpus of prior theoretical study to assure the correct choice of molecular electronic configuration. Not only is there a lack of data on the order of molecular orbitals on such species, but there is not much experimental data available to show that they exist. Herzberg⁵ quotes in the sixth Appendix of his book, Dixon et al⁵⁹, for the existence of SCN, and McKellar⁷³, and Kleman⁶⁸, for the existence of SiCC. In the experimental data quoted in the investigation of NCO, the species, SCN, is mentioned³⁶. The stability of SCC is likely, by analogy, but its undoubted high reactivity will give it a very transient existence. The ab initio investigation was mounted to enable a comparison between the bonding of oxygen and of sulphur in the carbenes to be made, with a view to determining analogous behaviour.

The ion, SCN^- , has been made the subject of an ab initio study by McLean and Yoshimine⁷⁴, and they used the electronic configuration:



as they have for their calculation on the species, SCO. This electronic configuration was taken as reference for the ab initio investigation of the carbene, SCC. The electronic configuration

used was:

$$\dots 5\sigma^2 1\pi^4 6\sigma^2 7\sigma^2 8\sigma^2 2\pi^4 9\sigma^2 3\pi^2 \dots {}^3\Sigma^-.$$

With this configuration, a double zeta basis was used, and the bond lengths optimized with respect to the energy. At the optimum geometry, the system was found to be bound with respect to the separated atoms. The energies of the atoms with a double zeta basis are given in the tables of Clementi²⁸, and, are: sulphur, 3P , -397.49051 hartree; carbon, 3P , -37.68668 hartree. The sum of the atomic energies for the triatomic system is -472.86386 hartree. The optimum energy for the molecule was calculated to be -473.03541 hartree. This is at a geometry of: a sulphur to carbon bond of 3.0599 bohr; and, a carbon to carbon bond of 2.4725 bohr. The species is, thus, more stable, by a margin of 0.17155 hartree over the separated atoms. The electronic configuration chosen, with the double zeta basis gives a system bound with respect to the separated atoms. An alternative electronic configuration would involve eleven occupied σ orbitals and two occupied π orbitals. This configuration was set as an alternative in the investigation of the species PCC - q.v. - and was found to have an energy that was not as low as that of the sum of the separated atoms; that is: this electronic configuration did not predict a bound system. The other configuration, on the other hand, did. It was assumed that this would be the case for SCC - especially as the binding energies for the double zeta basis and this configuration are similar for SCC and PCC: SCC 0.1716 hartree; PCC 0.1560 hartree.

The population analysis for the species is given in TABLE II.8, for the optimum geometry. The orbitals that are given in the table are the valence orbitals. The remaining orbitals fall into the

TABLE II.8Summary of the Population Analysis for SCC Ground State

Orbital	S	Centre C	C
$3\pi^2$	0.5568	0.4103	0.7330
$9\sigma^2$	0.0882	0.1151	1.7967
$2\pi^4$	1.9930	1.6858	0.3212
$8\sigma^2$	1.3505	0.5260	0.1235
$7\sigma^2$	0.5925	0.9290	0.4786
$6\sigma^2$	0.7343	0.7630	0.5027
Σ	15.6199	6.4252	5.9549

category of core orbitals. There are the usual $1s^2$ orbitals on each centre, but as one of the atoms is in the second row of the Periodic Table, the 2s shell is at an energy level close to that of the 1s shell of the first row. The fourth σ orbital of the molecule is predominantly s-type on sulphur, with density in the 1s and 2s shells. There are eight extra electrons on the sulphur centre, vis à vis oxygen, and the remaining six electrons fill the 2p shell of the atom. The $n = 3$ shell is left for bonding interaction. $5\sigma^2$ is of the form of a lone pair $2p^2$, on sulphur. The other four electrons form a π molecular orbital - as expected from a combination of $2p_x$ and $2p_y$ - the $1\pi^4$ orbital.

The bonding in the molecule is described by the interaction of the $n = 2$ shell of the carbon atoms and the $n = 3$ shell of the sulphur atom. By analogy with OCC, there are expected the following orbitals: two σ orbitals, giving bonding between the two pairs of atoms; two lone pairs on the terminal atoms; two π orbitals between the two pairs of atoms.

The extra charge in the sulphur nucleus contracts the atomic orbitals of low n . This effect is modelled by a large exponent value for the Slater functions for low principal quantum number. The Slater functions are: $\exp(-ar)$, where a is the supplied exponent value. The larger the value that a takes, the closer to the nucleus will be the peak of the electronic density, ψ^2 . In combination of atoms, atomic orbitals of the same symmetry interact to greatest extent with those nearest in energy, forming molecular orbitals. As calculated with a double zeta basis, orbital energies of sulphur and of carbon, together with molecular orbital energies for the carbene are given in TABLE II.9, indicating

TABLE II.9Orbital Energies for SCC (${}^3\Sigma$), S(3P), C(3P)

S(3P)	C(3P)	SCC(${}^3\Sigma$)
		$3\pi^2$ -0.4081
3p -0.4371	2p -0.4327	
		$9\sigma^2$ -0.4866
		$2\pi^4$ -0.5058
		$8\sigma^2$ -0.6479
3s -0.8791	2s -0.7043	
		$7\sigma^2$ -1.0065
		$6\sigma^2$ -1.1419

the closeness in energy of the $n = 2$ shell of first row atoms to the $n = 3$ shell of second row atoms.

Proceeding to a discussion of the valence orbitals 6σ and 7σ form the σ bonding orbitals of the system. They are, however, not clearly localized as the two σ bonding orbitals are in OCC, but are delocalized over the system as a whole. This can be rationalized by noting that the $n = 3$ shell is more diffuse than the $n = 2$ shell; but, some of the effect may derive from the smallness of the basis. The results from the species, PC, suggest however, that extending the basis is not going to have much effect on these bonds - as the increase in number of functions combined in these orbitals is not large. For 6σ , the larger contribution of the sulphur orbitals gives it a lower energy, and it does have more density between sulphur and carbon than carbon and carbon. As the 7σ molecular orbital also has more density between sulphur and carbon, to describe each as separate two-centre bonds is not accurate. 8σ is the orbital that corresponds to the lone pair on oxygen in OCC. It does not, however, have negligible density on the central carbon atom. This is ascribed to the diffuse nature of the $n = 3$ shell - to which can also be ascribed the large bond length, of 3.0599 bohr, compared with 2.121 bohr for OCC. 9σ is clearly localized on the terminal carbon atom, as a lone pair, as in OCC. This shows that the diffuseness of the other orbitals is due to the presence of the $n = 3$ shell. As for OCC, the π system is delocalized over the whole molecule, and they show the same pattern - the lower π orbital is largely between the sulphur and the central carbon atom; the higher between the two carbon atoms. That they are similar could be ascribed to the total σ distribution, beneath the π system,

being much the same in both species. Perhaps this is reading too much into the result - the π system is diffuse in OCC, and a greater diffuseness occasioned by the presence of the second row atom would make no discernable difference.

It can be concluded that prediction of the type of bonding present in species containing second row elements from results of calculations on first row species can be made; but, the greater diffuseness of orbitals of second row atoms renders the description of the bonding orbitals in terms of valence bonds between two atoms inadequate.

The usual molecular properties were calculated, and the results should give an order of magnitude value for the single configuration value for these properties - from consideration of the results obtained for the species, PC. The expectation values for the usual operators are given in TABLE II.10, the properties calculated therefrom in TABLE II.11. It is seen that the forces on the nuclei do not satisfy the Hellmann-Feynmann theorem. The basis set used is, therefore, inadequate, and one including polarization functions would be needed before there could be assumption of significance in the values of properties calculated. This point is repeated in the analysis of the results for SCN.

Both the dipole and quadrupole moments are calculated as being of the same sign and similar magnitude as for OCC; and, despite the inadequacies of the basis set, are probably of the right order of magnitude. The force constants as calculated for the carbon to carbon bond - 2.425 bohr in SCC, 2.58 bohr in OCC - are of similar magnitude, which gives support to the value calculated for SCC.

TABLE II.10Expectation Values for SCC Ground State

Operator	S	Centre C	C
z	52.5057	-33.1715	-102.402
z^2	266.490	207.329	542.534
e^2	37.0082	37.0082	37.0082
z/r^3	0.76942	-0.7509	-1.37378
$3z^2 - r^2/r^5$	-0.254292	1.08771	1.02682

TABLE II.11Properties for SCC Ground State

Property		Value (A.U.)	Value (C.G.S.)
Dipole Moment		-0.9519	-2.4193 D
Quadrupole Moment		-3.1732	-4.2677 barn
Force on Nucleii	S	0.7694	
	C	-1.5324	
	C	2.1739	
	Σ	1.4109	
Field Gradient	S	0.2354	
	C	3.1861	
	C	2.1973	
Force Constants f_{SC}		0.4358	$6.7841 \times 10^5 \text{ dyn cm}^{-1}$
f_{CC}		0.6480	$10.0874 \times 10^6 \text{ dyn cm}^{-1}$

Postulated Preparation

Carrington et al²⁶ in their investigation of the ESR spectrum of NCS make use of the preparative methods of Holland et al⁵⁹. These latter observed emission bands in the fluorescence spectrum of methyl thiocyanate and methyl isothiocyanate, irradiated with ultra violet light; and, from high frequency discharge through methyl thiocyanate. Dixon and Ramsey³⁶, as for NCO^{35} photolyse methyl and ethyl isothiocyanates at pressures of 1 to 10 Torr, with and without a large excess of argon. The lifetime of the NCS radical is longer than 250μ sec.

The absence of a suitable substrate from which the grouping SCC could be obtained makes use of this method inapplicable. A more useful parallel preparative route is that of Smoes et al¹¹⁴. They obtained atomisation energies for several small molecular species containing phosphorous, including PCC. The method involved use of mass spectroscopic techniques, and Knudsen cells. The technique is described in a paper by Drowart and Goldfinger³⁸, and involves production of molecular beams from a reaction vessel - the Knudsen cell - capable of being heated in the range 1000 to 2500 °K, and pressures of 1 to 10^{-9} Torr. The cells were made of graphite and contained GdP, which had been prepared separately by direct combination of the elements. The gaseous species emitted from the cell were of general formula C_nP_m , n and m integer and zero. A similar procedure for the preparation of carbon-sulphur species could be postulated.

Noting that OCC was observed on photolysis⁵⁵ and radiolysis¹³⁰ of carbon monoxide, photolysis of CS_2 vapour might give some C_2S molecules.

In such experiments with sulphur compounds, the quantity of material would have to be controlled - by dilution with inert gas, or by low pressure - to reduce the amount of polymeric sulphur accumulating in the vessels. The lifetime of SCC is not expected to differ much from that of SCN.

Section III: The Species, NCC, CNC, PCC

Introduction

Spectroscopic observation of these species has been made by Merer and Travis^{79,80}, and their evidence led them to expect the ground and first excited states of these species to be linear. They are species that are, again, of transient existence, and data from ab initio calculations would complement experimental data. For the ground states of these species, ab initio investigations have been made by Dr. Thomson, and reported¹²³. The basis sets used were of DZ and DZ+P quality, for the species in $C_{\infty v}$ symmetry for NCC and $D_{\infty h}$ symmetry for CNC. In the work discussed here, attempts were made to obtain wave functions for the first excited states of the two species.

Obtaining wave functions for these species was more difficult than obtaining those for the excited states of the carbene, OCC. For that species, there exists an excited state of the ground configuration, and the ground state wave function could be used as a first approximation for the SCF programme input. This produced a convergent analysis, and optimization of the $^1\Delta$ state could proceed. The energy of that state is close to that of the first state of the first excited configuration, $^3\pi$. The use of the $^1\Delta$ wave function as a first approximation to that of the $^3\pi$ state was successful in leading to a convergent SCF calculation, though, for the highest states considered, attainment of a set of vectors that would lead to a convergent SCF calculation became more difficult. For the species that form the subject of this section, the excited states are not as close to the ground state as for OCC. For this

species, the first excited state - that is, the $^1\Delta$ state - is at an energy 0.04 hartree above the ground state. The first excited configuration leads to an energy for the $^3\Pi$ state 0.06 hartree above the ground state. For the two species considered in this section, the excitation energies are: for NCC, ground state to $^2\Delta$ approximately 0.11 hartree; for CNC, 0.21 hartree. For the species of OCC, the total energies are taken from calculations with a BA+P basis, for NCC and CNC, with the lower quality double zeta bases; but all that is required from the figures/is an indication of which is the larger excitation energy. As the excited states of the NCC, CNC species are at greater energy differences from the ground state energy than the excited states of OCC, establishing a suitable set of vectors for programme input would be more difficult - as the ground state vectors are a poorer approximation to the excited state vectors. Obtaining a set of vectors that would lead to a convergent execution of the SCF routines in the ALCHEMY programme became more difficult as the size of the basis set was increased. In fact, use of the BA+P basis set in the $D_{\infty h}$ formalism gave sufficient difficulty, that the input data was rewritten in $C_{\infty v}$ form. For the problem in this form, a set of vectors leading to convergence was found, and the geometry of the species was expressed so as to maintain the applicability of the centre of inversion operator to the species.

For NCC, a basis of double zeta quality, taken from Clementi's tables²⁸, was used for the calculation of the wave function for the first excited state, $^2\Delta$. An optimum geometry with this basis was eventually found, and is given in TABLE III.1. It was found that optimization of each bond length was dependent on the value for the other in that unless the bond length being held constant was close

TABLE III.1Optimum Energies and Bond Lengths for the Species, NCC, and CNC

State	Basis	Bond Length		Total Energy	Virial Co- efficient
		NC	CC		
NCC $^2\Delta$	DZ	2.3066	2.3813	-129.84010	-1.99980
CNC Ground	BA+P	2.2987		-130.05425	-1.99993
CNC $^2\Delta$	DZ	2.3518		-129.75159	-1.99986
	DZ+P	2.3115		-129.83507	-2.00027
CNC $^2\Sigma$	DZ	2.3537		-129.72061	-1.99976
	DZ+P	2.3138		-129.80435	-2.00018

to the optimum, the other bond length was difficult to obtain. As the molecular energy is -129.84010 hartree, and the energy of the ground state of the species, calculated by Dr. Thomson¹²³, with the double zeta basis set, was -129.94687 hartree, the first excitation energy is 0.10677 hartree.

Isomeric with NCC is the species, CNC. This is also linear in the ground and first two excited states^{79,80}. Calculations on this species were performed for the two excited states of ${}^2\Delta$ and ${}^2\Sigma$, with bases of DZ, and DZ+P quality. The ground state has been studied with DZ and DZ+P bases by Dr. Thomson¹²³, and with the BA+P basis in this study. The ground state energies are:

- 129.95688 hartree (DZ basis);
- 130.04418 hartree (DZ+P basis);
- 130.05425 hartree (BA+P basis).

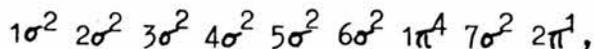
From these total energy values for the ground state, and the energies calculated for the excited states tabulated in Table III.1, excitation energies may be derived:

		Energy (hartree)	
Ground State	Excited State	DZ basis	DZ+P basis
CNC (${}^2\Pi$)	→ CNC (${}^2\Delta$)	0.20529	0.20911
CNC (${}^2\Pi$)	→ CNC (${}^2\Sigma$)	0.23627	0.23983

It is noted that the difference in excitation energies is predicted as being similar:

- 0.00382 hartree for the DZ basis;
- 0.00356 hartree for the DZ+P basis.

The ground state configuration of NCC is



and the first excited configuration is:

$$\dots 6\sigma^2 7\sigma^1 \pi^4 2\pi^2.$$

This configuration gives rise to the two possible electronic states of ${}^2\Delta$ and ${}^2\Sigma$ that have been examined. The species, CNC, has $D_{\infty h}$ symmetry, and the ground state and first excited states are:

$$1\sigma_g^2 2\sigma_g^2 1\sigma_u^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 \pi_u^4 3\sigma_u^2 1\pi_g^1, \\ \dots \dots 4\sigma_g^2 3\sigma_u^1 1\pi_u^4 \pi_g^2.$$

Calculations for the ground state wave function were performed with the BA+P basis. For the first excited states, calculations were performed with DZ and DZ+P bases. These calculations were carried out with the electronic configurations in $D_{\infty h}$ symmetry. Repeated attempts to derive wave functions for the excited states using the BA+P basis sets and $D_{\infty h}$ symmetry were met with failure. Calculations were attempted with the data rewritten in $C_{\infty v}$ symmetry. Some success was achieved, suggesting total energies for the states, as calculated with BA+P bases, some 0.063 hartree lower than the total energies as calculated with the DZ+P bases.

As is noted in the investigation of HBO in particular - Section VIII of this chapter - as the basis size is increased, the predicted bond lengths decrease. This is the case also for the species of CNC:

	DZ basis	DZ+P basis
CNC ${}^2\Delta$	2.35 bohr	2.31 bohr
CNC ${}^2\Sigma$	2.35 bohr	2.31 bohr

The calculations using the BA+P bases referred to above suggested a further reduction in bond lengths of similar magnitudes.

Bonding

In the previous section of this chapter, on the OCC species, the general bonding pattern for these triatomic species has been established. There are three core orbitals, each centred on one of the three atoms. Two σ symmetry molecular orbitals link the two pairs of atoms. A σ symmetry molecular orbital on each terminal atom is interpreted as a lone pair of electrons on each of these atoms. The π -system comprises two orbitals, both delocalised over the whole molecule, each having greater density over one of the two bonds.

This pattern is repeated for the $C_{\infty v}$ symmetry species of NCC. For the $D_{\infty h}$ species of CNC, the pattern is similar, with molecular orbitals in gerade and ungerade pairs. This pattern is the same as that for the species, OBO, in Section VII of this chapter.

Properties

The expectation values for the various operators are given in TABLE III.2, with the properties calculated from them in TABLE III.3. Values are given for those properties listed for the species, calculated at the optimum geometries for the species.

The dipole moment of the first excited state of NCC is 3.7D, comparing to the ground state value of 1.18 D - as calculated by Thomson¹²³. These compare with the values obtained for the species, OCC, ground and first excited, ${}^3\Pi$, states of -1.3D and 1.1D respectively. The value for the first excited state of NCO, ${}^2\Sigma^-$, is -2.4D - calculated with the DZ basis. This is a similar dipole moment to that of the first excited state of NCC.

TABLE III.2Expectation Values for the Quoted Operators

Operator	N	Centre C	C
NCC $^2\Delta$			
z	40.9364	-2.8890	-48.1337
Operator	C	Centre N	C
CNC Ground State			
z	43.6753	0.0000	-43.6753
z^2	180.567	80.1705	180.567
e^2	24.3641	24.3641	24.3641
z/r^3	1.60920	0.0000	-1.60914
$(3z^2 - r^2)/r^5$	1.10688	1.10508	1.10682

TABLE III.3Molecular Properties Calculated for the Species Indicated

		Value (A.U.)	Value (C.G.S.)
NCC $^2\Delta$			
Dipole Moment		1.4788	3.759 D
CNC Ground State			
Quadrupole Moment		-4.6061	-6.1958 barn
Force on Nucleii	C	-0.0035	
	N	0.0	
	C	0.0039	
	Σ	0.0004	
Field Gradient	C	0.1677	
	N	0.8703	
	C	0.1677	
Force Constant	f_{NC}	2.2400	$3.4872 \times 10^6 \text{ dyn cm}^{-1}$

It is noted in the section of this chapter on the species, NC - Section VI - that the numerical value of the dipole moment decreases as the basis size is increased from DZ to BA+P. As the value for the first excited state of OCC was obtained from a wave function with the latter basis, it may be assumed that the dipoles of all the first excited states of the three species, NCO, NCC, OCC, are of a similar magnitude. The Hartree-Fock limiting value for the first excited state of OCC is 1.1D. All of these species show the dipole as being directed from the most electronegative atom in the molecule. With the dipole for NC decreasing approximately threefold from DZ to BA+P, it can be estimated that the values for the dipoles of NCC and OCC will be close, and of a somewhat lower magnitude for OCN.

Comments on CNC

A summary of the population analysis for CNC ground state is given in TABLE III.4. The wave function was calculated in $C_{\infty v}$ symmetry, as noted above, with the BA+P basis; and, it is seen from this table that the wave function does show $D_{\infty h}$ symmetry. The expectation values and properties resulting are given in Tables III.2 and III.3 respectively.

The dipole moment for a wave function possessing $D_{\infty h}$ symmetry is expected to be zero, as the molecule is invariant to transformation across the centre of symmetry. With expectation values of the operator \hat{z} on the terminal atoms of equal magnitude and opposite sign, and of zero magnitude on the central atom, the dipole moment is indeed calculated as zero. It is also expected for a wave function of $D_{\infty h}$ symmetry, that the sum of

TABLE III.4Population analysis of CNC Ground State

Orbital	C	Centre N	C
$2\pi^1$	0.479	0.041	0.479
$7\sigma^2$	0.943	0.114	0.943
$6\sigma^2$	0.976	0.048	0.976
$1\pi^4$	0.708	2.584	0.708
$5\sigma^2$	0.471	1.059	0.471
$4\sigma^2$	0.462	1.076	0.462
Σ	6.036	6.929	6.036

the forces on the nuclei are also zero. The wave function, as shown by the population analysis summarised in Table III.4 does have $D_{\infty h}$ symmetry. The divergence from zero of the sum of the forces on the nuclei are, then, more a measure of the accuracy of the form of the calculation than of the quality of the wave function. This suggests that the calculation has significance up to three decimal places. The quadrupole exists, and at -6.2 barn compares with the value of -5.8 barn for OCC ground state, with the same BA+P basis.

The excitation energies of the two states with the DZ+P basis are 0.20911 hartree for the ${}^2\Delta$ state, and 0.23983 hartree for the ${}^2\Sigma$ state. Values using the BA+P basis would be expected to be of smaller magnitude. As indicated previously, such calculations as were done using the BA+P basis would suggest lower total energies. The resultant excitation energies would be some 0.053 hartree lower than the values obtained using the DZ+P basis. These values would be comparable to the excitation energy of OCC ${}^1\Pi$, obtained as 0.12412 hartree with the BA+P basis.

Symmetry and Restricted Hartree-Fock wave functions

In this work, wave functions were calculated in the Restricted Hartree-Fock symbolism. This was because the computer programme, ALCHEMY, had been developed using this symbolism. For a closed shell system, of $2N$ electrons, the wave function is expressed as a single determinant of N doubly-occupied orbitals. When open shell systems are considered, the programme, ALCHEMY, uses the formalism of Roothaan¹⁰⁶. As presented in a previous chapter,

this treats the problem of the open shell wave function as a closed shell problem with the addition of several correction terms. That is, the Roothaan procedure calculates wave functions for open shell species in single determinant form.

As discussed in a previous chapter, except for the case of a singly-occupied two-electron orbital, excited states are essentially multi-determinant states. A wave function produced fulfilling this criterion would be an Unrestricted Hartree-Fock wave function. That is, for species with open shells - apart from the case of the singly-occupied two-electron orbital - the Unrestricted Hartree-Fock wave function is a determinant belonging to a degenerate set of functions^{95,96}. That is, for species with open shell occupancies of, for example, $\sigma^1 \pi^2$, as for the excited states of CNC, a set of determinants should be considered. (Wave functions of closed shell species are single determinant functions in Unrestricted Hartree-Fock theory as well as Restricted Hartree-Fock theory.)

As Nesbet argues⁹², application of group theory to the Unrestricted Hartree-Fock system produces the result that the orbitals of an open shell Unrestricted Hartree-Fock determinant must show some distortion from the degree of symmetry used to describe a closed shell function. That is, an Unrestricted Hartree-Fock wave function calculated for a species should show a reduced symmetry over a Restricted Hartree-Fock wave function calculated for the same species. The Unrestricted Hartree-Fock wave function will necessarily produce a total energy lower than that produced from a Restricted Hartree-Fock wave function, even though the wave function will not have the correct

transformation properties.

It would follow that a symmetry distortion of a Restricted Hartree-Fock wave function would produce a closer approximation to the Unrestricted Hartree-Fock function. In this way, a reduction in total energy calculated should be possible. That a symmetry distortion of a Restricted Hartree-Fock wave function for a $D_{\infty h}$ species will produce a lower energy has been demonstrated for the species NNN by Archibald and Sabin¹⁶. They studied the ground state, which has an open shell, π^3 . They found that a displacement of the central atom gave a reduction in total energy from the symmetric geometry.

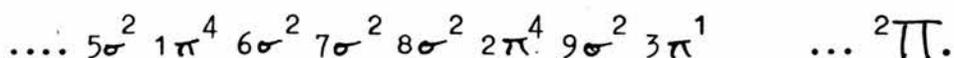
This discussion would suggest that, for an open shell species, a lower symmetry Restricted Hartree-Fock wave function would approach an Unrestricted Hartree-Fock wave function. This would be a closer approximation to the multiconfiguration function necessary for open shell species. If this aspect of theory is applied to experimental situations, the suggestion would be that excited states of species will show symmetry reduced over the ground state.

Properties of one-electron operators could be calculated for such wave functions. However, as the symmetry of the function is reduced, then criteria dependent on symmetry transformation would no longer hold. Such would be that the value of the dipole moment of a $D_{\infty h}$ species is zero. The criteria of an accurate wave function that the sum of the forces on the nuclei should be zero would still hold for the symmetry-distorted wave function.

The Species, PCC

In the previous section of this chapter, the analogue of the carbene containing a second row element was considered. The species containing the next element in the second row is PCC, and calculations on this species are reported here.

Smoes et al ¹¹⁴ have obtained atomisation energies for various species containing the element phosphorus, including the species PCC, by mass spectroscopic methods. They assumed that the geometry of the species would be analogous to the first row species; that is, they would be linear. This, however, does not finalise the choice of the electronic configuration. By comparison with calculations on SCN⁻ performed by McLean and Yoshimine ⁷⁴, the configuration they chose would suggest a configuration for PCC of:



There is another possibility, with eleven σ orbitals and two π orbitals. Which of these giving the lower energy depends on which gives a better description of the core orbitals. Both configurations were investigated with a double zeta basis, obtained from the tables of Clementi ²⁸. For all geometries chosen, the energy of the latter configuration - that is: that configuration with only two orbitals of π symmetry - gave an energy higher than that of the

sum of the separate atoms, calculated with the same basis. As the other configuration gave a lower energy for the species, predicting it to be bound, the electronic configuration is concluded to be that written out above. Curve-fitting the energy results for the other configuration did not suggest that there would be a geometry at which it would be stable with respect to the isolated ground state atoms.

The usual geometry optimization of the energy was performed for the species, resulting in an energy of -416.21867 hartree for the minimum geometry, which was: P-C bond length, 3.0927 bohr; C-C bond length 2.4309 bohr. As for the species, SCC, the bond to the second row atom is nearer to three bohr than to two. Again, this indicates that the $n=3$ shell is more diffuse than the $n=2$ shell. The sum of the atomic energies, obtained from Clementi²⁸, is -416.06266 hartree. The energy difference from that for the molecule is 0.15601 hartree - the contribution to the dissociation energy with this basis. To the DZ basis were added polarisation functions of $3d$ and $4f$ on all centres for each molecular symmetry. Calculating a wave function at the same geometry as the minimum geometry for the DZ basis, the total energy obtained was -416.29273 hartree - an improvement of 0.07406 hartree. This indicates that the results for the DZ basis set are rather far from optimum for the single configuration approximation. The results obtained with the species, PC, reported in Section VI of this chapter, indicate that the DZ+P basis would give a good wave function for the species.

Bonding

The bonding in the species parallels that of the first row

analogue - which is described by Thomson¹²³. This pattern has been reported in the previous section for the species, SCC. As reported there, the bonding of the species can be predicted from that of the first row species, with some modification owing to the diffuseness of the $n=3$ shell.

The lowest five σ orbitals and the lowest π orbital, which are all fully occupied, form the core orbitals, with density close to the nucleus - compared to bond lengths. The bonding orbitals form around this set, which, with the nucleus, form a strongly-localised charge distribution, having little influence on the bonding pattern of the species.

The valence orbitals follow the usual pattern, and the population analysis for them is summarised in TABLE III.5. The sixth and seventh σ molecular orbitals give the two σ bonding pairs in the species. Unlike SCC, where both orbitals had substantial density on all three centres, for PCC, 6σ is clearly a phosphorus to carbon bond, with some density on the terminal carbon atom; and, 7σ is definitely a carbon to carbon bond. The s orbital contributing to the bonding in the phosphorus to carbon bond is the expected $3s$ orbital. $8\sigma^2$ is the lone pair on phosphorus, more $3sp$ in character than $3p$ alone. $9\sigma^2$ is the lone pair on the terminal carbon atom, sp symmetry.

$2\pi^4$ is a π -symmetry molecular orbital extending over the whole molecule, having a density bias towards the central carbon atom. The last molecular orbital - the $3\pi^1$ open shell - is centred largely in phosphorus. Concluding the comparison of the bonding in SCC and PCC, that in SCC is seen to be more diffuse, which suggests that: for accurate modelling of the electron distribution, polarisation functions on the centres are essential. This is not

TABLE III.5Population Analysis for the Ground State of PCC

Orbital	P	Centre C	C
$7\sigma^2$	0.3102	0.8855	0.8043
$6\sigma^2$	0.7810	0.9709	0.2482
$8\sigma^2$	1.4333	0.3615	0.2052
$9\sigma^2$	0.1581	0.1328	1.7091
$2\pi^4$	0.9552	2.3010	0.7438
$3\pi^1$	0.6890	0.0641	0.2469
Σ	14.3346	6.7080	5.9574

to say that d-orbitals are involved in the bonding of sulphur to other centres; but, simply that the bonding is more diffuse, and the way of modelling this effect with an atomic basis set is to add polarization functions, of n and l values larger than those occupied in the ground states of the atoms involved. This conclusion would have to be considered by reference to explicit calculation.

The population analysis results can, by use of the total population on each centre, indicate the presence of a dipole moment. In the case of PCC, the direction indicated is that from phosphorus to carbon.

The wave function produced with the DZ basis gave a virial coefficient of -2.00024 , which is not far from the theoretical value of -2.0 . The DZ+P calculation at this geometry gave a value of -2.00060 , which is further from the limit, as expected, as this is not the optimum geometry for the basis set. For both bases, the usual properties were calculated. The expectation values are given in TABLE III.6, together with those for the DZ+P calculation. The values for the properties for both bases are given in TABLE III.7.

As the DZ+P calculation is not at the optimum geometry for that basis, comparison of the two sets of data are not entirely valid. There is an improvement in the sum of the forces on the nuclei, in the direction of satisfaction of the Hellmann-Feynman theorem. The values for the other properties are of the same order of magnitude with both bases. For the dipole and quadrupole moments, the DZ+P basis gives a reduction in the absolute value. From the results of the calculations on the species, PC, given in a later section of this chapter, this reduction in the values of properties is a real effect, and not just occasioned by the DZ+P being not at optimum

TABLE III.6Expectation Values for the Quoted Operators for PCC Ground State

The values given below are those calculated with the DZ basis.

Operator	P	Centre	
		C	C
z	53.2222	-30.2807	-95.9150
z^2	269.700	198.749	505.518
r^2	306.014	253.063	541.833
e^2	36.3142	36.3142	36.3142
z/r^3	0.781277	-0.58307	-1.38328
$(3z^2 - r^2)/r^5$	1.04851	1.02092	1.12812

TABLE III.6 (continued)

The values given below are those calculated with the DZ+P basis.

Operator	P	Centre	
		C	C
z	53.0822	-30.4207	-96.0550
z^2	267.441	197.356	504.806
r^2	303.432	233.347	540.797
e^2	35.9918	35.9918	35.9918
z/r^3	0.821308	-0.56296	-1.46991
$(3z^2 - r^2)/r^5$	1.09229	1.12456	1.13325

TABLE III.7Properties for the species PCC

Values are those calculated with the DZ basis.

Property		Value (A.U.)	Value (C.G.S.)
Dipole Moment		-1.5244	-3.8743 D
Quadrupole Moment		-5.3609	-7.2099 barn
Force on Nucleii	P	-0.6408	
	C	-0.1810	
	C	0.7363	
	Σ	-0.0855	
Field Gradient	P	-0.5717	
	C	0.8287	
	C	-0.1147	
Force Constants f_{PC}		0.654	$1.018 \times 10^6 \text{ dyn cm}^{-1}$
	f_{CC}	0.637	$9.913 \times 10^5 \text{ dyn cm}^{-1}$

TABLE III.7 (continued)

Values are those calculated with the DZ+P basis.

Property		Value (A.U.)	Value (C.G.S.)
Dipole Moment		-1.3844	-3.5185 D
Quadrupole Moment		-3.7892	-5.0961 barn
Force on Nucleii	P	-0.0397	
	C	-0.0604	
	C	0.0474	
	Σ	-0.0527	
Field Gradient	P	-0.6154	
	C	0.7250	
	C	-0.1199	

geometry. The direction of the dipole moment is directed as in the first row analogue, and not as suggested by the population analysis.

The values for the two electric multipole moments, at -3.9 D and -7.2 barn for PCC are in the same direction and of similar magnitude to those obtained for SCC, at -2.4 D and -4.3 barn. This is a striking similarity, as the detail of the electron distribution is not at all similar.

Section IV: The Species, NCN, NNC

Introduction

The paper written by Dr. Thomson giving the report of his calculations on the ground states of the species, CNC, NCC¹²³ includes, also, data on the ground states of the species, NNC, NCN. The absorption spectra of NCN was obtained by Herzberg and Travis⁵⁸, after flash photolysis of diazomethane. U.V. and I.R. spectroscopy of matrix-isolated NCN has given further evidence for the existence of the species, and for the assumption that it is linear⁸¹. Electron Spin Resonance spectroscopy has also produced experimental evidence for this species⁷⁹. NNC has been observed from matrix isolation experiments by electron spin resonance, ultra-violet, and infra-red spectroscopic methods^{79,80}.

Both these species are reactive intermediates, with limited free lifetimes. As for the species, NCC, CNC, Thomson¹²³ found that the symmetric species had the more stable ground state. For the first excited state, it would appear from this study that it is the asymmetric isomer that is the more stable.

Again, as for the symmetric species of the previous section, difficulty was experienced in obtaining convergent solutions of the eigenproblem, using the BA+P basis set. As for the species of CNC, attempts were made to achieve convergence by rewriting the data in $C_{\infty v}$ symmetry.

For NNC, the first excited state was investigated, using the DZ+P basis. TABLE IV.1 reports the results of optimising the energy with respect to the geometry of the species indicated.

TABLE IV.1Optimum Energies and Bond Lengths for the Species Indicated

State	Basis	Bond Length		Total Energy	Virial
		N-N	N-C		Coefficient
NNC $^3\Pi$	DZ+P	2.1596	2.2721	-146.53542	-2.00037
NCN $^3\Pi$	DZ	-	2.347	-146.39046	-2.00034

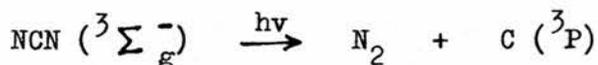
From the tables of Clementi²⁸, the sum of the atomic energies from DZ basis calculations may be found. The sum of the ground state energies for two nitrogen atoms and one carbon atom is -146.48242 hartree. The reason for choosing this sum has been given in the preceding section of this chapter. From the table, the energy of the first excited state of NNC - the $^3\Pi$ - state - is -146.53542 hartree. The species is thus predicted as being stable with respect to the separate atoms, by an energy of 0.05300 hartree. As the ground state energy of this species is -146.68096 hartree¹²³, the excitation energy to the first excited state is 0.14554 hartree, calculated with the DZ+P basis. Calculations on the $^1\Pi$ state were also attempted. Those that gave convergence indicated an energy above that of the $^3\Pi$ state, as expected from Hund's rules.

The $^3\Sigma$ ground state of NCN has been investigated by Thomson¹²³ with a DZ+P basis. He found a binding energy of 0.21253 hartree for that basis - that is: the difference between the sum of the constituent atom energies and the calculated molecular energy of -146.69495 hartree. As part of this work, attempts were made to obtain a molecular energy using a BA+P basis set. Such results as were obtained would suggest a ground state energy some 0.013 hartree below the DZ+P ground state energy. This compares with the results obtained for CNC ground state and reported in the previous section of this chapter. There, the ground state energy using the BA+P basis is some 0.010 hartree below the energy obtained using the DZ+P basis.

Referring again to the tables of McLean and Yoshimine⁷⁴, the sum of the ground state energies for two nitrogen atoms and one carbon atom, using the BA basis is found to be -146.49048 hartree. The calculations performed would support the conclusions from the DZ+P results that the species is stable with respect to the constituent atoms.

With the DZ basis, the first excited state of NCN has an energy of -146.39046 hartree. (Such calculations as were performed with the BA+P basis would suggest an energy some 0.184 hartree lower).

In a paper by Milligan and Jacox⁸², the decomposition of the species, NCN, is suggested as being:



The atomic energy of carbon in the ${}^3\text{P}$ state has been calculated by McLean and Yoshimine⁷⁴, using a BA basis, as -37.68862 hartree. With a near Hartree-Fock energy for molecular nitrogen of -108.9956 hartree¹⁶, and a suggested value for the molecular energy of -146.707 hartree, from calculations performed as part of this work, this reaction would be endothermic by some 0.023 hartree.

Bonding

The bonding pattern in these species follows that established for the other linear triatomics that have been studied in this work. For $\text{C}_{\infty v}\text{NNC}$, the molecular orbitals are: three 'core' orbitals - $1s^2$ on each of the three atomic centres; 4σ and 5σ representing σ bonds between each pair of centres; 6σ and 7σ representing lone pairs on the terminal nitrogen

and carbon atoms respectively. The two π symmetry molecular orbitals show the usual pattern of having density over the whole molecule: 1π having more density between the two nitrogen atoms; 2π between the nitrogen and the carbon atoms.

The form of $D_{\infty h}$ molecular orbitals is given in Section VII of this chapter, for the species, OBO.

Properties

As OCC and NCN/NNC are isoelectronic, some similarity is expected in their properties. As has been seen, the bonding pattern of these species is similar - which it is for all these linear triatomics. The bond lengths of OCC ground state as calculated using the BA+P basis set are:

O-C 2.2121 bohr;

C-C 2.58 bohr.

The calculations performed for NCN using the BA+P basis would suggest a length of 2.27 bohr for each nitrogen to carbon bond. This bond length is similar to the oxygen to carbon bond length of the ground state of OCC. For NNC, with the DZ+P basis, the bond lengths for the ground state are:

N-N 2.16 bohr;

N-C 2.27 bohr.

The directions of properties should be similar for these species, the values will, of course, differ, as the nuclei have different charges. For the species of NCN, the presence of a centre of inversion renders properties that cannot be compared with the $C_{\infty v}$ species. For the excited state of NNC, expectation values calculated for the various operators are given in TABLE.IV.2,

TABLE IV.2Expectation Values for the Quoted Operators

Operator	Centre		
	N	N	C
z	40.9599	-2.23214	-47.6741
z^2	160.045	76.4091	189.801
p^2	21.4365	21.4365	21.4365
z/r^3	1.77225	-0.339253	-1.71998
$(3z^2 - r^2)/r^5$	0.891709	1.40981	0.511129

with the properties calculated from them, together with the usual force constants for bond vibration, in TABLE IV.3. For NNC, as the basis is of DZ+P quality, the properties for the first excited state are not going to be far from the single configuration limit.

Using the value for the nuclear electric quadrupole moment of ^{14}N given by Ramsey⁹, the coupling constant for this isotope has been calculated, related as it is to the field gradient at the particular nucleus. The value calculated for the terminal nitrogen atom - N_t in Table IV.3 - is almost an order of magnitude different from that calculated for the central nitrogen atom - N_c in Table IV.3. The ^{14}N coupling constant of 1.4 MHz for NCO ground state was obtained from a BA+P calculation described in Section V of this chapter.

For all these properties, meaningful comparisons of molecular values can be made if, and only if, the most diffuse orbitals - that is, the open shells - are adequately modelled.

TABLE IV.3Molecular Properties Calculated for the Species Indicated

NNC $^3\Pi$, DZ+P Basis		Value (A.U.)	Value (C.G.S.)
Dipole Moment		0.7475	1.900 D
Quadrupole Moment		-1.9361	-2.604 barn
Field Gradient	N	8.300	
	N	-2.601	
	C	-9.845	
^{14}N Coupling Constant	N_t	4.624×10^{-9}	30.42 MHz
	N_c	1.449×10^{-9}	9.535 MHz
Force on Nucleii	N	-0.2332	
	N	-0.0095	
	C	-0.0379	
	Σ	-0.2806	
Force Constants	f_{NN}	0.3185	$4.958 \times 10^5 \text{ dyn cm}^{-1}$
	f_{NC}	0.7355	$1.145 \times 10^6 \text{ dyn cm}^{-1}$

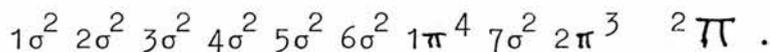
Section V: The Radical, NCO

Introduction

Ab initio investigations of this species with DZ and BA+P bases have been performed. For comparison, the analogue species, SCN, has also been considered, using a DZ basis. The results for NCO ground state have been published¹²⁶.

In flash photolysis of HNCO vapour, Dixon reports^{33, 34} observation of a transient species in the emission spectra. He assigned the bands to a linear species, NCO. Without isotopic data, he was unable to assign the bond lengths, but obtained an upper limit on their sum as 4.5505 bohr. Apart from this study of the electronic spectrum, Milligan and Jacox⁸⁴ studied the UV and IR spectra in argon matrix-isolation experiments. More recently, gas phase electron spin resonance techniques, developed by Carrington, have been used by him and coworkers²⁶ to study several molecular parameters of NCO.

Previous theoretical study of the species is lacking; however, McLean and Yoshimine⁷⁴ have investigated the anion, NCO^- . The electronic configuration of the ground state of NCO was assumed by Dixon to be:



This configuration was used for the ground state calculations, comparing with the configuration used by McLean and Yoshimine for NCO^- .

The optimum geometry for the ground state using the DZ basis was obtained by examination of plots of energy against bond lengths. For the BA+P basis, use was made of the curve-fitting programme

described previously. These optimum geometries, with total energies and virial coefficients are given in TABLE V.1. From electron diffraction work on isocyanic acid, HNCN, Fyster et al⁴² postulated bond lengths of 2.27 bohr for the two bonds. This length is similar to the bond lengths obtained for the NCO radical with the DZ basis.

The sum of the atomic energies, taken from Clementi's Tables²⁸, for the DZ basis is -166.8887 hartree; so, the species is predicted as being **stable** by 0.1238 hartree. Similarly, for the BA+P basis, with the atomic energies given by McLean and Yoshimine⁷⁴, the sum of these energies is -166.89893 hartree, and the species is predicted as being **stable** by 0.28905 hartree. The usual increase in this energy with the near Hartree-Fock basis is observed.

Bonding

The population analysis for the BA+P basis is summarised in TABLE V.2. As noted for OCC, there are three 'core' orbitals, and the population results for these are omitted from the table. These orbitals correspond to $1s^2$ on oxygen, nitrogen and carbon, respectively. The fourth σ molecular orbital is a carbon to oxygen σ bond, of sp character on carbon, s on oxygen. 5σ is a nitrogen to carbon σ bond, s character on nitrogen, sp on carbon. The sixth and seventh σ orbitals are lone pairs, of sp character, on the oxygen and nitrogen atoms. The two π symmetry molecular orbitals, although extending over all three centres, are predominantly carbon to oxygen and nitrogen to carbon respectively. Again, the general bonding pattern of these first row triatomic species is upheld. The total atomic population shows only a small transfer of charge along the molecule to the oxygen centre. This is supported by the value of the dipole

TABLE V.1Optimum Energies and Bond Lengths for NCO:

Basis	Bond Length		Total	Virial
	N-C	C-O	Energy	Coefficient
DZ	2.38	2.25	-167.01256	-2.00068
DZ+P	2.38	2.25	-167.00401	-2.00608
BA+P	2.3167	2.1426	-167.18798	-2.00008

TABLE V.2Summary of Population Analysis for NCO Ground StateBA+P Basis

Orbital	Centre		
	N	C	O
$4\sigma^2$	0.0228	0.5369	1.4403
$5\sigma^2$	1.2054	0.7653	0.0294
$6\sigma^2$	0.0537	0.2106	1.7357
$1\pi^4$	0.1064	1.2493	2.6434
$7\sigma^2$	1.7375	0.2118	0.0507
$2\pi^3$	1.9431	0.7588	0.2982
Σ	7.0679	5.7339	8.1983

moment calculated: as only approximately 0.5 D; and, of sign indicating electronic charge accumulation on oxygen. The dipole is considered as small, as the values obtained for the other triatomic species considered are usually nearer to one Debye unit; for example: OCC ground state has a value of 1.3 D.

Properties.

The usual one electron properties were calculated with the BA+P basis. The expectation values of the operators are given in TABLE V.3, the properties derived therefrom in TABLE V.4. The Π -radical, NCO, is isoelectronic with N_3 . An ab initio treatment of this system and its two monoions has been performed by Sabin and Archibald¹⁶, using a basis of Gaussian functions, of quality approximating to Slater double zeta; and, obtaining, as their optimum, an assymmetric, $C_{\infty v}$, geometry with bond lengths of 2.345 and 2.160 bohr. These values are similar to those found in this work for NCO, the values being closer for the BA+P than for the DZ optimum geometry. They calculated a force constant, for symmetric stretching, of $1.57 \times 10^6 \text{ dyn cm}^{-1}$, and a value for the dipole moment of 0.67 Debye. This force constant is remarkably close to the value, $f_{CO} = 1.589 \times 10^6 \text{ dyn cm}^{-1}$, obtained here for NCO. Their dipole moment compares also to the value of 0.50 Debye for NCO. Dixon³⁴ gives a value for the sum of the force constants as approximately $3 \times 10^6 \text{ dyn cm}^{-1}$. As he lacked data from an isotopic molecule, he was unable to factorize this value. The sum of the two force constants calculated for NCO is $2.69 \times 10^6 \text{ dyn cm}^{-1}$, which is in tolerable agreement.

As the NCO grouping in isocyanic acid is linear⁴², the evalua-

TABLE V.3Expectation Values for Quoted Operators for NCO Ground State:

The values given are those calculated with the BA+P basis set.

Operator	Centre		
	N	C	O
z	49.3761	0.725432	-44.2692
z^2	205.896	89.8260	183.123
e^2	22.5898	22.5898	22.5898
r^2	228.756	112.686	205.983
z/r^3	1.53470	0.436745	-1.67081
$(3z^2 - r^2)/r^5$	0.79988	1.74542	0.548970

TABLE V.4Properties for the species, NCO

Property		Atomic Units	C.G.S. Units
Dipole Moment		0.1985	0.5044 Debye
Quadrupole Moment		-7.0489	-9.480 barn
Rotational g values, g_s		0.5044	
	g_r	0.1074	
Force on Nucleii	N	0.1201	
	C	0.0068	
	O	-0.1321	
	Σ	-0.0052	
Field Gradient	N	0.3457	
	C	1.0172	
	O	0.8289	
^{14}N Quadrupole			
Coupling Constant		1.9256×10^{-10}	1.2670 MHz
Force Constants	f_{NC}	0.7094	$1.1043 \times 10^6 \text{ dyn cm}^{-1}$
	f_{CO}	1.0208	$1.5890 \times 10^6 \text{ dyn cm}^{-1}$

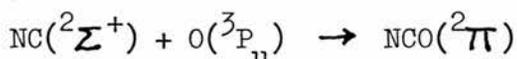
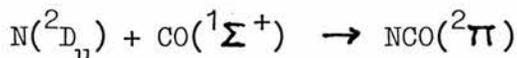
tion by Eysel and Nachbaur⁴¹ of stretching force constants from Raman spectra as $f_{\text{NC}} = 1.4286 \times 10^6 \text{ dyn cm}^{-1}$, and $f_{\text{CO}} = 1.4419 \times 10^6 \text{ dyn cm}^{-1}$, can be compared with those from this work. These being $1.1043 \times 10^6 \text{ dyn cm}^{-1}$; and $1.589 \times 10^6 \text{ dyn cm}^{-1}$ respectively, agreement is not good. The values, $f_{\text{NC}} = 1.082 \times 10^6 \text{ dyn cm}^{-1}$ and $f_{\text{CO}} = 1.293 \times 10^6 \text{ dyn cm}^{-1}$, obtained for the radical by Milligan and Jacox⁸⁴ are closer to those calculated. As they were estimated using bond lengths of 2.324 bohr for N-C and 2.230 bohr for C-O, it would be expected that the experimental value for f_{NC} would be less and that for f_{CO} greater than those calculated from the ab initio results.

In the paper by Carrington et al²⁶, a value for the nitrogen atom quadrupole coupling constant is given, as -2.2 MHz. Using the value for the nitrogen nuclear electric quadrupole of +0.0156 C.G.S. units from Ramsey⁹, the value for the coupling constant is calculated as 1.26 MHz. This is a similar magnitude to the experiment, but of opposite sign. Carrington, et al, state that they chose the sign of the coupling constant to be the same as that for the NO molecule given in an ab initio study on NO by Green⁴⁹. The field gradient at the nitrogen atom that was calculated with the BA+P basis is of positive sign, in contrast to that of NO, as calculated by Green. It is suggested, therefore, that the sign of the coupling constant is positive.

In their paper, Carrington, et al, give a value for the dipole moment of 0.742 ± 0.05 Debye. The value obtained with the near-Hartree-Fock wave function is 0.5044 D. This is certainly of the same sign and order of magnitude, which is encouraging for the utility of those dipole moments calculated for the other species

with the BA+P basis. The numerical deviation is ascribed to the effects of electron correlation.

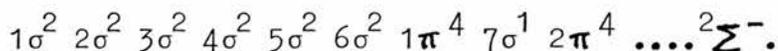
In the paper by Dixon³⁴, two possible reaction pathways are given for the formation of the NCO radical:



The DZ calculations are considered first. The DZ-derived energy of carbon monoxide is -112.7588 hartree⁹⁰, and the atomic energy of nitrogen is -54.3979 hartree²⁸. These give the first reaction pathway to be endothermic by $+0.1441$ hartree. For the second pathway, the energy of the NC species is given in the section of this chapter on NC and PC, as -92.1285 hartree. Together with the atomic energy of oxygen²⁸, this gives an exothermicity for the second reaction of -0.0799 hartree.

For the BA+P calculations, the atomic energies and the molecular energy of carbon monoxide are given in the tables of McLean and Yoshimine⁷⁴. The energy for NC using the BA+P basis is given in the appropriate section of this chapter. The respective energies are now $+0.00206$ hartree and -0.15872 hartree.

Dixon includes in the first paper⁸⁷, the first excited state of NCO:



The geometry of this species was investigated using a DZ+P basis set. This basis set gives an energy of -167.0040 hartree at the geometry optimised for the ground state, using the DZ basis. An electron has been promoted from the seventh σ to the second π

orbital. These two orbitals have energies -0.7115 and -0.4757 hartree respectively. The energy difference is 0.2358 hartree. This, however, is not a reasonable approximation to the energy required for promotion, as, on removal of the electron from the one orbital, some stabilisation energy is lost, and although some is regained from extra stabilisation in the higher orbital, this would be unlikely to be as large. The total electronic energy of the excited state at this geometry is -166.7513 hartree - that is, an energy higher than that of the ground state by 0.2527 hartree. The difference is taken from the energy calculated with the DZ+P wave function produced at the optimum geometry of the minimum DZ energy. The optimum geometry of the ground state is not that of the excited state, and minimisation of the energy with respect to the geometry gave an energy of -166.8131 hartree at a geometry of: N-C bond of 1.9863 bohr; C-O bond of 2.2096 bohr.

The orbital energies given by the DZ+P calculation at the geometry of N-C bond 2.38 , C-O 2.25 bohr, and the orbital energies given by the optimum calculation for the excited state are given in TABLE V.5. From this table, it is seen that the highest σ orbital in the ground state drops in energy to below that of the $6\sigma^2$ orbital, the single electron in the lone pair orbital of nitrogen being at a lower energy than the lone pair of the oxygen atom.

The population analysis, summarised in TABLE V.6, shows that the bonding pattern is not as clear as for the ground state - to which the lower flexibility of the basis will be contributing. It is clear, however, that the two lowest σ molecular orbitals correspond to σ bonds between the oxygen and carbon atoms, and the

TABLE V.5Orbital Energies Of NCO Ground State, and First Excited State

Values as calculated with the DZ+P basis

Ground State		Excited State	
Orbital	Energy	Orbital	Energy
$2\pi^3$	-0.4757	$2\pi^4$	-0.4810
$1\pi^4$	-0.6642	$1\pi^4$	-0.6960
$7\sigma^2$	-0.7115	$6\sigma^2$	-0.7221
$6\sigma^2$	-0.7966	$7\sigma^1$	-0.9375
$5\sigma^2$	-1.3158	$5\sigma^2$	-1.4201
$4\sigma^2$	-1.5067	$4\sigma^2$	-1.4882

TABLE V.6Summary of Population Analysis for NCO $^2 \Sigma^-$

Values as calculated with the DZ+P basis

Orbital	Centre		
	N	C	O
$2\pi^4$	1.919	-0.012	2.093
$1\pi^4$	1.874	0.969	1.157
$6\sigma^2$	-0.001	0.245	1.756
$7\sigma^1$	0.998	-0.001	0.004
$5\sigma^2$	0.576	0.570	0.854
$4\sigma^2$	0.850	0.525	0.625
Σ	8.221	4.293	8.486

carbon and nitrogen atoms. The orbital labelled as $6\sigma^2$ is the lone pair on oxygen, and $7\sigma^1$ is the orbital corresponding to the lone pair on nitrogen.

Although the wave function calculated for this species gives a virial coefficient of -2.00024 , the wave function is not reliable for the prediction of one electron properties - the Hellmann-Feynman force is calculated as being large. The expectation values of the usual operators are given in TABLE V.7, and the resulting properties in TABLE V.8.

The field gradient on the nitrogen atom has the same sign as and a similar value to that of the ground state. The dipole, however, is of opposite sign. In the analysis of the properties of HBO, Section VIII of this chapter, the coupling constant is not sensitive to the basis set; and, as it is close to the value for the ground state, it should be a fair indication of the true value. In that analysis, the value of the dipole is sensitive to the quality of the basis; and, considering the value for the Hellmann-Feynman force, the reliability of the dipole calculated for the species should not be too high.

In their paper on the ESR spectrum of NCO, Carrington et al²⁶ indicate that Renner splitting of the π -symmetry molecular orbitals occurs. Although an investigation of bent configuration was not undertaken, the splitting of the π -symmetry molecular orbital of the species HBO - Section VIII - indicating that Walsh's rules¹²⁸ hold, suggests that splitting of the π orbitals would occur for this species.

TABLE V.7Expectation Values for the Quoted Operators, for $NC0 \ ^2\Sigma^-$

Values calculated with the DZ+P basis

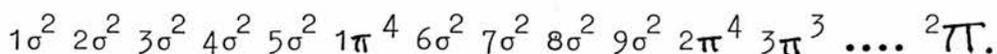
Operator	Centre		
	N	C	O
z	46.4277	4.71540	-41.6882
z^2	181.863	80.2771	161.968
e^2	23.5612	23.5612	23.5612
z/r^3	1.97420	-0.044126	-1.58176
$(3z^2 - r^2)/r^5$	1.36545	1.75166	0.093787

TABLE V.8Properties Calculated for NCO $^2\Sigma^-$

Property		Atomic Units	C.G.S. Units
Dipole Moment		-0.9427	-2.3960 Debye
Quadrupole Moment		-1.4823	-1.9935 barn
Force on Nucleii	N	-0.0067	
	C	0.5492	
	O	0.3581	
	Σ	0.9006	
Field Gradient	N	0.3824	
	C	1.5179	
	O	1.2081	
^{14}N Quadrupole Coupling Constant		2.1303×10^{-10}	1.4017 MHz
Force Constants	f_{NC}	0.5333	$8.303 \times 10^5 \text{ dyn cm}^{-1}$
	f_{CO}	7.1038	$11.059 \times 10^6 \text{ dyn cm}^{-1}$

The Second-row Radical, SCN

As for OCC, the sulphur-containing analogue was made the subject of an ab initio study, using a DZ basis set. The ultra-violet spectrum of this species has been obtained by Dixon and Ramsay³⁶. The electronic configuration adopted for the ab initio calculations was chosen as an analogue of that for NCO, and by comparison with that used for the anion by McLean and Yoshimine⁷⁴, that is:



Minimisation of the total energy with respect to the two bond lengths gave an energy of -489.7277 hartree, with bond lengths of:
 sulphur to carbon 3.3054 bohr;
 carbon to nitrogen 2.2098 bohr.

With the sum of the atomic energies derived from the DZ basis, given in Clementi's tables²⁸, equal to -489.5751 hartree, the stabilisation energy for the molecule is 0.1527 hartree.

Bonding

For each molecular orbital, the sum of the atomic populations are given in TABLE V.9. As noted for the previous second-row analogues considered, the first six orbitals of the molecular set are core orbitals. Again, the effect of the optimised atomic orbital exponent values having placed the low n-value orbitals close in to the nucleus is to give a description of the valence orbitals in terms of sulphur 3s and 3p interacting with carbon and nitrogen 2s and 2p. For this species, the molecular bonding pattern is clearer than that for SCC:

$6\sigma^2$ is a largely s-type σ bond, between carbon and nitrogen;

TABLE V.9Summary of Population Analysis for SCN Ground State

Values calculated with the DZ Basis

Orbital	Centre			Orbital Energy
	S	C	N	
$6\sigma^2$	0.0598	0.6616	1.2786	-0.2934
$7\sigma^2$	1.3417	0.6078	0.0505	-1.0451
$8\sigma^2$	0.9572	0.5870	0.4559	-0.6730
$9\sigma^2$	0.3354	0.2566	1.4080	-0.5808
$2\pi^4$	0.1018	2.0033	1.8949	-0.5440
$3\pi^3$	2.8217	-0.0150	0.1933	-0.4589
Σ	15.6212	6.0979	7.2809	

$7\sigma^2$ is the sulphur to carbon σ bond; $8\sigma^2$ is a lone pair on sulphur, with appreciable electron population on carbon and nitrogen; $9\sigma^2$ is the sp^2 lone pair on nitrogen; $2\pi^4$ is a predominantly carbon to nitrogen π -bond; $3\pi^3$ is centred largely on sulphur. The total populations give an indication of a charge drift from sulphur to nitrogen, suggesting a dipole directed from sulphur to nitrogen. This is not supported by explicit calculation of the expectation values of the z operator. This is calculated as -3.0528 D directed from sulphur to nitrogen. This is, however, the same direction as for NCO; and, is therefore acceptable.

The prediction of $6\sigma^2$ to lie below $7\sigma^2$ in energy is somewhat suspect. For SCC, although both these orbitals are more diffuse, and extend over all three centres, the predominantly sulphur to carbon bond does lie at a lower energy than the carbon to carbon bond. The prediction for SCN may be an artifact of the basis used. The atomic orbitals of second-row atoms being more polarisable than those of first row atoms, the addition of polarisation functions to the basis might give a reordering of these two molecular orbitals.

The optimum geometry for the DZ basis used was obtained as:
 sulphur to carbon bond length 3.3054 bohr; and,
 carbon to nitrogen bond length 2.2098 bohr.

This geometry compares with that obtained for SCC as:

sulphur to carbon bond length 3.0599 bohr;
 carbon to carbon bond length 2.4725 bohr.

Properties

The expectation values for the usual operators are given in TABLE V,10; and, the calculated properties derived therefrom in

TABLE V.10Expectation Values for Quoted Operators for SCN Ground State

Values calculated with the DZ basis

Operator	Centre		
	S	C	N
z	59.6399	-36.2167	-100.301
z^2	305.565	228.142	529.819
e^2	36.0758	36.0758	36.0758
z/r^3	0.711218	-1.107112	-1.55425
$(3z^2 - r^2)/r^5$	0.957320	1.18488	1.19451

TABLE V.11.

It is noted that the dipole in SCN is of the same direction as in NCO - that is, directed from nitrogen. The quadrupole moments are of the same order of magnitude - this is all the comparison that can be made, as the DZ basis for this second-row species is nowhere near as accurate as the BA+P basis used for the calculations on NCO. The Hellmann-Feynman force's being -0.142 , it can be assumed that the wave function is not predicting these properties to high accuracy. The corresponding value in NCO is -0.0052 .

The ^{14}N coupling constant is calculated as having a sign opposite to that for NCO, which is interesting, considering the discussion made there; however, as the wave function is not too reliable, conclusions about the sign will not be made.

The force constants for bond stretching are given in the table. For f_{NC} are of the same order; but, for f_{SC} , the value is less than that for f_{CO} ; however, when the bond length is, in the one case, 3.3 bohr, and in the other, 2.3 bohr, it cannot be expected that the value for this force constant will be larger.

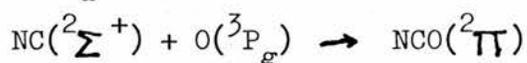
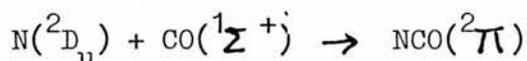
For a more reliable estimation of these properties, a larger basis is required. Polarisation functions in particular are needed; however, a larger s and p basis is required before these can be assumed to be acting as polarisation functions only - noting the results obtained for PC. For predictions of the same accuracy as the BA+P for NCO, a basis of the level of the 'BA+P' set used for PC would be required.

TABLE V.11Properties Calculated for SCN Ground State

Property		Atomic Units	C.G.S. Units
Dipole Moment		-1.20114	-3.0528 Debye
Quadrupole Moment		-4.77094	-6.4164 barn
Force on Nuclei	S	-1.089	
	C	4.252	
	N	-3.305	
	Σ	-0.142	
Field Gradient	S	-0.5416	
	C	0.2883	
	N	-0.5005	
¹⁴ N Quadrupole Coupling Constant		-2.788×10^{-10}	-1.835 MHz
Force Constants	f_{SC}	0.3545	$5.597 \times 10^5 \text{ dyn cm}^{-1}$
	f_{CN}	0.9470	$14.742 \times 10^5 \text{ dyn cm}^{-1}$

Section VI: The Diatomic Species, NC and PCIntroduction

In the paper by Dixon³⁴, noted in the section on the NCO radical, there are given the possible reaction pathways to its formation:



Energy results are available for the atoms in the tables by Clementi²⁸ and McLean and Yoshimine⁷⁴ for DZ and BA bases. The latter also give energies for CO. For NC, although Schaefer¹⁰⁸ has analysed the wave function, optimum geometries and energies are required with the bases used in the investigation of NCO. In TABLE VI.1 are listed the total energies and bond lengths of these species. They are used to establish the correlations given in the section on NCO.

As is seen from this table, the most important improvement in terms of the energy of the system is inclusion of polarisation functions. Giving the largest basis to the PC system improves the energy over the previous function by only 0.0061 hartree; however, the bond length is decreased by 0.0143 bohr, which is near to the decrease in bond length - of 0.0166 bohr - that is achieved in taking the system from the DZ+P to the Cl+P basis set. The properties calculated with these two large basis sets should show differences.

Properties and Discussion

In TABLE VI.2 expectation values are given for the species, NC,

TABLE VI.1Optimum Energies and Bond Lengths for the Species Indicated

Species	Basis	Bond Length	Total Energy	Source
CO	$1\Sigma^+$			
	DZ	2.132	-112.7588	a
	BA+P	2.132	-112.7891	b
NC	$2\Sigma^+$			
	DZ	2.342	-92.12847	c
	DZ+P	2.2809	-92.21455	c
	BA+P	2.2708	-92.21988	c
PC	$2\Sigma^+$			
	DZ	3.3985	-378.3857	c
	DZ+P	3.0896	-378.4505	c
	DZ+P(opt)	3.0896	-378.4556	c
	Cl+P	3.073	-378.4657	c
	BA+P	3.0587	-378.4728	c

Sources:

- a Nesbet 90
- b McLean and Yoshimine 74
- c this work

TABLE VI.1 (continued)Atomic Energies Used in the Text

Atomic Species	Basis	Total Energy	Source
N 2D_u	DZ	-54.39787	d
	BA	-54.40093	b
O 3P_g	DZ	-74.80418	d
	BA	-74.80938	b
P 2D_u	DZ	-340.6893	d
	BA	-340.7186	d

Sources:

b	McLean and Yoshimine ⁷⁴
d	Clementi ²⁸

TABLE VI.2Expectation Values for the Quoted Operators for NC,at the Optimum Geometries

Values Calculated with the DZ Basis

Operator	Centre	
	N	C
z	13.9459	-16.5001
z^2	44.2738	50.2556
r^2	60.6353	66.6172
e^2	16.3616	16.3616
z/r^3	0.890180	-1.11711
$(3z^2 - r^2)/r^5$	1.10323	1.15518

TABLE VI.2 (continued)

Values Calculated with the DZ+P Basis

Operator	Centre	
	N	C
z	13.6723	-15.9794
z^2	41.4808	46.7431
r^2	57.4503	62.7126
ρ^2	15.9695	15.9695
z/r^3	1.13078	-1.32311
$(3z^2 - r^2)/r^5$	1.24338	1.20692

TABLE VI.2 (continued)

Values Calculated with the BA+P Basis

Operator	Centre	
	N	C
z	13.5898	-15.9306
z^2	41.1186	46.4343
r^2	56.8886	62.2043
e^2	15.7700	15.7700
z/r^3	1.17251	-1.35459
$(3z^2 - r^2)/r^5$	1.26484	1.23743

and properties calculated therefrom in TABLE VI.3.

The two larger bases produce values for the sum of the electrostatic forces on the nuclei that come close to satisfying the Hellmann-Feynman theorem. In fact, the value is numerically larger for the BA+P basis than for the DZ+P basis. This might suggest that the DZ+P basis is as large as is necessary for a single configuration model of the system. That the values for the other one electron properties are not much altered by the change to the larger basis supports this. That the forces on each nucleus are significantly reduced from the DZ+P to the BA+P values does show that the latter function is superior.

Ab initio calculations were performed also on the species, PC, for correlation with PCC, and for comparison with NC. Calculations were performed with a double zeta basis, taken from Clementi's tables²⁸. The optimum energy geometry and the energy are given in Table VI.1. Polarization function exponents of:

$$\begin{array}{ll} 3d\sigma = 3.1 & 3d\pi = 3.1 \\ 4f\sigma = 2.8 & 4f\pi = 2.8 \end{array}$$

were added to the phosphorus centre, and

$$\begin{array}{ll} 3d\sigma = 2.072 & 3d\pi = 1.211 \\ 4f\sigma = 1.6 & 4f\pi = 2.243 \end{array}$$

to the carbon centre. The optimum geometry and energy with these are given as the second entry in the section of Table VI.1 referring to PC. The values for the polarization functions on phosphorus were guessed by reference to the paper by Mulliken and Liu on P_2 and PO ⁸⁸. The σ symmetry polarization functions on phosphorus were then optimised to:

TABLE VI.3Properties Calculated for the Species, NC

Values Calculated with the DZ Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		0.1061	0.2696 Debye
Quadrupole Moment		-3.4125	-4.5895 barn
Force on Nuclei	N	-1.4260	
	C	0.9547	
	Σ	-0.4713	
Field Gradient	N	-0.1691	
	C	-0.0653	
^{14}N Quadrupole Coupling Constant		0.9419×10^{-10}	619.73 kHz
Force Constant		1.1657	$1.8148 \times 10^6 \text{ dyn cm}^{-1}$

TABLE VI.3 (continued)

Values Calculated with the DZ+P Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		0.0131	0.0333 Debye
Quadrupole Moment		-2.3086	-3.1049 barn
Force on Nuclei	N	-0.1576	
	C	0.1349	
	Σ	-0.0226	
^{14}N Quadrupole Coupling Constant		1.2931×10^{-10}	850.8 kHz
Force Constant		1.4140	$2.2014 \times 10^6 \text{ dyn cm}^{-1}$
Field Gradient	N	-0.2321	
	C	-0.0271	

TABLE VI.3 (continued)

Values Calculated with the BA+P Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		0.0305	0.0775 Debye
Quadrupole Moment		-2.3679	-3.1846 barn
Force on Nucleii	N	0.0626	
	C	0.0174	
	Σ	0.0800	
Field Gradient	N	-0.2400	
	C	-0.0418	
^{14}N Quadrupole Coupling Constant		1.3372×10^{-10}	879.8 kHz
Force Constant		1.0592	$1.6490 \times 10^6 \text{ dyn cm}^{-1}$

$$3d\sigma = 1.8700$$

$$4f\sigma = 1.9255,$$

by adjusting their value to give minimum total energy, by use of least-square analysis.

The resulting total energy was lowered by 0.00519 hartree over the value obtained with the unoptimised functions. Both functions were optimized to smaller values; therefore, closer to the nucleus. This suggests that the basis is incomplete with respect to s and p functions.

An extended basis for phosphorus was taken from the table, number 24, in Clementi's publication²⁸. The basis used on the carbon centre was the 'accurate' Best-Atom set, taken from the tables of McLean and Yoshimine⁷⁴; that is, the functions as used in the BA+P calculations performed on the first-row species. The energy result from this molecular basis has been labelled as 'Cl+P' in Table VI.1 and referred to as such in the text. The energy lowering over the result with the previous basis is 0.01003 hartree.

The virial coefficients are:

DZ	-2.00042
DZ+P	-1.99990
DZ+P (opt)	-1.99995
'Cl+P'	-1.99991
'BA+P'	-2.00000 (to six significant places)

These indicate an improvement in the wave function from DZ through to DZ plus the optimized polarization functions, with a drop for the 'Cl+P' basis, the final wave function giving a good virial coefficient.

It was felt that the 'Cl+P' basis was not adequately balanced -

there are only three 3p functions in the phosphorus basis, for interaction with four 2p functions on the carbon basis. In the paper of Mulliken and Liu⁸⁸, in which an optimised set of basis functions is provided for P₂, the basis set includes four 3p functions, as well as a larger number of s-symmetry functions. A set of calculations on PC using this basis, with the BA basis for carbon were performed, with polarization functions on phosphorus those used by Mulliken and Liu on PO, and the polarization functions used by them on oxygen, set on the carbon centre. This gave an energy improved over that with the 'Cl+P' basis of 0.0071 hartree.

The expectation values for the usual operators are given in TABLE VI.4, and the properties calculated therefrom in TABLE VI.5.

The sum of the forces on the nuclei improves from the calculation with the DZ to the DZ+P bases; however, on going to the 'Cl+P' basis, this improvement is lost, to be regained on going to the 'BA+P' basis.- the effect noted with the virial coefficients. The changes in value for the properties are in the same direction, except for the 'Cl+P' basis. It is suggested that these results support the assertion that the 'Cl+P' basis is not balanced. The virial coefficient and the Hellmann-Feynman force indicate that the DZ+P is a superior wave function to the 'Cl+P' wave function. For NC, the property results indicate that a DZ+P wave function is an adequate function, and, that a larger basis set is not necessary for a single configuration investigation. For PC, it is found that the DZ+P wave function is a reasonable function - in that it produces properties that are not far removed from those produced from the wave function over the largest basis set, which, in the Hellmann-Feynman and virial sense, is a 'good' function - and, the

TABLE VI.4Expectation Values for PC, Ground State

Values Calculated with the DZ Basis

Operator	Centre	
	P	C
z	20.8713	-50.4972
z^2	88.6215	189.305
r^2	117.180	217.863
e^2	28.5585	28.5585
z/r^3	0.469127	-1.20111
$(3z^2 - r^2)/r^5$	0.693421	0.944672

TABLE VI.4 (continued)

Values Calculated with the DZ+P Basis

Operator	Centre	
	P	C
z	19.2966	-45.5850
z^2	75.6331	156.854
r^2	103.009	184.230
e^2	27.3763	27.3763
z/r^3	0.615779	-1.53627
$(3z^2 - r^2)/r^5$	1.16906	1.15259

TABLE VI.4 (continued)

Values Calculated with the Cl+P Basis

Operator	Centre	
	P	C
z	19.2864	-45.2466
z^2	74.9845	154.760
r^2	102.724	182.500
e^2	27.7394	27.7394
z/r^3	0.629842	-1.59247
$(3z^2 - r^2)/r^5$	1.20137	1.17648

TABLE VI.4 (continued)

Values Calculated with the BA+P Basis

Operator	Centre	
	P	C
z	19.2509	-44.9818
z^2	74.6932	153.397
r^2	102.636	181.339
e^2	27.9424	27.9424
z/r^3	0.64305	-1.60724
$(3z^2 - r^2)/r^5$	1.21783	1.16506

TABLE VI.5Properties for PC Ground State

Values Calculated for DZ Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		-0.4803	-1.2208 Debye
Quadrupole Moment		-4.1321	-5.5573 barn
Force on Nucleii	P	-0.7554	
	C	0.5857	
	Σ	-0.1697	
Field Gradient	P	-0.3877	
	C	-0.1804	
Force Constant		0.4234	$6.592 \times 10^5 \text{ dyn cm}^{-1}$

TABLE VI.5 (continued)

Values Calculated for DZ+P Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		-0.7590	-1.9291 Debye
Quadrupole Moment		-3.3622	-4.5218 barn
Force on Nucleii	P	-0.1917	
	C	0.2108	
	Σ	0.0191	
Field Gradient	P	-0.7622	
	C	-0.1354	
Force Constant		0.4455	$6.935 \times 10^5 \text{ dyn cm}^{-1}$

TABLE VI.5 (continued)

Values Calculated for Cl+P Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		-0.8484	-2.1560 Debye
Quadrupole Moment		-2.9996	-4.0342 barn
Force on Nucleii	P	-0.0829	
	C	-0.0243	
	Σ	-0.1072	
Field Gradient	P	-0.7879	
	C	-0.1427	
Force Constant		0.5814	9.052×10^5 dyn cm ⁻¹

TABLE VI.5 (continued)

Values Calculated for BA+P Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		-0.8987	-2.2839 Debye
Quadrupole Moment		-3.3336	-4.4834 barn
Force on Nucleii	P	0.0251	
	C	-0.0221	
	Σ	0.0030	
Field Gradient	P	-0.7985	
	C	-0.1167	
Force Constant		0.4789	7.456×10^5 dyn cm ⁻¹

basis that has been labelled 'Cl+P' produces a wave function inferior to that with the DZ+P basis.

Conclusion

These investigations were mounted to obtain energy values for use in previous sections of this chapter; but, have also shown that, for species containing elements from only the first row of the Periodic Table, the results from the DZ+P basis set calculation for the molecular properties are close to those predicted by the near-Hartree-Fock basis, the BA+P - for dipole and quadrupole moments if not for forces on nuclei.

For species containing an element from the second row of the Periodic Table, for which PC is the example, use of the 'Cl+P' basis gives a poorer set of property predictions than the DZ+P basis. Again, for this species, the DZ+P result is not far from the BA+P predictions. The important conclusion is that, for second-row containing species, the DZ+P basis gives a good set of properties; and, to obtain an improved set, a very expensive - in terms of required computer time - calculation must be mounted. This basis must show greater flexibility than the DZ+P basis. The basis as used by Mulliken and Liu fulfills this criterion.

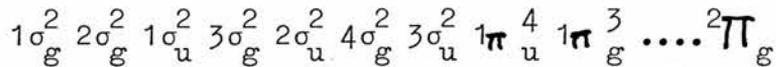
The bonding of the species PCC has been compared with that of SCC in a previous section. It was seen that the bonding in the sulphur-containing species is much less localised than in the phosphorus-containing species. It is presumed, therefore, that the use of the BA+P basis of Mulliken and Liu would be more necessary.

After this section had been written, there appeared a suitable basis set for sulphur by Green¹⁴⁸. This consists of a basis of

seven s type functions and six p type functions. This basis, with four polarization functions he gives as producing near Hartree-Fock wave functions.

Section VII: The Species OBOIntroduction

This species was reported from study of electronic emission spectra in flames and electric arcs by Johns⁶⁶, with a bond length of 2.3905 bohr, and a symmetry point group of $D_{\infty h}$. The electronic configuration is given as:



The species is isoelectronic with the radical, NCO. However, comparison of molecular properties is not possible as the species forming the subject of this section possesses a centre of symmetry.

In the ab initio investigation, the electronic configuration used was that written above, and calculations were performed with DZ and DZ+P bases. The DZ basis was taken from Clementi²⁸, and, for the DZ+P basis, the added polarization functions on both atoms were taken from the calculation on the species, BF, performed by McLean and Yoshimine⁷⁴. No optimization of these functions was attempted - as before, it is assumed that the accuracy of the wave function is much more sensitive to the presence of these functions than to their precise value. The minimum energies and geometries for these two bases are given in TABLE VII.1, together with that value for the energy obtained by adding polarization functions to the DZ result. This energy depression is 0.1101 hartree; and, on optimizing the geometry, gives, with a shorter bond length, an energy depression of 0.1126 hartree from the DZ result. This reduction in bond length, from the optimum geometry with a smaller basis, on reaching the optimum geometry with a larger basis has been noted before. This enables a more informed guess for the

TABLE VII.1Optimum Energies and Geometries for OBO Ground State

Basis	Bond Length	Total Energy	Virial Coefficient
DZ	2.3829	-174.3446	-2.0006
(DZ+P	2.3829	-174.4546	-2.0011)
DZ+P	2.3282	-174.4572	-1.9999
OBO ⁺			
DZ+P	2.2382	-173.9575	-1.9999
OBO ⁻			
DZ+P	2.3282	-174.5881	-1.9985

geometry of the larger basis set calculation to be made. The sum of the atomic energies, taken from Clementi's tables²⁸, is -174.1362 hartree. The species is predicted as being bound by both bases, by 0.2083 hartree with the DZ basis, improving to 0.3210 hartree with the optimized geometry and the DZ+P basis.

Bonding

Considering the other species investigated, it is expected that the bonding analysis will show: three core orbitals; two two-centre σ bonding orbitals, between the two pairs of atoms; two σ symmetry lone pairs on the terminal atoms; and two π symmetry molecular orbitals, again between the two pairs of atoms, though more diffuse than those of the σ set.

The population analysis is given in TABLE VII.2 for the optimum DZ+P wave function. In the table are given the total population on each centre for each of the valence orbitals. There are, indeed, three core orbitals. These are: $1\sigma_g^2$ and $1\sigma_u^2$, which are formed from the linear combination of the two equivalent centres of oxygen, in symmetric and asymmetric sum of the atomic 1s orbitals; the third core orbital is the 1s atomic orbital of the boron atom. This being at the centre of the molecule, it is a gerade symmetry orbital, $2\sigma_g^2$. As the two oxygen atoms are equivalent centres - about the centre of inversion of the $D_{\infty h}$ point group, each atomic orbital on each of these centres is equivalent. The molecular orbitals that form the molecular set are, thus, in pairs, and the set of orbitals given in Table VII.2 fall into pairs: $3\sigma_g^2$ is a boron to oxygen σ bond, with equal density on each of the two, terminal oxygen atoms; the $2\sigma_u^2$ is the antisymmetric counterpart

TABLE VII.2Summary of Population Analysis for the Species, OBO

Orbital	Centre		
	O	B	O
$1\pi_g^3$	1.439	0.122	1.439
$1\pi_u^4$	1.557	0.885	1.557
$3\sigma_u^2$	0.904	0.191	0.904
$4\sigma_g^2$	0.895	0.210	0.895
$2\sigma_u^2$	0.891	0.218	0.891
$3\sigma_g^2$	0.912	0.177	0.912
Σ	8.600	3.798	8.600

Total Populations for the Anion and Cation of OBO:

OBO ⁺	8.262	3.475	8.262
OBO ⁻	8.914	4.172	8.914

thereof. These two orbitals form the equivalent pair of σ bonding pairs that, in the $C_{\infty v}$ cases, are described as the two two-centre bonds. For $D_{\infty h}$ systems, such orbitals are necessarily delocalized over the whole system. The orbitals, $4\sigma_g^2$ and $3\sigma_u^2$ form the equivalent of the lone pairs, and are again, three centre bonds. The π molecular orbitals are delocalized over the three centres, as expected.

Returning to the first molecular orbitals, the orbitals $3\sigma_g$ and $2\sigma_u$ should give the σ bonding orbitals for the two boron to oxygen bonds. There should be at least as much charge on the boron centre as on the oxygen centres. As is noted in the discussion of the species, HBO, boron is showing its usual character of being electron deficient. If the populations for each centre are summed for these two molecular orbitals, and compared with the sum from the two lowest bonding orbitals of NCO ground state, an indication of the extent of this electron-deficiency can be obtained. (The values for NCO were obtained with the BA+P and those for OBO with the DZ+P basis.)

For the species, OBO:

	O	B	O
$2\sigma_u + 3\sigma_g$	1.803	0.395	1.803

And, for the species, NCO:

	N	C	O
$5\sigma + 4\sigma$	1.426	1.095	1.479

This comparison suggests a charge deficit on the central atom of almost one unit of charge. Consideration of the total charge population indicates that the boron centre is one unit of charge deficient. As the species is $D_{\infty h}$, the dipole moment will be zero;

but, because of the large charge deficiency on the boron centre, the quadrupole moment is expected to be large.

At the optimum geometry for the DZ+P basis, wave functions for the two monoions were obtained, giving the total energies for each of these two systems, and the ionisation energies are:

$$\text{OBO} \rightarrow \text{OBO}^+ \quad 0.4997 \text{ hartree}$$

$$\text{OBO} \rightarrow \text{OBO}^- \quad -0.1309 \text{ hartree}$$

Production of the anionic state forms a closed shell system, and extra stabilisation is expected.

The total populations are given in Table VII.2. For the cation, charge is lost over the whole system, with the positive charge centred on the boron atom. The anion shows the added electronic charge being spread over the whole system, the oxygen atoms acquiring extra charge density despite the boron centre's remaining highly electron deficient.

Properties

The expectation values for the indicated operators, calculated with the DZ+P wave function are given in TABLE VII.3, and the properties calculated therefrom in TABLE VII.4.

The quadrupole moment does have a large value, of -6.02 barn. This compares with the value of -9.5 barn for the asymmetric NCO ground state. As the system is in $D_{\infty h}$ symmetry, the sum of the forces on the nuclei is bound to be zero; so, the Hellmann-Feynman theorem is of no use in estimating the quality of the wave function. The virial coefficient, at -1.9999 , does indicate that the wave function is not too far from the limit. The force constant calculated with this basis, at $f_{\text{OB}} = 2.534 \times 10^6 \text{ dyn cm}^{-1}$, compares

TABLE VII.3Expectation Values for Quoted Operators, for OBO Ground State

Values Calculated with DZ+P Basis

Operator	Centre		
	O	B	O
z	48.8880	0.0	-48.8880
z^2	215.772	101.961	215.772
r^2	237.283	123.472	237.283
p^2	21.5107	21.5107	21.5107
z/r^3	1.26791	0.0	-1.26791
$(3z^2 - r^2)/r^5$	0.816749	1.47494	0.816749

TABLE VII.4Properties for OBO Ground State

Property		Atomic Units	C.G.S. Units
Quadrupole Moment		-4.47723	-6.02142 barn
Force on Nucleii	O	-0.1879	
	B	0.0	
	O	0.1879	
	Σ	0.0	
Field Gradient	O	-0.8167	
	B	1.0607	
	O	-0.8167	
Force Constant	f_{OB}	1.6275	$2.534 \times 10^6 \text{ dyn cm}^{-1}$

with that obtained with the BA+P basis for HBO, of $f_{OB} = 1.564 \times 10^6$ dyn cm⁻¹, and is for a longer bond - being 2.3282 bohr for this species, with that in HBO being 2.2284 bohr.

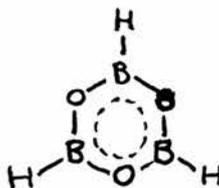
Section VIII: The HBO Molecule

Introduction

Ab initio calculations have been carried out to give a near Hartree-Fock wave function for the ground state of this species. Some of the results of this work have been published¹²⁷. Further investigations of this species have been made using configuration interaction.

The work on the ground state was prompted by a report by Porter and Lory¹⁰¹. After photolysis of $H_2B_2O_3$, and using matrix isolation techniques, Infra-Red spectroscopy suggested the presence of a linear species to which they assigned the structure, H-B-O. This species is normally of only transient existence, the trimer, boroxine, forming readily.

Boroxine:



The anion, HBO^- , has been the part subject of an Unrestricted Hartree-Fock study by Claxton²⁷. This calculation followed the reported observation, by electron spin resonance spectroscopy, of HBO^- . This species was discovered to be bent¹²¹.

As for the other species considered in this work, basis sets of increasing size were used in the investigation of the ground state wave function. The total energy was minimised with respect to the two bond lengths for:

- 1) minimal basis set;
- 2) DZ+P basis set;
- 3) 'nominal' BA+P basis set;
- 4) BA+P basis set.

The energies and geometries are given in TABLE VIII.1. The DZ exponents were obtained from Clementi's tables²⁸, the two BA bases from the tables of McLean and Yoshimine⁷⁴. The functions on hydrogen, including polarisation functions, were taken from the latter's calculation on HCN. Polarisation functions for boron were taken from their calculation on BF, and, for oxygen, on CO.

The DZ+P basis gives an energy lowering of 0.37212 hartree for the molecular species over the isolated atoms. The atomic energies for boron and oxygen are from Clementi²⁸. For hydrogen, the energy, of -0.49999 hartree was obtained by using the ATSCF programme¹⁰³. Using this value for the energy of the hydrogen atom, and the values for the other two atoms given in the tables of McLean and Yoshimine⁷⁴, the binding energies were obtained as shown in Table VIII.1. It is noted that use of the 'nominal' basis gave an energy poorer than that obtained with the DZ+P basis.

The 'nominal' basis is reported by Bagus, Gilbert, and Roothaan¹⁸. It is intended to be of similar quality as the DZ basis. It is a larger basis than the DZ basis, with four s type and six p type functions per atom, as against four s type and four p type for DZ. Bagus et al indicate that the 'nominal' basis should give a better molecular energy than the DZ basis. This is not to claim that this larger basis will give a near Hartree-Fock wave function. For the boron atom, the energy

TABLE VIII.1Optimum Energies and Bond Lengths for HBO Ground State

Basis	Bond Lengths		Total	Virial	Energy
	H-B	B-O	Energy	Coef.	Diff.
Minimal	2.2792	2.2914	-99.80883	-2.00955	
DZ+P	2.228	2.225	-100.20418	-2.00018	0.37212
'nominal'+P	2.178	2.256	-100.20126	-2.00013	0.36312
BA+P	2.1913	2.2284	-100.20870	-1.99986	0.37027

(Last column gives; the difference in energy between the sum of the atomic energies, and the molecular energy.)

is poorer than DZ by 0.000033 hartree. In the calculations of the molecular energy of HBO, the energy as calculated with the 'nominal' +P basis is poorer than that obtained using the DZ+P basis, by 0.00292 hartree.

In view of this result, in the calculations for the other species forming the subject of this work, the 'nominal' basis was not used. Calculations with basis sets larger than DZ+P were performed using the BA+P basis set.

The BA+P basis giving a near Hartree-Fock wave function^{74,76}, the energy difference between the molecular energy and the sum of the atomic energies should be within 0.005 hartree of the Hartree-Fock dissociation energy. For HBO, this was calculated to be 0.37027 hartree.

Bonding

For consideration of the molecular bonding in the species, a summary of the population analysis results are given in TABLE VIII.2. The two lowest orbitals are 'core' orbitals: $1s^2$ on oxygen and boron respectively. The other orbitals form the valence molecular orbitals of the set: 3σ is the boron to oxygen σ bond, s on oxygen, sp on boron; 4σ is the hydrogen to boron bond, s character on hydrogen, sp on boron; 5σ is a lone pair, predominantly of p character, on oxygen. The π orbital is a boron to oxygen π bond. The total populations on the system suggest a dipole directed towards the oxygen atom.

Considering the contribution of the polarisation functions, for core orbitals and for the σ molecular orbitals, population density on them is small to be negligible. For the π orbital,

TABLE VIII.2Summary of Population Analysis, for Species indicated

Values Calculated with the BA+P Basis

HBO Ground State

Orbital	Centre		
	H	B	O
$3\sigma^2$	0.013	0.326	1.661
$4\sigma^2$	0.798	0.759	0.443
$5\sigma^2$	0.280	0.350	1.370
$1\pi^4$	-0.023	0.737	3.287
Σ	1.070	4.167	8.763

TABLE VIII.2 (continued)

HBO ⁻			
Orbital	Centre		
	H	B	O
3σ ²	0.013	0.326	1.661
4σ ²	0.795	0.759	0.446
5σ ²	0.282	0.352	1.366
1π ⁴	-0.023	0.737	3.286
2π ¹	-0.002	1.002	0.0
Σ	1.067	5.171	8.762

HBO ⁺			
Orbital	Centre		
	H	B	O
3σ ²	0.012	0.279	1.709
4σ ²	0.845	1.084	0.076
5σ ²	0.045	0.194	1.761
1π ³	-0.009	0.311	2.698
Σ	0.895	3.864	8.241

however, there is a reduction in population from DZ+P to BA+P bases. The total population contributions over the molecules are:

DZ+P p 3.897; d 0.089; f 0.014

BA+P p 3.953; d 0.034; f 0.013

In the BA basis, there are twice as many p basis functions as there are in the DZ basis. For both bases, the total p population is close. There are the same number of d functions in both basis sets. Yet, for the DZ+P calculation, the d population is more than twice that of the BA+P calculation. This would suggest that electron density is being put into the d functions in the DZ+P calculation to compensate for an insufficient number of p functions in the π -symmetry DZ basis.

At the geometry obtained with the BA+P wave function for the neutral species, SCF calculations for the wave functions for the two monoions were performed. Population analysis gives the two core orbitals as being almost unaltered, reorganisation of charge taking place in the valence orbitals. For the anion, the valence orbitals also remain largely unaltered, the extra electron being accommodated in a bond of π symmetry, localised on the boron centre. The cation shows loss of charge almost uniformly over the whole system, the resultant dipole being very little altered from the neutral parent.

The analysis for the boron centre indicates a high level of electron deficiency, amounting to almost one unit of charge for the neutral species. For the cation, this is increased further, with most of the overall positive charge centred on boron -

there remaining some negative charge excess on the oxygen centre. On adding an electron to the neutral species, the electron deficiency is cancelled, with the overall charge of the molecule being localised on the oxygen centre.

Properties

For the neutral ground state, various properties were calculated for the basis sets used. The calculated expectation values are given in TABLE VIII.3, and the resulting properties in TABLE VIII.4. For comparison, the dipole moments and the forces on the nuclei are given for the two ionic states, as calculated with the BA+P basis. Considering the properties of the BA+P wave function as limiting values, those produced by the minimal basis are a poor approximation, those with the two larger bases are better, the DZ+P recovering most of the difference.

It is seen that the sum of the forces on the nuclei decrease with increase in size of the basis set, and the closeness of the last value to zero indicates that the one-electron properties derived from this wave function should be reliable. Comparison with experiment is possible for the stretching force constants. In evaluation of these, Porter and Lory¹⁰¹ assumed bond lengths of: H-B 2.23 bohr; and, B-O 2.27 bohr. The latter value they took from the bond length of the diatomic species, BO. The values they obtained for the two stretching force constants were;

$$f_{\text{HB}} = 4.27 \times 10^5 \text{ dyn cm}^{-1}$$

$$f_{\text{BO}} = 13.86 \times 10^6 \text{ dyn cm}^{-1}$$

From Table VIII.4 it is seen that all the bases used give values

TABLE VIII. 3Expectation Values for the Quoted Operators

Values Calculated with the Minimal Basis

Property	Centre		
	H	B	O
z	48.628	16.719	-15.361
z^2	206.15	57.209	54.096
e^2	16.198	16.198	16.198
z/r^3	1.2807	1.3069	-0.6762
$(3z^2 - r^2)/r^5$	0.3790	0.7608	0.6101

Values Calculated with the DZ+P Basis

Property	Centre		
	H	B	O
z	47.961	16.7690	-14.3810
z^2	199.41	55.1919	49.879
r^2	215.69	71.473	66.160
e^2	16.281	16.281	16.281
z/r^3	1.4309	1.4252	-1.0348
$(3z^2 - r^2)/r^5$	0.4435	1.0545	0.8289

TABLE VIII.3 (continued)

Values Calculated with the Nominal Basis

Property	Centre		
	H	B	O
z	47.6201	17.1281	-14.4559
z^2	197.38	56.3598	50.331
p^2	16.046	16.046	16.046
z/r^3	1.4602	1.3485	-1.0498
$(3z^2 - r^2)/r^5$	0.4557	1.0419	-1.6466

Values Calculated with the BA+P Basis

Property	Centre		
	H	B	O
z	47.597	16.919	-14.279
z^2	196.88	55.500	49.616
r^2	231.00	71.622	65.738
p^2	16.122	16.122	16.122
z/r^3	1.4512	1.3909	-1.0755
$(3z^2 - r^2)/r^5$	0.45438	1.0569	0.82471

HBO⁻

z	49.768	16.898	-16.528
z/r^3	1.4511	1.3908	-1.0755

HBO⁺

z	44.247	15.760	-13.209
z/r^3	1.4502	1.3647	-1.0558

TABLE VIII.4Properties for HBO Species

Values Calculated with the Minimal Basis

Property		Atomic Units	C.G.S.Units
Dipole Moment		-0.6671	-1.6954 Debye
Quadrupole Moment		-0.2210	-0.2972 barn
Force on Nucleii	H	-0.0648	
	B	-0.1213	
	O	2.5918	
	Σ	2.4058	
Field Gradient	H	0.6331	
	B	0.4001	
	O	-1.4623	
^2H Quadrupole Coupling Constant		0.6191×10^{-10}	407.3 kHz
Force Constants	f_{HB}	0.16891	2.63×10^5 dyn cm $^{-1}$
	f_{BO}	10.571	16.46×10^6 dyn cm $^{-1}$

TABLE VIII.4 (continued)

Values Calculated with the DZ+P Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		-1.1970	-3.0421 Debye
Quadrupole Moment		0.4875	0.6557 barn
Force on Nucleii	H	0.0209	
	B	0.0320	
	O	0.2136	
	Σ	0.2665	
Field Gradients	H	0.6370	
	B	0.2360	
	O	-1.7651	
^2H Quadrupole Coupling Constant		0.6265×10^{-10}	411.9 kHz

TABLE VIII.4 (continued)

Values Calculated with the 'nominal'+P Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		-1.2581	-3.198 Debye
Quadrupole Moment		0.2796	0.3760 barn
Force on Nuclei	H	-0.0007	
	B	-0.0627	
	O	-0.1324	
	Σ	0.1958	
Field Gradient	H	0.6958	
	B	0.1580	
	O	-1.6466	
^2H Quadrupole Coupling Constant		0.6803×10^{-10}	447.6 kHz
Force Constants	f_{HB}	0.2633	$4.10 \times 10^5 \text{ dyn cm}^{-1}$
	f_{BO}	9.1522	$14.25 \times 10^6 \text{ dyn cm}^{-1}$

TABLE VIII.4 (continued)

Values as Calculated with the BA+P Basis

Property		Atomic Units	C.G.S. Units
Dipole Moment		-1.2831	-3.2612 Debye
Quadrupole Moment		0.2646	0.3559 barn
Force on Nuclei	H	0.0134	
	B	-0.0119	
	O	-0.0190	
	Σ	-0.0275	
Field Gradients	H	0.6726	
	B	0.4311	
	O	-1.7505	
^2H Quadrupole Coupling Constant		0.6576×10^{-10}	432.7 kHz
Force Constants	f_{HB}	0.2760	$4.297 \times 10^5 \text{ dyn cm}^{-1}$
	f_{BO}	10.045	$15.64 \times 10^6 \text{ dyn cm}^{-1}$

TABLE VIII.4 (continued)

Values for the Ions, Calculated with BA+P Basis

Property		Atomic Units	C.G.S. Units
HBO⁻			
Dipole Moment		-0.0246	-0.0626 Debye
Force on Nuclei	H	0.0133	
	B	-0.1196	
	O	-0.0174	
	Σ	-0.1137	
HBO⁺			
Dipole Moment		-1.3616	-3.4649 Debye
Force on Nuclei	H	-0.0006	
	B	-0.1903	
	O	0.0023	
	Σ	-0.1886	

of the same order of magnitude. These values are:

Minimal Basis	$f_{\text{HB}} = 2.63 \times 10^5 \text{ dyn cm}^{-1}$
Nominal Basis	$f_{\text{HB}} = 4.10 \times 10^5 \text{ dyn cm}^{-1}$
BA+P Basis	$f_{\text{HB}} = 4.297 \times 10^5 \text{ dyn cm}^{-1}$;
Minimal Basis	$f_{\text{BO}} = 16.46 \times 10^6 \text{ dyn cm}^{-1}$
Nominal Basis	$f_{\text{BO}} = 14.25 \times 10^6 \text{ dyn cm}^{-1}$
BA+P Basis	$f_{\text{BO}} = 15.64 \times 10^6 \text{ dyn cm}^{-1}$.

For the predictions using the BA+P wave function, both values are predicted as being larger than Porter and Lory's results. The bond lengths they used, however, were only assumed. Their H-B bond length, 2.23 bohr, is close to the value as calculated with the BA+P basis of 2.1913 bohr. The force constants of theoretical calculation and experiment are in close agreement - only 0.63 larger than experiment. Their B-O bond length, 2.27 bohr, as larger than the calculated value of 2.2284 bohr. This would produce a smaller value for the experimentally-derived constant than the theoretically-derived value. Porter and Lory's value is $13.86 \times 10^6 \text{ dyn cm}^{-1}$, compared to the theoretical prediction of $15.64 \times 10^6 \text{ dyn cm}^{-1}$.

Bonding

The molecular orbitals described follow the format suggested by Walsh¹²⁸. This would predict the following:

On bending, the core orbitals should remain at about the same energy, as should the B-O bonding orbital - $3\sigma/3a'$. The two higher molecular orbitals should rise in energy. The π orbital should be resolved into the two molecular orbitals, $1a''$, and $6a'$. Of these, $6a'$ should rise in energy, with $1a''$ remaining much

the same.

Using the POLYCAL programme package, bending of the species can be achieved, with the Slater functions used in this work. With a minimal basis set, the hydrogen atom was bent away from the boron to oxygen axis. The total and molecular orbital energies are given in TABLE VIII.3. It is clear that the three lowest molecular orbitals are remaining at their respective levels. 4σ is slowly dropping in energy as it transforms into $4a'$. 5σ is increasing in energy as it transforms into $5a'$. The resolution of the π orbital into one orbital which remains at the same level, $1a''$, and, another which becomes less bonding, $6a'$, is also clear. Fitting the total energy against angle curve to a quadratic function for these three results gave a predicted minimal angle of 179.9° , supporting the assumption that the HBO molecule is linear. As the energies were obtained with a minimal basis, this is further support that a minimal basis is sufficient to predict the general geometry of a species.

Configuration Interaction Calculations

A limited configuration interaction analysis of the system was attempted, using the programme, POLYCAL, which had been set up on the St. Andrews Computing Laboratory's IBM 360/44 by Dr. Thomson. A minimal basis set was used for the SCF orbital set from which the programme creates the CI matrix, using promotions to virtual orbitals. It is noted from a paper by Allen et al¹⁵, that the contribution to the total correlation energy from a doubly-occupied p orbital is greater than from an s orbital. It is expected that correlation of the ground

TABLE VIII.5Total and Orbital Energies of Bent HBO, with Minimal Basis

Orbital	Angle			Orbital
	180°	170°	160°	
		-0.4923	-0.4901	6a'
1π	-0.4931	-0.4931	-0.4931	1a''
5σ	-0.5680	-0.5677	-0.5667	5a'
4σ	-0.6466	-0.6468	-0.6475	4a'
3σ	-1.3422	-1.3421	-1.3420	3a'
2σ	-7.7012	-7.7012	-7.7010	2a'
1σ	-20.7268	-20.7268	-20.7269	1a'
Total				
Energy	-99.8088	-99.8075	-99.8034	

state of the system with matrix elements containing promotions from those molecular orbitals with large p content will be the most important. Schaefer¹² reports Moser, et al⁵⁴ as finding that, in configuration interaction study of carbon monoxide, and, despite Brillouin's theorem²⁴, single excitation matrix elements are important. It is expected, then, that the configuration interaction description of HBO will contain important contributions from single-excitation components from the π -symmetry boron to oxygen molecular orbital, and from the lone pair on oxygen.

From the work on the single configuration wave function, the minimum basis wave function is deficient in its description of these π -symmetry molecular orbitals, and extension of the description of these orbitals will give an improvement in the wave function. Also, from this reasoning, those excitations from the π -symmetry molecular orbitals should be the most important.

In the configuration interaction investigation that was undertaken, excitation from the core orbitals were assumed to give small contributions to the configuration interaction wave functions and were omitted from the study. This left: the two σ symmetry bonding molecular orbitals - boron to oxygen, hydrogen to boron; the lone pair on oxygen; and, the π -symmetry molecular orbitals to consider. There are two π orbitals, as, in ALCHEMY, the π orbitals are considered as being fully occupied when they have received four electrons - that is, the degeneracy of the two - π_x and π_y - orbitals is

implicit; and, in the POLYCAL programme, this degeneracy is not assumed.

There being eleven basis functions in the set, there are produced eleven molecular orbitals in the single configuration SCF calculation. Of these, seven are occupied in the ground state, the other four being virtual orbitals. The promotions considered were from the upper five molecular orbitals to the four virtual orbitals. Promotions only within symmetry groups being considered. There are 41 possible excitations given by these constraints:

double to double:

each of $3^2, 4^2, 5^2$	to each of $10^2, 11^2$	6 excitations
each of $6^2, 7^2$	to each of $8^2, 9^2$	4 excitations

double to single:

each of $3^2, 4^2, 5^2$	to $10^1/11^1$	3 excitations
each of $6^2, 7^2$	to $8^1/9^1$	2 excitations

twin single promotions:

$3/4, 3/5, 4/5,$	to each of $10^2, 11^2$	6 excitations
$3/4, 3/5, 4/5,$	each to $10^1/11^1$	6 excitations
$6/7$	to each of $8^2, 9^2$	2 excitations
$6/7$	to $8^1/9^1$	2 excitations

single to single promotions:

each of $3, 4, 5,$	to each of $10^1, 11^1$	6 excitations
each of $6, 7$	to each of $8^1, 9^1$	4 excitations

This gives a total of forty-one excitations.

Because of the way the POLYCAL programme permutes its excitations, some of the above promotions are included in others; so, a total of only 38 configurations was requested from the programme for a full consideration of these excitations. The SCF energy at the optimum geometry of the minimum basis calculations of: hydrogen to boron bond length 2.2792 bohr, boron to oxygen bond length 2.2914; was obtained by the POLYCAL programme as -99.80884 hartree. The total energy as calculated with this set of excitations was -99.89978 hartree. The difference in energy is 0.09094 hartree. The combination coefficient for each of the excitations chosen is given in TABLE VIII.6.

The first point to be noted is, that, for this closed shell species, the single configuration wave function is a good approximation. If the coefficient is expressed as a fraction, the ground state function forms 96.6% of the configuration interaction wave function. Apart from this ground state configuration, the three excitations that are most important in the configuration interaction matrix are excitations from the π symmetry molecular orbitals. The most important of these is an excitation to an electronic state with four open shells. Both π molecular orbitals lose one electron and each electron is promoted to a separated virtual orbital. This is an excitation of a similar sort to that which Schaefer¹² reports Das and Wahl³² finding as being important in the configuration interaction matrix of the flourine molecule. The first σ promotion - that is, promotion from a σ symmetry molecular orbital - is from the

TABLE VIII.6Combination Coefficients from the CI Matrix for HBO

Excitation	Coefficient at SCF Minimum Geometry	Coefficient at CI Minimum Geometry
Ground	0.9656	0.9637
6,7 - 9 ¹ / 8 ¹	0.142	-0.404 x 10 ⁻¹
7 ² - 9 ²	-0.122	-0.226 x 10 ⁻¹
6 ² - 8 ²	-0.122	-0.226 x 10 ⁻¹
4 ² - 10 ²	-0.541 x 10 ⁻¹	-0.554 x 10 ⁻¹
6 - 8 ¹	-0.501 x 10 ⁻¹	-0.132 x 10 ⁻¹
7 - 9 ¹	-0.501 x 10 ⁻¹	-0.132 x 10 ⁻¹
4,5 - 11 ¹ / 10 ¹	0.400 x 10 ⁻¹	0.309 x 10 ⁻¹
5 ² - 10 ²	-0.378 x 10 ⁻¹	-0.405 x 10 ⁻¹
6,7 - 8 ¹ / 9 ¹	0.336 x 10 ⁻¹	-0.134 x 10 ⁻¹
4,5 - 10 ²	-0.330 x 10 ⁻¹	0.332 x 10 ⁻¹
4 ² - 10 ¹ / 11 ¹	0.312 x 10 ⁻¹	0.314 x 10 ⁻¹
3 ² - 10 ¹ / 11 ¹	-0.185 x 10 ⁻¹	-0.187 x 10 ⁻¹
5 ² - 11 ²	-0.181 x 10 ⁻¹	-0.196 x 10 ⁻¹
4 ² - 11 ²	-0.175 x 10 ⁻¹	-0.179 x 10 ⁻¹
3,5 - 10 ²	-0.166 x 10 ⁻¹	-0.170 x 10 ⁻¹
3,5 - 11 ¹ / 10 ¹	-0.162 x 10 ⁻¹	0.751 x 10 ⁻¹
7 ² - 8 ²	-0.157 x 10 ⁻¹	-0.118
6 ² - 9 ²	-0.157 x 10 ⁻¹	-0.118

TABLE VIII.6 (continued)

$3^2 - 11^2$	-0.139×10^{-1}	-0.141×10^{-1}
$3,5 - 10^1 / 11^1$	0.136×10^{-1}	-0.208×10^{-1}
$3^2 - 10^2$	-0.134×10^{-1}	-0.134×10^{-1}
$3,5 - 11^2$	-0.133×10^{-1}	-0.141×10^{-1}
$4,5 - 10^1 / 11^1$	-0.112×10^{-1}	-0.311×10^{-1}
$4,5 - 11^2$	-0.101×10^{-1}	0.958×10^{-2}
$5 - 11^1$	0.850×10^{-2}	0.959×10^{-2}
$3,4 - 10^2$	-0.700×10^{-2}	0.715×10^{-2}
$3,4 - 10^1 / 11^1$	0.680×10^{-2}	-0.720×10^{-2}
$5^2 - 10^1 / 11^1$	-0.574×10^{-2}	-0.735×10^{-2}
$5 - 10^1$	0.443×10^{-2}	0.532×10^{-2}
$3,4 - 11^2$	-0.352×10^{-2}	0.382×10^{-2}
$4 - 11^1$	-0.313×10^{-2}	0.308×10^{-2}
$3 - 11^1$	-0.307×10^{-2}	-0.340×10^{-2}
$4 - 10^1$	0.305×10^{-2}	-0.368×10^{-2}
$3,4 - 11^1 / 10^1$	-0.228×10^{-2}	0.250×10^{-2}
$3 - 10^1$	-0.210×10^{-2}	-0.247×10^{-2}
$6 - 9^1$	0.168×10^{-5}	-0.520×10^{-1}
$7 - 8^1$	-0.106×10^{-5}	0.520×10^{-1}
$7^2 - 8^1 / 9^1$	-0.846×10^{-6}	0.367×10^{-1}
$6,7 - 8^2$	0.845×10^{-6}	-0.367×10^{-1}
$6^2 - 8^1 / 9^1$	0.788×10^{-6}	-0.367×10^{-1}
$6,7 - 9^2$	-0.788×10^{-6}	0.367×10^{-1}

fourth σ molecular orbital. This is the hydrogen to boron bond, and the hydrogen possesses no p type atomic functions. The importance of this excitation is presumably in default of the presence of polarisation functions on this centre - the 'polarisation induced configuration mixing' of Milliken⁸⁷. After this excitation, the most important σ excitation is another, giving four singly-occupied orbitals in the species.

Of the first six π excitations, four are such as to give open shell configurations. For the first six σ excitations, only three give open shell configurations. Their coefficients in the combination matrix indicate that they are about half as important as the π excitations. Only the last of these six σ type configurations is a promotion from the third σ molecular orbital - the boron to oxygen bond.

As expected, the major correlation effects are in the highest energy valence orbitals - those orbitals in which p-type atomic functions are present in the single-configuration wave function. However, as the basis set is not of high quality, quantitative deductions are not possible. The assumptions about the most important configurations are, however, supported by the data of Table VIII.6.

It is also clear from Table VIII.6 that some configurations are of negligible importance. Those with combination coefficients of order 10^{-5} and 10^{-6} are certainly so. As all those combination coefficients of order 10^{-2} contribute less than one per cent of the whole matrix, these also were left out of a further configuration interaction calculation. Twenty-two excitations were requested of the programme, giving twenty-

five configurations in the configuration interaction matrix. It would certainly not be expected that the same energetic order would be obtained; but, the same conclusions should be capable of being drawn as for the more complete investigation. The excitations used, the first twenty-five of Table VIII.6, are given in TABLE VIII.7 with the combination coefficients. The SCF energy remaining at -99.80884 hartree, the configuration interaction wave function energy being -99.89928 hartree, the energy difference is now 0.09044 hartree. The energy difference between SCF and the larger configuration interaction expansion being 0.09094 hartree, this new energy difference represents 99.5% of it. This was achieved with the computer programme taking one third of the time for the configuration interaction part of the calculation. This set of configurations was chosen for the ground state; and, the energies calculated for the excited states with this set of excitations are much inferior to those from the larger expansion.

This reduced set of excitations has the same set of π excitations as the first six. All but the last of the first six of the σ excitations are as before. The other excitations are in the same order as for the larger calculation, apart from the placing of the pair of excitations labelled as 4,5 to the twin open set of 10^1 and 11^1 , which are at the end of this subset of excitations, one of them taking the place of the excitation from the third σ symmetry molecular orbital. The order of the rest of the excitations is much the same as in the larger set. Although, in the larger set, all the excitations had combination coefficients in the configuration interaction matrix not less

TABLE VIII.7Combination Coefficients from the Reduced Matrix

Excitation	Coefficient
Ground	0.9660
6,7 - $9^1/8^1$	-0.140
$7^2 - 9^2$	-0.122
$6^2 - 8^2$	-0.122
$4^2 - 10^2$	-0.540×10^{-1}
6 - 8^1	-0.482×10^{-1}
7 - 9^1	-0.482×10^{-1}
7,6 - $9^1/8^1$	0.421×10^{-1}
$5^2 - 10^2$	-0.368×10^{-1}
4,5 - 10^2	-0.332×10^{-1}
$4^2 - 10^1/11^1$	0.309×10^{-1}
4,5 - $10^1/11^1$	0.302×10^{-1}
4,5 - $11^1/10^1$	-0.294×10^{-1}
3,5 - $10^1/11^1$	-0.198×10^{-1}
$3^2 - 10^1/11^1$	-0.187×10^{-1}
$5^2 - 11^2$	-0.179×10^{-1}
$4^2 - 11^2$	-0.176×10^{-1}
3,5 - 10^2	-0.169×10^{-1}
$6^2 - 9^2$	-0.157×10^{-1}
$7^2 - 8^2$	-0.157×10^{-1}

TABLE VIII.7 (continued)

$3^2 - 11^2$	-0.140×10^{-1}
$3^2 - 10^2$	-0.134×10^{-1}
$3,5 - 11^2$	-0.134×10^{-1}
$4,5 - 11^2$	-0.106×10^{-1}
$3,5 - 11^1 / 10^1$	0.693×10^{-2}

than 0.1×10^{-1} , here, the excitation with the smallest coefficient is one giving four resultant open shells, labelled as $3,5 - 11^1/10^1$. The coefficient is 0.69×10^{-2} , in contrast to the previous 0.75×10^{-1} . All the other coefficients are close in value. It is concluded that this small matrix is a good approximation to the larger, giving a close prediction of the total configuration interaction energy. This statement holds for the ground state, and not the excited states.

For a single configuration calculation, the minimal basis gives an energy far from the Hartree-Fock limit. On increasing the size of the basis set, the geometry predicted by the single configuration calculation alters by reduction of bond length. There will be a dependence of the energy predicted with the configuration interaction analysis on geometry, and this should differ from the dependence of the single configuration analysis. The bond lengths were altered in turn, and the optimum geometry was obtained as H-B 2.3133 bohr, B-O 2.3386 bohr. The energy produced at this larger geometry is -99.90096 hartree $- 0.00118$ hartree lower than the energy obtained with the optimum geometry of the single configuration calculation. The gain in energy is not worth the effort of calculation. That the energy is lower would seem to suggest, given the variation theorem, that this is a better wave function. The combination coefficients of this calculation are given as the last column of Table VIII.6. It is seen from the values, that those configurations that had least importance in the former calculations have coefficients increased over several orders of magnitude. This shows that the geometry of the species must be carefully minimised in the single

configuration calculation.

If the difference between the SCF and configuration interaction energies is plotted against the altering bond length, a linear relation is obtained. That is, the correlation energy increases linearly with bond length. Adding this to the energy from the single configuration calculation is bound to give a lower energy at a larger geometry. The variation theorem indicates that, for the same molecular species, a lower energy is a closer approximation to the real energy. This applies to only the lowest member of a particular spectral series; therefore, it cannot be said that the variation theorem indicates that the lower energy configuration interaction wave function is an improvement; that is, a closer approach to the real system.

The geometry obtained is larger than that of the single configuration calculation with BA+P basis. This could be taken as suggesting that the bond lengths predicted by the BA+P basis are too short.

The total energy obtained with the larger configuration interaction matrix is -99.89978 hartree, at the geometry of: H-B 2.2792 bohr; B-O 2.2914 bohr. This energy compares with the energy obtained with the DZ+P basis of -100.20418 hartree. As the lowering from the single configuration SCF energy was 0.09094 hartree for the minimal basis, it should be possible to obtain a wave function beyond the Hartree-Fock limit, which is at an energy not lower than -100.21370 hartree - that is, the -100.20870 hartree optimum energy of the BA+P wave function plus -0.005 hartree - by use of configuration interaction and a double zeta basis set.

Although the DZ basis is larger than the minimal, π symmetry excitations are still going to be important, as the hydrogen basis does not contain any π symmetry functions. In the DZ basis, there are twenty-two atomic functions, giving fifteen virtual orbitals, of which six will have π symmetry. There will, thus, be an even larger set of possible excitations. For reducing the time spent establishing which of these are the most important in the configuration interaction matrix, the calculation could be set with only π excitations considered. As the two symmetries are independent, then this should give those excitations which are most important for that symmetry.

As the basis is more complete, there should be less interaction from the excited configurations for the set of σ molecular orbitals. The importance of excitations from 3σ should be reduced, although this would not be of much assistance in deciding which excitations to omit.

It was noted in the chapter on molecular properties that Green had performed a set of configuration interaction calculations on the closed shell species, $\text{CS}^{51,52}$. As there is an experimental dipole moment known for this species, reliable estimates of the level of computation required for prediction of the dipole moment can be made. He estimated that the limiting restricted Hartree-Fock wave function gives a dipole accurate to the order of 10^{-1} Debye. To obtain improved accuracy, addition of configuration interaction is required, and he gives the estimated accuracy with the configuration interaction wave function of the order of 10^{-2} Debye.

In choosing the particular excitations to be included in the

configuration interaction matrix, Green ignored excitations from the core orbitals - as has been done for the species considered in this section. This gave slight over-correction to the value of the dipole moment. The values taken from the paper by Green⁵² are:

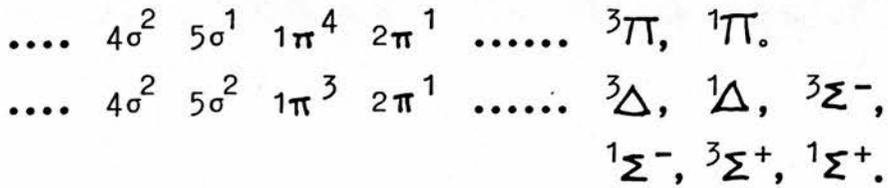
SCF	1.56 Debye
Fixed Core	2.095 Debye
Free Core	2.03 Debye
Experiment	1.97 Debye

The wave function referred to as 'free core' included excitations from the core orbitals.

For the species, HBO, the starting function for the configuration interaction matrix was not the Hartree-Fock limiting function, but an inferior function. The addition of configuration interaction would then take the predicted dipole moment only towards a prediction of an experimental value. For a DZ+CI function, with the dipole for the single configuration function being of the order of the limiting restricted Hartree-Fock value, that wave function should give a good prediction of the experimental value.

Green^{51,52} confirms that, despite first assumptions from Brillouin's theorem²⁴, single excitations are important in the molecular wave function matrix.

Schaefer et al¹⁰⁹ have produced wave functions for some excited states of HCN. This species is isoelectronic with HBO. Their method of performing the ab initio calculations is not straightforward, as they use a form of configuration interaction to estimate the energies of these states. The excited states they considered were of the forms:



Some of these states Schaefer et al predict as being bent, but they do claim that predictions from the Walsh diagrams for these states are qualitatively correct. Such excited states for HBO would be subject to the same Walsh rules, and it would be interesting to discover if they too agreed.

CHAPTER 5CONCLUDING DISCUSSIONIntroduction

With less than the BA+P basis set, wave functions are far from the Hartree-Fock limit. The molecular one electron properties calculated with the various bases differ quite widely - as each basis set produces different optimum bond lengths, differences are bound to occur. It is known, however, that, when an exact Hartree-Fock wave function is used to calculate one electron properties of a species, correlation effects will cause only a second order error in the expectation values¹²⁴. The near Hartree-Fock wave functions calculated in this work should, then, give values for the molecular properties of the species that are close to experimental values.

The other source of error that will give deviation from experiment is the effect of vibrational averaging. In a paper by Stevens et al¹²⁵ on the properties of the ammonia molecule, molecular one electron properties were derived at the equilibrium geometry for a near Hartree-Fock wave function. These values were corrected to give values for the first two vibrational states. The results indicate that the error is of the order of a few per cent only - for the dipole moment they obtain an alteration of approximately 5%, and this is the largest change. Such alterations of the properties from the near Hartree-Fock values are not sufficiently large to significantly reduce the usefulness of the values calculated in the present work.

Comparison of the Properties of the Species

It has been seen that the excitation energies for isomeric species are similar; but isomers of different symmetry do give different properties - as in the $C_{\infty v}$ and $D_{\infty h}$ isomers, NNC and NCN. For species that are merely isoelectronic, as OBO and NCO, there is less correspondence in value between properties. The consistent general bonding pattern has been noted for all the first row species - which is expected.

For second row species, PCC, SCC, SCN, there is some similarity in properties between all three - the force constants, dipole and quadrupole moments are of the same order of magnitude. Those of PCC and SCN are more similar to each other than to SCC:

	PCC	SCN	SCC
Dipole Moment	-3.87	-3.05	-2.42
Quadrupole Moment	-7.21	-6.42	-4.27

This is assignable to the similarity of the open shell; in PCC this is $3\pi^1$, in SCN $3\pi^3$, with SCC $3\pi^2$.

Basis Set Conclusions

Molecular one electron properties for the species HBO and NC were calculated from wave functions with various bases. The values for the properties thus obtained were compared with those from the near Hartree-Fock function for each species. It was seen that properties calculated with a minimal basis are far from the Near Hartree-Fock values, and must be useless for predictive use. With NC and a DZ basis, the properties still differ from the limit by a substantial margin. Adding polarization functions, however,

produces a set of properties much closer to the near Hartree-Fock values. The agreement is to better than an order of magnitude for each property, apart from the dipole and the vibrational force constant. The precise value of the latter is dependent on the precise value of the total energy at each geometry; and, the dipole is always a difficult property to predict - the CO problem is reviewed by Schaefer²¹.

In the section on the species HBO, properties as calculated with the DZ+P basis are closer to the near Hartree-Fock values; and, even the dipole, at -3.0 D is comparable, to -3.3 D. For the triatomic system, the DZ+P basis is an even better approximation to the near Hartree-Fock system than for the diatomic system. Also for the species, PC, several bases were used, with the DZ+P basis again predicting properties close to the near Hartree-Fock values.

For a single configuration wave function, a DZ+P basis gives a set of molecular properties close to those of a near Hartree-Fock function. It has been suggested that the BA+P basis optimises at bond lengths shorter than experimental. This will affect values of properties predicted by virtue of different contributions of nuclear electrostatic terms at least.

For a description of the system that is going to give predictions closer to experimental than the single configuration function with the DZ+P basis, then the use of a configuration interaction function is necessary. A CI description using a DZ basis should introduce correlation effects into the system.

It has been seen that molecular properties depend chiefly on the open shell orbitals. The 'core' orbitals remain virtually unchanged from ground to excited states or to ions. The quality

of the description of these open shell orbitals determines the values of the properties.

Comments on the Computer Programme

The programme ALCHEMY was adapted to fit on the 360/44 by division into integral and SCF programmes. All routines in the programmes pass large numbers of parameters as arguments. If this is done by address as opposed to value, large increases in speed are possible. Experimentation indicated that implementation of this would increase the speed of the integral programme by perhaps more than an order of magnitude. Integrals are evaluated by quadrature, the appropriate networks of points over which this is done being set by initialising the quadrature routine. As the same routine is used for more than one type of integral, altering the passing of arguments is non trivial - duplicate quadrature routines would have to be supplied. This would involve some reprogramming, during which the Overlay structure of the programme could be improved.

The other disadvantage of the ALCHEMY integral package is non-provision of a facility for stopping an integral run and picking up in another job at the same point. Implementation of this would require further programming additions.

An improvement in the speed of the SCF programme by altering the passing of arguments would be useful; but, the main difficulty encountered was non-convergence by failure of the normalization processing. This became more troublesome as basis size increased. A method is suggested for improving the chance of success. It is noted that the molecular orbitals form into two groups - 'core' and 'valence' orbitals. The core orbitals have the characteristic

of having density in one atomic orbital of one centre - for $C_{\sigma v}$, the rest of the elements of the vector being almost zero. If, for terms involving these small elements, the routines are directed to omit any calculation, then the size of the problem has been reduced. This reduction in the number of terms to be normalized should improve the chance of this being successfully accomplished, particularly if the normalization threshold is relaxed for the first attempt.

If the vector set is maintained in this form - a 'frozen core' with free valence orbitals, - and the routines that control the SCF iterations are directed not to alter any of the coefficients of these core orbitals during the run, the amount of computation to be done will be reduced. Taking the example of the first row triatomics, this would reduce the number of vectors to be varied in the σ block from seven to four. For the species containing second row elements, the number of valence orbitals is the same, there being four extra core orbitals for each second row atom present. The reduction in the size of the SCF problem would be substantial.

The use of the frozen core orbitals could be continued to reduce the divergence threshold part of the way towards the converged condition. The iterative procedure could then be switched to include all the orbitals. As the small elements of the core orbital vectors are small, the change to full iteration would not be expected to create much difficulty, although the normalization condition might have again to be relaxed for the first attempt.

CONCLUSION

Near Hartree-Fock wave functions have been obtained for the ground states of several linear triatomics. Single configuration wave functions for several excited states have been produced using the same basis sets. Values for one electron properties have been calculated for all species. It has been indicated that molecular properties from a DZ+P wave function are not far from the Hartree-Fock limit. For some of the species, wave functions with this basis have been produced.

Some indications of the properties and bonding in systems including elements of the second row of the Periodic Table have been made. Again, the use of the DZ+P basis would seem to give an adequate approximation for the single configuration result. To obtain an accuracy greater than this, there must be a large increase in the size of the basis.

As any piece of work is never finished, suggestions on how a DZ CI investigation of the ground state of the species HBO could be undertaken, based on the minimal basis CI results are made.

Some suggestions for improving the computer programmes are made.

The overall conclusion must be that for open-shell species; and, in particular, for excited states, the single-configuration wave function is an inadequate approximation, and a form of multi-configuration is essential. For species where a single configuration wave function is a good approximation - that is, for ground states and closed shell ground states in particular - electronic well properties as well as molecular geometry are predicted/if a DZ+P basis set is chosen.

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APPENDIX IConversion Factors from Atomic Units to C.G.S. Units

Dipole Moment	1 AU = 2.54158	Debye
Quadrupole Moment	1 AU = 1.3449	barn
Distance(bohr)	1 AU = 0.529167	Ångstrom
Energy(hartree)	1 AU = 27.2107	eV
	= 2.1947462 x 10 ⁵ cm ⁻¹	
Quadrupole Coupling		
Constant	1 AU = 6.5797 x 10 ⁹	MHz
Force	1 AU = 1.5568 x 10 ⁶	dyn cm ⁻¹

These values are from McLean and Yoshimine⁷⁷.

APPENDIX IIThe Born-Oppenheimer Approximation

The approximation was proposed by Born and Oppenheimer in 1927²². The following notes are based on Slater¹³.

The space dependent Schrödinger wave equation is

$$\left(-\sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_j \frac{\hbar^2}{2m_e} \nabla_j^2 + V(X_i, x_j) \right) \psi(X_i, x_j) = E \psi(X_i, x_j) \quad \dots 1$$

where: X_i are coordinates of nuclei; x_j of electrons; M_i nuclear, m_e electronic masses.

If the positions of the nuclei are fixed - that is, each electronic LCAO MO SCF calculation at a particular geometry - then the following equation can be written:

$$\left(-\sum_j \frac{\hbar^2}{2m_e} \nabla_j^2 + V(X_i, x_j) \right) u(X_i, x_j) = E(X_i) u(X_i, x_j).$$

$E(X_i)$ is now used as a potential energy function to describe the nuclear motion - a Schrödinger equation of the form:

$$\left(-\sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + E(X_i) v(X_i) \right) = E v(X_i) \quad \dots 2$$

The Born-Oppenheimer approximation states that E of equation 2 is a good approximation to the E of equation 1; and,

$$u(X_i, x_j) v(X_i) \quad \dots 3$$

is a good approximation to $\psi(X_i, x_j)$.

This is shown by substituting the identity, 3, in equation 1,

and noting that the error terms are small:

$$\left(- \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_j \frac{\hbar^2}{2m_e} \nabla_j^2 + V(X_i, x_j) \right) u(X_i, x_j) v(X_i) + \sum_i \frac{\hbar^2}{2M_i} \left(2 \frac{\partial u}{\partial X_i} \frac{\partial v}{\partial X_i} + \frac{\partial^2 u}{\partial X_i^2} v \right) = E u(X_i, x_j) v(X_i).$$

In the second term of the error bracket, u depends on the X_i 's as much as it does on the x_j , as it depends on the coordinates of the electrons with respect to whatever positions the nuclei happen to be in; that is, on $(x_j - X_i)$. Hence, $\frac{\partial^2 u}{\partial X_i^2}$ is the same order of magnitude as $\frac{\partial^2 u}{\partial x_j^2}$.

This, multiplied by $\frac{\hbar^2}{2m_e}$ would be of the order of the energy of the electrons - an appreciable fraction of the energy of the system; but, as M_i is thousands of times larger than m_e , these energy terms can be neglected.

As an approximation, uv forms a solution to the problem, and is justified in the use of the electronic energy as a potential function for the nuclei. These elements determine the rate of transitions between different electronic levels.

POST SCRIPTUM

"The Hartree-Fock approximation is the last hand-hold for elementary physical intuition before it is forced to work directly in terms of the superposition of wave amplitudes that depend on large numbers of independent variables. It can be argued that any attempt to think in terms of physical models, rather than pure mathematics, past this point, is **necessarily deceptive.**" - R.K. Nesbet⁹⁵.

"Now, here, you see, it takes all the running you can do, to keep in the same place. If you want to get somewhere else, you must run at least twice as fast ..." - The Red Queen, 'Through the Looking Glass', L. Carroll.