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Commentationes

Non-Empirical LCAO-MO-SCF-CI Calculations on Organic Molecules with Gaussian Type Functions

Part I. Introductory Review and Mathematical Formalism*

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This paper (Part I) describes the theoretical and computational bases of some non-empirical calculations on small organic molecules to be reported in later papers (Parts II et seq).

Approximate solutions for the usual fixed nucleus electronic Hamiltonian, in the term of wave functions composed of Slater determinants, are discussed, with particular emphasis on their computational utility. Possible choices of basis functions, from which to form the determinants are examined, and the advantages of Gaussian type functions (GTF) centered on the component atoms are pointed out. Some of the properties of molecules which can be calculated using such approximate wave functions are outlined. Finally an attempt is made to discuss the current limitations of non-empirical calculations of the type described here, and some guesses are made about their future.

Brief outlines as a set of appendices are given of the mathematical formalism and computational details of the calculations.

Cet article (1ère partie) décrit les fondements théoriques et pratiques de quelques calculs non semi-empiriques sur de petites molécules organiques qui seront exposés dans des articles ultérieurs (2è partie et suivantes).

On s'y intéresse, dans l'hypothèse adiabatique, à des solutions approchées utilisant des déterminants de Slater, en insistant particulièrement sur l'utilité, pour les calculs, d'une telle approximation. Des choix possibles de fonctions de base utilisables pour la constitution des déterminants sont examinés et les avantages de fonctions du type gaussien (GTF) centrées sur les atomes sont soulignés. On donne un aperçu des propriétés moléculaires calculables à l'aide de ces fonctions d'onde approchées. Enfin une tentative est faite pour discuter des limites habituelles des calculs non semi-empiriques du type de ceux décrits ici, et certaines prédictions concernant leur avenir sont effectuées.

Le formalisme mathématique et les détails de calcul sont esquissés brièvement dans une série d'appendices.

Diese Arbeit (Teil I) beschreibt die theoretischen und rechentechnischen Grundlagen einiger nicht-empirischer Rechnungen an kleinen organischen Molekülen, über die in späteren Arbeiten berichtet wird (Teil II und folgende).

Im Rahmen der Born-Oppenheimer-Näherung werden aus Slaterdeterminanten zusammengesetzte Näherungslösungen im Hinblick auf ihre rechentechnische Nützlichkeit diskutiert. Es wird geprüft, welche Wahl von Basisfunktionen zum Aufbau von Slaterdeterminanten nützlich ist, und die Vorteile der Gaußfunktionen dargelegt. Es wird ein Überblick über die

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Moleküleigenschaften gegeben, die mit diesen Funktionen berechnet werden können. Schließlich wird der Versuch unternommen, die gegenwärtigen Grenzen der nicht-empirischen Rechnungen der beschriebenen Art zu diskutieren, und es werden Vermutungen über die Zukunft geäußert.

Ein kurzer Auszug aus dem mathematischen Formalismus und rechentechnischen Details wird im Anhang gegeben.

1. Introduction

It has been the desire of organic chemists for the last 100 years to establish correlations between molecular structure and chemical behaviour. Such correlations became possible in principle in the late 1920's with the discovery of wave mechanics and a fuller realization of the role that the electron played in chemical binding. Practical use of the discovery, however, for organic compounds is only just becoming feasible. With the development of fast automatic digital computers, the prospects for non-empirical calculations on small and medium sized molecules seems now, rather promising. In this series of papers some calculations on such systems are reported in an attempt to find how far we can get with the present generation of computers.

This first part of the present series is intended to serve four purposes.

(1) In a "Theoretical Discussion" (Section 2) the basic ideas of non-empirical molecular quantum mechanical calculations are reviewed with particular reference to the present approach.

(2) The "Computational Discussion" (Section 3) indicates the problems of implementing this approach, and the methods adopted for its solution.

(3) In Section 4 some results of the present approach on very simple systems are presented, together with a discussion of the accuracy and potential of the methods discussed.

(4) In a set of "Appendices" (Section 5) the detailed mathematical formalism needed in later papers is provided, and some of the computational details are discussed.

2. Theoretical Discussion

The fundamental problem with which we are concerned is that of obtaining a solution of the Schrödinger equation for electronic motion in the field of fixed nuclei:

$$\mathscr{H}\,\Psi_e = E_e\,\Psi_e \tag{1}$$

where $\mathscr{H}$ is the usual Hamiltonian operator, which is (in Hartree atomic units):

$$\mathscr{H} = \sum_i \left[-\tfrac{1}{2}\nabla^2(i) + V(i)\right] + \sum_{i>j}\frac{1}{r_{ij}} \equiv \sum_i h(i) + \sum_{i>j}\frac{1}{r_{ij}} \tag{2}$$

the sums extending over all electrons. E_e is the electronic energy of the system, and Ψ_e is the electronic wavefunction, which must be antisymmetric with respect to interchange of the coordinates of any two electrons. There is at present no method of obtaining an exact solution Ψ_e for many electron systems, and some approximation is necessary.

The most powerful method of finding an approximate solution of (1) is by use of the Variation Principle, which states that any approximate solution Ψ is such that the quantity

$$E = \frac{\int \Psi^* \mathscr{H} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} \tag{3}$$

where integration is over all space and spin coordinate of the electrons, will be not less than E_e, and will only be equal to E_e if Ψ is the exact solution. The problem that we attempt to solve is thus that of choosing Ψ to minimize E. The computed value E will generally be used as a criterion of accuracy for the wave function but other criteria (eg. dipole moment) could equally well be used.

2.1 Many Determinantal or Polydetor (Valence Bond and Configuration Interaction) Wave Functions

The requirement that Ψ be antisymmetric makes it possible to expand Ψ without loss of generality as a linear combination of functions Φ_p which are themselves antisymmetric:

$$\Psi = \sum_p c_p \Phi_p \, . \tag{4}$$

The state Ψ to be investigated belongs to an irreducible representation of the space and spin symmetry group of the molecule, and so we may restrict consideration to those Φ_p which belong to such a representation. Boys and Cook [7] refer to a Ψ of form (4) as a poly-detor wave function and to the individual Φ_p's as co-detors. These Φ_p's can be considered to be simple linear combinations of detors, i.e. the usual Slater determinants (5) as shown for an N electron problem; in detail:

$$(N!)^{-1/2} \begin{vmatrix} \phi_{p1}(1)\, w_{p1}(1) & \phi_{p2}(1)\, w_{p2}(1) & \cdots & \phi_{pN}(1)\, w_{pN}(1) \\ \phi_{p1}(2)\, w_{p1}(2) & \phi_{p2}(2)\, w_{p2}(2) & \cdots & \phi_{pN}(2)\, w_{pN}(2) \\ \vdots & \vdots & & \\ \phi_{p1}(N)\, w_{p1}(N) & \phi_{p2}(N)\, w_{p2}(N) & \cdots & \phi_{pN}(N)\, w_{pN}(N) \end{vmatrix} \tag{5}$$

Or in an abbreviated form:

$$(N!)^{-1/2} \det \left| \phi_{p1}(1)\, w_{p1}(1) \quad \phi_{p2}(2)\, w_{p2}(2) \cdots \phi_{pN}(N)\, w_{pN}(N) \right| .$$

The functions $\phi_r(i)$ and $w_r(i)$ are functions of the spatial and spin coordinates respectively of a single electron i. It can be shown that if the functions ϕ_r form a mathematically complete set of one-electron functions, the set of all determinants which can be formed from them is also complete, so in principle, at least, a polydetor wave function can be made to approximate the exact solution to any required degree of accuracy.

Substitution of (4) into (3) transforms the minimization of E into the solution of the secular equation

$$\sum_p c_p \left(H_{pq} - E\, S_{pq}\right) = 0 \qquad q = 1, 2 \ldots \tag{6}$$

where

$$H_{pq} = \int \Phi_p^* \mathscr{H} \Phi_q \, d\tau \tag{7}$$

$$S_{pq} = \int \Phi_p^* \Phi_q \, d\tau \tag{8}$$

integration being over all electronic coordinates.

It should be noted that the great majority of calculations on molecular systems have been performed using wave functions of the form described above, or wave functions which could easily be put in this form. The seemingly great differences between many calculations are merely due to different choices of the functions ϕ_r and Φ_p. This choice arises because in practice it has been found impossible to use anything like a complete set of functions for ϕ_r. Even with an incomplete set of ϕ_r, the number of Φ_p can still be very large.

In the *Valence Bond* (VB) method, the ϕ_r are chosen to be functions centered on the various atoms (atomic orbitals: AO's). The co-detors Φ_p are formed from spin eigenfunctions called structures, which correspond to possible allocations of the electrons to these AO's. The early calculations on H_2 by HEITLER and LONDON [*22*] exemplify well the valence bond approach. Its application to more complicated molecules is discussed by EYRING et al. [*14*] as well as by recent textbooks [*15*, *44*].

After a number of early successes the method was very little used in a priori calculations. This was largely due to the fact that the non-orthogonality of the orbitals on the different centres made such calculations on large systems extremely difficult. Recently, however, there have been attempts to rehabilitate the method [*28*, *29*].

In the method of *Configuration Interaction* (CI) the ϕ_r are allowed to be many-centre functions. This freedom in the ϕ_r allows them to be orthogonal, simplifying the formulae for the matrix elements between the Φ_p's. By a careful choice of the ϕ_r, the expansion can usually be made in such a way that a single co-detor predominates, and that co-detor alone provides a reasonable and simple approximation to the correct wave function. This may be achieved as follows. A single co-detor wave function is constructed in which the ϕ_r are considered to be variable functions. The energy of this wave function is then minimized with respect to variations in the ϕ_r. In practice this minimization is effected by a self-consistent field (SCF) procedure and the resulting ϕ_r's are called *self-consistent field molecular* orbitals (SCF–MO's).

It is usually found also, that the number of effective Φ_p which can be formed from the SCF–MO's is much smaller than the total number of Φ_p possible. Only these co-detors which differ from the dominant co-detor by less than three orbitals play an important part in the expansion (4). In the ensuing work we shall consider only such a limited set of co-detors and refer to this method as self-consistent field configuration interaction (SCF–CI). The co-detors Φ_p are called configurations because they may be considered as approximate single co-detor wave functions for the appropriate excited states of the molecule.

In actual calculations on molecules it has not yet proved possible to determine the SCF–MO's exactly, in a manner analogous to that used in determining SCF atomic orbitals. Instead the ϕ_r are expressed as linear combinations of a set of basic functions η_i $(i = 1, N)$:

$$\phi_r = \sum_{i=1}^{N} Y_{ri}\, \eta_i \tag{9}$$

and the coefficients Y_{ri} are considered to be the variables in the SCF procedure. As the basis functions most often used are atomic orbitals, the method is called the linear combination of atomic orbitals (LCAO) MO–SCF method.

In both approaches the constructed many-determined wave functions are used as approximations to the exact electronic wave function Ψ_e. It seems to be fair to say as a comment on the success of these attempts that in most cases VB provides lower total energy values for the molecule (and in a sense better wave functions) than a single co-detor (i.e. MO–SCF) but even fairly limited CI is superior to the VB approach [*29, 10*]. However, it should be noted that this is true only because of the various approximations generally made in the two methods and in theory if one includes all possible configurations or structures that can be formed from a given set of atomic orbitals, the CI and VB wave functions will be identical.

The computational simplicity of LCAO–MO–SCF calculations and the ease of interpretation of the results in terms of chemical concepts has made this method very popular [*11, 49*]. Since the LCAO–MO–SCF calculations is essential for CI, the various features of it will be discussed in the next section.

2.2 Single Determinant (Molecular Orbital) Wave Functions

In the hierarchy of molecular wave functions a single configuration (co-detor) is the simplest unit that exhibits the required symmetry properties. In some cases, this co-detor can be chosen to be a single determinant of doubly occupied orbitals

$$\begin{aligned}\Phi_0 &= \frac{1}{\sqrt{(2M)!}} \det \left| \phi_1(1)\,\alpha(1)\,\phi_1(2)\,\beta(2) \ldots \phi_M(2M\text{-}1)\,\alpha(2M\text{-}1)\,\phi_M(2M)\,\beta(2M) \right| \\ &= (\left| \phi_1 \overline{\phi_1} \ldots\ldots\ldots\ldots\ldots \phi_M \overline{\phi_M} \right|) \qquad (10)\end{aligned}$$

where the $2M$ by $2M$ determinant Φ_0, describes $2M$ electrons in M molecular orbitals. A state which can be represented by such a wave-function will be referred to as a closed shell, a definition which includes the intuitive chemical concept of a closed shell state. All other states will be referred to as open shells.

As most molecules have closed shell ground states we shall be largely interested in wave functions like Φ_0. In this section we shall outline the method used for determining the constituent molecular orbitals of such a function, and later [Appendix 5.1 (*ii*)] we shall extend the discussion to some of the cases where the co-detor is composed of more than one Slater determinant.

As mentioned in the previous section, the molecular orbitals ϕ_r are generally expressed as linear combinations of basis functions with variable coefficients. The basis functions are considered fixed and the required molecular orbitals are found by determining the coefficients which minimize the energy of the single co-detor wave function.

In the case of co-detors like Φ_0 ROOTHAAN [*38*] has shown that the coefficients may be determined by a procedure involving the iterative solution of the eigenvalue problem, (which is ideally suited for automatic computation):

$$\boldsymbol{F}\,\boldsymbol{Y}_r^\dagger = \boldsymbol{G}\,\boldsymbol{Y}_r^\dagger\,\varepsilon_r\,. \qquad (11)$$

The scalar quantity ε_r is called the orbital energy of the orbital ϕ_r, and $\boldsymbol{F}$ and $\boldsymbol{G}$ are N by N matrices with elements as defined in Appendix 5.1 (*ii*).

As can be seen the solution of (11) will yield N new vectors $\boldsymbol{Y}_r$ each associated with an orbital energy ε_r. There are however only M molecular orbitals involved in Φ_0, and these are usually called the *occupied orbitals* (the remaining N-M being called *unoccupied* or *virtual* orbitals).

If it is desired to represent the ground state (i.e. the state of lowest energy) of a system the occupied molecular orbitals are chosen as those which correspond to the lowest M orbital energies. That this choice is reasonable can be seen from considering the physical significance of the orbital energy. It is the energy that a single electron would posses in the field of the nuclei and all the other electrons.

It should perhaps be noted at this point that if the atomic orbitals (η) form a complete set, the molecular orbitals resulting from it would be the best possible orbitals within the single determinant restriction. The best possible molecular orbitals are referred to as the *Hartree-Fock* molecular orbitals. As is well known it is possible to obtain by numerical methods such orbitals for atoms in singlet states, and recently it has been shown [*40*] that very good approximations to these orbitals can be obtained using the analytic procedure outlined above. The many electron wave function that describes the ground state $(\Psi = \Phi_0)$ which is assembled from Hartree-Fock molecular orbitals is called the Hartree-Fock wave function.

Table 1. *The number of one (p) and two (q) electron integrals associated with various size (N) basis sets*

N Size of Basis Set	Number of Molecular Integrals	
	One-Electron Integrals (p)	Two-Electron Integrals (q)
10	55	4 540
20	210	22 155
30	465	108 345
40	820	336 610
50	1 275	814 725
100	5 050	12 751 250
200	20 100	202 015 050
300	45 150	1 019 261 250

The whole SCF procedure (11) can be made automatic [see Appendix 5.1 (*ii*)], after the atomic orbitals (η) are chosen and the one-electron integrals $(\eta_i \mid \eta_j)$, $(\eta_i \mid h \mid \eta_j)$ and the two-electron integrals $(\eta_i \eta_j \mid \eta_k \eta_l)$ are evaluated. Usually the atomic orbitals are real, so there are at most $p = N(N+1)/2$ distinct integrals of each of the one-electron types and $q = p(p+1)/2$ of the two electron type. Since q varies roughly as the fourth power of N, the number of two-electron integrals rapidly becomes enormous as N increases. To illustrate this difficulty, the number of integrals to be evaluated for various values of N is tabulated in Tab. 1. It is this large number of integrals which is really the limiting factor in molecular orbital calculations.

In the attempt to keep N within manageable limits, much consideration has been given to the form of the basic functions (η). The numerical Hartree-Fock (H.F.) atomic orbitals are perhaps the most obvious choice. However, they are rejected for larger molecules because of the difficulty of calculating integrals over numerically defined quantities. Also, there is no theoretical reason to believe that self-consistent H.F. atomic orbitals would approximate molecular orbitals more accurately than a set of appropriately selected analytic functions.

Up to the present time the nodeless Slater functions have been the most widely used atomic orbitals. Their general form is:

$$\eta = N r^{n-1} e^{-\alpha r} S_{l,m} (\vartheta, \varphi) \tag{12}$$

where n, l, m are quantum numbers ($n = 1, 2, 3, \ldots; l < n; -l \leq m \leq l$), N is a radial normalizing factor, and $S_{lm} (\vartheta, \varphi)$ a normalized spherical harmonic. The radial distance from the centre considered is r and α is the *orbital exponent* (sometimes called the *effective nuclear charge*). The Slater functions are quite similar to the shape of the Hartree-Fock orbitals both near the nucleus and at large distances from it. Consequently linear combinations of very few of them have been shown to approximate the Hartree-Fock orbitals in atoms very closely. They would seem therefore to be ideally suited for composing molecular orbitals, but their use in polyatomic calculations presents a severe difficulty.

As can be seen the two electron integrals $(\eta_i \eta_j \mid \eta_k \eta_l)$ may involve orbitals centred on one, two, three or four different atoms. The one and two centre integrals offered no particular difficulty and there are a number of good methods of evaluating them accurately and quickly [*39, 42, 43*]. The three and four centre integrals do, however, present considerable difficulties and to date only two acceptable methods have been proposed for their evaluation [*2, 46*]. To obtain accurate values by either of these methods involves much complicated calculation. Even with modern computing machinery there are integrals that may take of the order of minutes to evaluate. As three and four centre integrals usually constitute the bulk of the integrals in a polyatomic calculation, the difficulties are obvious.

To combat this difficulty it has been suggested [*5*] that the radial portion r^{n-1} $e^{-\alpha r}$ of the Slater orbital [*15*] be replaced with a gaussian function $r^{2(n-1)}$ $e^{-\alpha r^2}$. This would enable the many centre integrals to be done very easily and quickly. In principle, since the gaussians form a complete set, the exact molecular orbitals may be expressed in term of them. Unfortunately the behaviour of the gaussians near the nucleus and far away from it is incorrect, so many more gaussians than Slater functions are needed to approximate the exact orbitals to the same degree of accuracy. It is possible, however, to evaluate the integrals over gaussian orbitals something like a thousand times as fast as integrals over Slater orbitals, so that provided there is space in the computer to hold all the integrals, it is possible to include enough gaussians to hope for success using them. Furthermore, if numerical accuracy is not the primary object, semi-quantitative results might be obtained with a minimal gaussian basis set for quite large molecules.

2.3 Calculable Properties of Molecules

So far discussion has been limited to methods of obtaining an electronic wave function for a system of electrons and nuclei in the Born-Oppenheimer (fixed nucleus) approximation neglecting relativistic effects. Implicitly only isolated systems have been considered. The next stage is to obtain information about the properties of the system whose wave function has been calculated. In discussing these it is convenient to adopt the classification of them given by BOYS and COOK [*7*]. This classification associates a group of properties with distinct computational stages of what may be called a *complete quantum prediction*.

Boys and Cook consider four types of properties, which they classify as primary, derivative, induced and interaction properties. *Primary properties* can be calculated from the density kernels already obtained. These include, for example dipole moment and electron density in addition to energy. *Derivative properties* can be obtained by performing the calculations again for different nuclear configurations. Examples of derivative properties are force constants. *Primary induced properties,* such as polarizability and refractive index, involve the effect of fields on the system and for their calculation require knowledge of a manifold of excited states. Finally the calculations of *Interaction properties* between systems.

In future papers the main concern will be with certain of the primary and derivative properties and these are discussed in a little more detail here.

a) Primary Properties

The primary properties to be considered are the total energy of a system in its ground and excited states, the molecular binding energy and ionization potentials the one electron densities, and the electric dipole moments.

In the fixed nucleus approximation the total energy of the molecule obtained simply by adding the nuclear repulsion energy to the total electronic energy obtained from the solution of (6) in the CI treatment or from (11) in the SCF treatment. Although the total energy of the system is not a quantity of particular physical or chemical interest, the binding energy defined as the difference between the total molecular energy and the energy of the separated atoms, is. As this is a small quantity formed by the substraction of two very large quantities it is, of course, very sensitive to errors in the latter. It is usual to calculate the electronic energies of the atoms using the same basis set on the free atom as was used in the molecule, in the hope of cancellation of errors by subtraction.

It is possible to calculate the ionization potential of an electron in a molecule by finding the energy of the ion and subtracting the energy of the molecule from it, but here once more it is the small difference between two large quantities. In SCF calculations it is customary to invoke Koopmans' theorem [*25*] which states that an ionization potential is approximately equal to the negative of the appropriate orbital energy.

In performing a configuration interaction calculation, a theorem originally due to MacDonald [*27*] and later extended by Davies [*12*], enables us to say that each of the higher roots resulting from the solution of the secular problem are upper bounds to the energies of the appropriate excited states of the molecule if the ground state conformation is preserved in the excited state. In practice it is found that, the excited state energies calculated from the roots are, in all but the lowest few, rather poor bounds. As the lowest are generally those of greatest interest however this is not such a severe disability. In the SCF approach a wave function consisting of just one of the terms in the CI expansion (single co-detor) is generally chosen to describe an excited state. The total energy of this function is usually a very poor approximation to the energy of the actual state, and is an upper bound only if the excited state co-detor differs from the SCF ground state co-detor by one orbital alone.

Another primary property is the one electron density of the molecule. In theory one can obtain the picture of the molecule that would be obtained by x-ray or electron diffraction methods. In practice one cannot be so accurate, but nevertheless a useful general picture of the disposition of change over the nuclei may quite readily be obtained using the one particle density matrix, and the basis orbitals [Appendix 5.1 (*iii*)]. As these pictures are somewhat cumbersome to use, a rough semi quantitative idea of the electron density distribution in molecule may be obtained by the method of population analysis [*33, 30*]. The actual mechanics of this process are described in Appendix 5.1 (*iv*).

Finally the electric dipole moment, which is defined for electronic states i and j of a molecule as:

$$(\Psi_i \mid \sum_n \alpha_n \mid \Psi_j) = \mu_\alpha^{ij} \tag{13}$$

where α_n is a position co-ordinate (x, y or z) of the n-th electron. This quantity is closely related to the absorption (and transmission) coefficients, and determines the selection rules, for electronic transitions. The α component of the permanent dipole moment of a molecule in state i is

$$\mu_\alpha = \mu_\alpha^{ii} + \sum_n Z_n \alpha_n \tag{14}$$

where Z_n is the charge on the n^α nucleus, and α_n its a co-ordinate.

b) Derivative Properties

The simplest derivative property of interest is the equilibrium conformation of the molecule. This may be determined by performing a series of calculations each for a different conformation of the system until the conformation of lowest total energy has been found.

The force constants for nuclear vibration are found in the present approximation by a similar series of calculations. Here however, the electronic energy of the system is expressed as a function of the nuclear co-ordinates and the force constants obtained from the appropriate derivatives of this function with respect to nuclear displacement co-ordinates [*15*].

3. Computational Discussion

3.1 The Polyatom System

The preceding sections have presented the theory of non-empirical molecular calculations as seen from the authors viewpoint, with some reference to feasibility. The present section presents some details of programs comprising the Polyatom system [*14*], which represents their attempt to implement such calculations on the IBM 709/90/94 computers. First, however, is presented the general philosophy of the system, which differs somewhat from the one usually adopted.

First, the system is designed to be as open-ended as possible. This stems naturally from the fact that the four authours have rather different approaches to the subject, and each would like to be in a position to incorporate his own programs in the system without causing any great inconvenience to the others. This necessitated a division of the system into blocks which could be considered more or less independent. Each block was to be implemented by a separate program, which was to take data from tapes, and parameters from cards, and leave its results on tape, with printed output if required. Thus each calculation would consist of the execution of several programs which could be executed together, or separately if the intermediate tapes were saved. The different configurations of programs which could be required necessitated a rather general scheme for the manipulation of intermediate tapes, which has been reported elsewhere [*17*].

Secondly, generality has often been preferred to efficiency. That is, where there has been a choice between a general-purpose and a special-purpose one, the former has been chosen, even though it may not always operate at maximum efficiency. Some attempt has been made, however, to obtain efficiency when the programs are working at their upper limit.

Thirdly, simplicity has been preferred to efficiency. That is, all except the most basic programs are written in FORTRAN II, and these are heavily subroutinized to preserve readability and versatility. It should be noted that this and the preceding principle have been adopted not because of majestic indifference to the finances of such calculations but because it is generally felt that much work in this field has been duplicated because of unduly specialized programs and excessive pride in writing programs which no-one else can understand. The authors feel that adherence to these principles has resulted in a system of immense potential power, which is at the same time simple to use, and simple to extend. However, as experience of the system has accumulated, the bottlenecks in the calculations have become more pronounced, and it is expected that much useful work could be devoted to stream-lining these portions.

The preparation of these programs has been reported earlier [*3*] and it has been noted that it is essentially the extension of a preliminary system developed by C. M. Reeves, M. C. Harrison and R. Fletcher for a Pegasus computer at Leeds University. The present programs are specified and their functions outlined in Appendix 5.2 (*i*).

3.2 Selection of Gaussian Basis Sets

The choice of the orbital exponents for atomic or molecular calculations has been, until fairly recently, largely a matter of guesswork. The basis was usually the Slater rules for atoms, which gave a rough empiric fit to the optimum values of the exponents for a minimum basis of Slater functions. These values were often used in molecules also, but have been shown [*9*] to give results which are definitely inferior to the optimum values. It is now recognized that careful optimization of parameters can be very useful in improving the results for a given basis size. However, rigorous minimization of a function of many non-linear parameters is a lengthy process, usually requiring much more calculation than the use of a basis set twice as large. Two reasons can be given for the attempt to find optimum parameters. The first is that as basis sets are increased in size, in an attempt to reduce the 'criticalness' of the parameters, problems of linear dependence arise. The second is the hope that there will emerge sufficient regularity in the values for a general set of rules to be formulated.

A fair amount of work has been done over the years using Slater functions, and there is sufficient evidence to provide at least intuitive estimates of parameter values, and possible accuracy of these wave functions. For Gaussian functions this was quite lacking until rather recently, when it appeared that bases of between two and three times the size of a Slater basis would give comparable energies. The larger basis size implies a more difficult optimization problem, but also suggests that the solution may not be quite as critical as for STO's. Fairly systematic investigations have been made by REEVES [*35*], and REEVES and HARRISON [*36*] using small basis sets, in which scaling and minimization of overlap are used to simplify the optimization. KRAUSS [*25*] also follows the scaling hypothesis, while ALLEN [*1*] suggested a least square fitting to the atomic Hartree-Fock orbitals. Recent results by HUZINAGA [*23*] give optimum values of exponents for the atoms up to Ne, and these will be undoubtedly very valuable in future work. The work reported in later papers in the present series was started before HUZINAGA obtained his results, and a cruder optimization procedure was used. This procedure, together with extrapolated values for the atoms required in further papers, is given in Appendix 5.2 (ii).

4. Some Simple Examples and Remarks

Here the results of previous calculations on some systems using the methods outlined above, are reviewed and some new calculations are presented to provide a background for future work. The systems discussed are chosen not so much because of their chemical interest as because they examplify aspects of the present method rather well, and many other calculations on them are available for comparison.

To give some idea of the sort of accuracy that may be expected using GTF's in the SCF approximation total energies here been calculated for the ^4S state of the N atom. The results are given in Tab. 2 for basis set $3^s + 1^p$, $5^s + 2^p$ and $7^s + 3^p$, together with the energy given by a minimal STO basis and accurate Hartree-Fock orbitals. We see that the minimal STO energy is slightly worse then that given by the $7^s + 3^p$ GTF set.

Further information is available from previously reported calculations on hydrogen fluoride [*20*]. It was found that a $5^s + 2^p$ basis on the F atom gave lower orbital energies then the minimal STO Basis, but higher total energy. A $5^s + 3^p$ basis set on F gave about the same total energy as the minimal STO basis, but in many respects might be expected to give a superior wave function. A $9^s + 5^p$ basis set was within about 0.045 a.u. of the Hartree-Fock energy, slightly better then an STO calculations using half as many functions.

The results of these calculations (A, B, C, D) are summarized in Tab. 3, together with another (E), performed with only 2^s on the hydrogen to see how the calculated properties alter when the hydrogen is more poorly represented. The equilibrium interatomic distance (R_e) and the force constant (k_e) of the stretching motion are also shown in Tab. 3. Graphs of the variation of R_e and k_e obtained from calculations A, B, C, and D are shown in Fig. 1. It is interesting to see that while the energy values (primary properties) vary monotonically with basis set, the derivative properties pass through local minima or maxima before tending to converge.

Calculations on H_2 and H_3^+ [*54*, *55*] and calculations on larger molecules appear to be consistent with these results. KRAUSS' work [*25*] on CH_4 as well as on other molecules [*13*, *26*] and calculations by HARRISON and MOSKOWITZ on OH^-, H_2O and H_3O^+ [*32*] and C_2H_4 [*31*], gave no reason to suspect hidden drawbacks.

However properties which are critically dependent on the shape of the wave function near the nucleus, such as isotropic hyperfine splitting, will have to be carefully investigated.

There is considerably less information available about the effectiveness of CI. Early work using STO's was rather inconclusive. Much of the promising work used AO's instead of MO's (i.e. valence bond calculations) and so the effects of CI were difficult to assess. However recent work on small systems (2, 3 and 4 electrons) gave very accurate results [*41*, *52*]. Many interesting results were obtained by Foster and Boys, and in particular their H_2CO calculation [*16*], in which they used localised MO's for CI.

Table 2. *Orbital exponents (α) used and Total Energies calculated for nitrogen atom (^4S-state) by various methods of investigation*

Method		Hartree-Fock	STO	GTF		
Basis Set	Type	—	$1s + 2s + 2p$	$3^s + 1^p$	$5^s + 2^p$	$7^s + 3^p$
	Size	—	5	6	11	16
Type of Orbital			Orbital Exponents (α)			
s		—	6.66523 (1*s*)	.894	.424	.217
s		—	1.92372 (2*s*)	7.05	2.16	.857
s		—	—	55.8	11.0	3.37
s		—	—	—	55.6	13.3
s		—	—	—	282.	52.5
s		—	—	—	—	206.
s		—	—	—	—	811.
p		—	1.91696 (2*p*)	.550	.363	.257
p		—	—	—	2.13	1.33
p		—	—	—	—	6.89
Method			Total Energy (a.u.)			
SCF		−54.4105[a]	−54.269	−51.0255	−53.9110	−54.2846

[a] The experimental value is −54.61357 a.u. [*21*, *48*].

Only a few calculations using GTF's in CI are available. Reeves Calculations [*35*] on N and NH showed little improvement over the SCF results, but the basis

Table 3. *Calculated Properties of Hydrogen Fluoride with various Gaussian Basis Sets*

Basis Set[a]	No. of GTF	Total SCF Energy (a.u.)			Bond Distance		Force Constant	
		R (a.u.)			R_e[c]	ΔR	k_e[d]	Δk
		1.65	1.75	1.85	(a.u.)	(%)	mdyn/Å	%
A	23	−100.01512	−100.01758	−100.01404	1.7418	+ 0.519	10.1817	+ 5.29
B	17	− 99.39937	− 99.40371	− 99.40163	1.7676	+ 2.01	9.9948	+ 3.36
C	14	− 98.87468	− 98.88383	− 98.88517	1.8172	+ 4.87	12.1563	+25.7
D	12	− 95.36483	− 95.34717	− 95.32455	1.5331	−11.52	16.4753	+70.4
E	11	− 95.34523	− 95.32236	− 95.34916[b]	1.4878	−14.14	16.7662	+73.4

[a] *A* F($9^s + 5^p$) + H($3^s + 1^p$), *B* F($5^s + 3^p$) + H(3^s), *C* F($5^s + 2^p$) + H(3^s), *D* F($3^s + 2^p$) + H(3^s), *E* F($3^s + 2^p$) + H(2^s).

[b] This value was calculated with an interatomic distance of 1.35 a.u.

[c] At the experimental interatomic distance (1.7328 a.u.) the experimental total energy is −100.50278 in contrast to the values obtained by the analytic Hartree-Fock (−100.05754 a.u.) and by minimal Slater basis set (−99.53614) [*20*].

[d] $k_e^{\mathrm{exp}} = 9.67$ mdyn/Å at $R_e^{\mathrm{exp}} = 1.7328$ a.u. [*4*].

sets were obviously inadequate. Similarly inadequate basis sets were used by Reeves and Harrison [*36*] for ammonia, but the results were much more encouraging. CI appeared to provide about half the correlation energy of the three bonds. It also appeared that GTF's might be more effective for CI then STO's.

To supplement this information the results of some calculations on the beryllium atom are given in Tab. 4. In these calculations SCF orbitals were determined for the atom and used to form the basis functions for the CI calculation.

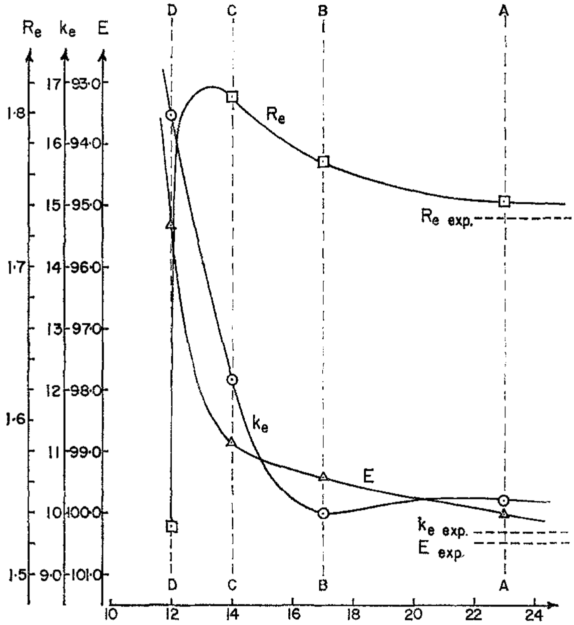

Fig. 1. The variation of calculated primary and derivative properties of hydrogen fluoride with the size of the basis set

The results were obtained using a general set of programs and, in theory, the extension to larger systems is just a matter of inserting different parameters. However, in molecules of any size the number of configurations is likely to be astronomical. For beryllium it was possible to include initially all useful configurations. Clearly a method of selecting the most useful configurations in advance will be essential in any future application. Second-order perturbation theory seems the simplest method and this is currently been used, but this does not overcome the fundamental difficulty of slow convergence with number of configurations. Work is now in progress investigating this feature but much work remains to be done before a realistic assessment of the usefulness of CI can be obtained. However the results for Be are good and could probably be improved with little effort. Less extensive CI calculations on Be_2 and HF are given in Tab. 5 the results being quite

Table 4. *Configuration Interaction* (CI) *calculations on Beryllium Atom*

Basis Set	Number of GTF's	Number of Configurations	Total Energy (a. u.)
$3^s + 2^p$	9	29	−13.80183
$5^s + 3^p$	14	59	−14.53263
$7^s + 5^p$	22	211	−14.63105
Numerical SCF[a]		1	−14.57302
STO-CI[b]		55	−14.66090

[a] Ref. [*29*]. [b] Ref. [*51*].

promising. However the numerical results particularly in the case of HF, indicate (cf. Tab. 5) that CI cannot overcome the shortcomings of the original SCF wave function.

Any discussion of large scale molecular calculations is incomplete without consideration of the practical difficulties of computation. The method of calculating SCF wave functions described above implies a computation time that varies rapidly as the fourth power of the size of the basis set. Experience has suggested that a computer with a cycle time of one or two microseconds can handle a basis set of 60 GTF's in about 10 hours for an SCF calculation. This corresponds to a calculation on ethylene giving a total energy within 0.05 a.u. of the Hartree-Fock limit, or a very rough benzene calculation, a few atomic units away in total energy but possibly of qualitative interest. In order to extend these SCF calculations to naphthalene, for instance, we would require something like 100 to 2000 hours in computer time for the rough and accurate calculations respectively.

Table 5. *Configuration interaction calculations on* HF *and* Be_2 *with limited basis set*

System	Type of Basis	No. of GTF's	SCF Energy (a. u.)	No. of Configurations	CI Energy (a. u.)
HF	2^s and $3^s + 2^p$	11	−95.3452	111	−95.4267
Be_2	$5^s + 3^p$ and $5^s + 3^p$	28	−33.1697	145	−33.2644
Be_2	$5^s + 3^p$ and $5^s + 3^p$	28	−33.1697	889	−33.2978[a]

[a] Estimated by second order perturbation theory.

Estimates of computer time required for additional CI calculations over these SCF calculations are only available for very small systems, but will certainly be much greater then SCF times.

At the moment time it appears that non-empirical calculation over these SCF calculations are only available for very small systems, but will certainly be much greater then SCF times.

At the present time it appears that non-empirical calculation in the LCAO–MO–SCF–CI framework reach their limits, as a result of technical difficulties associated with computation, sooner than might have been hoped. It is natural than to ask what systems of chemical interest can be studied at present ? As a general principle it is pointless to provide answers to questions which can be answered quicker and cheaper by experiment. Attention should preferably be concentrated on systems for which experiment is as yet, impossible or very difficult. However before any significance can be attached to results of calculations of this kind it is essential to perform calculations on many systems of known properties in order to establish estimates of accuracy.

Finally it must be asked, what can be done for systems too large for calculations using the methods outlined here ? It appears that semi-empirical calculations based securely on valid approximations may provide the optimum solution. The results of non-empirical calculations should provide a valuable basis for these approximations.

In an attempt to extend the limited experience of small atoms and molecules to systems of more chemical interest, a number of calculations have been performed on the formyl series (HCOX) using different sized basis set and different conformations. These are described in the following papers.

5. Appendices

5.1 Mathematical Formalism

The notation in this section is given in a uniform manner, however for brevity only the essential mathematical formalism is presented. For further details the reader should consult the references given.

(i) Integrals

One of the most formidable problems in the application of quantum mechanics to problems of chemical interest has been the evaluating of the multicentre integrals:

$$(\eta_i \mid \eta_j) = \int \eta_i^*(1)\, \eta_j(1)\, d\tau_1 \tag{15}$$

$$(\eta_i \mid \mathcal{O} \mid \eta_j) = \int \eta_i^*(1)\, \mathcal{O}(1)\, \eta_j(1)\, d\tau_1 \tag{16}$$

$$(\eta_i \eta_j \mid \eta_k \eta_l) = \int \eta_i^*(1)\, \eta_k^*(2)\, \frac{1}{r_{12}}\, \eta_j(1)\, \eta_l(2)\, d\tau_1\, d\tau_2 \tag{17}$$

where $\mathcal{O}$ is any one electron operator e.g. h, x, y, z etc. For the class of orbitals based on the Gaussian functions,

$$\eta(A, \alpha, a) = X_A^{a_1}\, Y_A^{a_2}\, Z_A^{a_3}\, (r_A^2)^{a_4}\, e^{-\alpha r_A^2} \tag{18}$$

where, $X_A = X - A_X$, etc.

$$r_A^2 = X_A^2 + Y_A^2 + Z_A^2\,, \tag{19}$$

the formulae for the integrals can be obtained explicity. The essential step in the reduction of the multicentre integrals is the application of the following theorem. The product of two Gaussians [*46*] having different centres A and B is itself a Gaussian (apart from a constant factor) with a centre somewhere on the line segment AB. Specifically

$$e^{-\alpha r_A^2} = \text{const.}\ e^{-\alpha r_B^2}\,. \tag{20}$$

The formulas between basic (1*s*-type) Gaussians were first derived by Boys, and it was shown that the formulae for orbitals with higher angular quantum numbers may be derived by applying differentiation and substitution operators to the basic formulae. If we define a substitution operator $P(r \mid s)$ which acts on the function written after if and replaces r by s, i.e.

$$P(r \mid s)\, f(r) = f(s)\,, \tag{21}$$

then we have the results,

$$P(a_1 \mid a_1 + 1)\, \eta(A, \alpha, a) = \frac{1}{2\alpha}\left[\frac{\partial}{\partial A_x} + a_1 P(a_1 \mid a_1 - 1)\right] \eta(A, \alpha, a)$$

for

$$a_4 = 0 \tag{22}$$

and

$$P(a_4 \mid a_4 + 1)\, \eta(A, \alpha, a) = -\frac{\partial}{\partial \alpha} \eta(A, \alpha, a) \tag{23}$$

for general a_4.

Since the parameters A, α, a etc. appear only within the definitions of the corresponding orbitals, the operations may be taken over and applied to the integrals as well. Thus if one denotes any one of the integrals,

$$I(a_1 + 1) = \tfrac{1}{2}\alpha \frac{\partial}{\partial A_x} I(a_1) = \frac{a_1}{2a} I(a_1 - 1) \tag{24}$$

for $a_4 = 0$ and

$$I(a_4 + 1) = -\frac{\partial}{\partial a} I(a_4) \tag{25}$$

for general a_4.

The formula for any integral may be generated by applying the above relations a sufficient number of times. The method is well adapted to implementation by digital computers.

There are times when it is advantageous to work with general integral formulas. Such a general formula may be derived through the use of Fourier transforms [*46*, *53*].

$$\frac{1}{|r|} = \int \frac{d\vec{k}}{2\pi} \frac{e^{i\vec{k}\cdot\vec{r}}}{k^2}\,. \tag{26}$$

The method is adaptable to the computation of operators of the form

$$\frac{3Z_{12}^2 - r_{21}^2}{r_{12}^5} = \frac{\partial^2}{\partial Z_{12}^2}\,;\, \frac{1}{r_{12}} = -\int \frac{d\vec{k}\,(k_Z^2 - k^2)}{2\pi^2\, k^2}\, e^{i\vec{k}\cdot\vec{r}_{12}} \tag{27}$$

which arise from the magnetic dipole-dipole interactions terms in the Hamiltonian.

A generalization of BOYS' original Gaussian orbitals was proposed by SINGER [*47*], which allows orbitals of the form

$$\sum_k p_k\, e^{-Q_k} \tag{28}$$

where Q_k is any positive definite quadratic form in the space coordinates, and p_k is a polynomial in all or some of these coordinates. This allows explicit dependence of the wave function on the interelectronic distance. BOYS has suggested the inclusion of Gaussian correlation functions [*6*],

$$e^{-ar_{12}^2} \tag{29}$$

while BROWN and POSHUSTA [*8*] have proposed the use of ellipsoidal Gaussian orbitals,

$$e^{(-\alpha x^2 - \beta y^2 - \gamma z^2)}\,. \tag{30}$$

Formulae for the above orbitals may all be obtained in a tractable form.

(ii) LCAO-MO-SCF *Formalism*

ROOTHAAN has shown [*39*] that when the total electronic energy can be written in a certain form, the optimum molecular orbitals

$$\phi_r = \sum_{i=1}^{N} Y_{ri}\, \eta_i \qquad r = 1, 2 \ldots N \tag{31}$$

are such that the coefficients Y_{ri} satisfy the equation

$$\boldsymbol{F}\,\boldsymbol{Y}_r^\dagger = \varepsilon_r \boldsymbol{G}\,\boldsymbol{Y}_r^\dagger \tag{32}$$

where $\boldsymbol{y}_r$ is the column vector consisting of the coefficients of the orbital ϕ_r. $\boldsymbol{G}$ is the overlap matrix given by

$$G_{ij} = (\eta_i \mid \eta_j) = \int \eta_i^*(1)\, \eta_j(1)\, dv_1 \tag{33}$$

the integration being over the spatial coordinates of electron 1. The Fock matrix $\boldsymbol{F}$ is given by

$$\boldsymbol{F} = \boldsymbol{H} + \boldsymbol{P} - \boldsymbol{Q} + \boldsymbol{R} \tag{34}$$

with

$$\boldsymbol{P} = 2\boldsymbol{J}^t - \boldsymbol{K}^t \tag{35}$$

$$\boldsymbol{Q} = 2\alpha \boldsymbol{J}^o - \beta \boldsymbol{K}^o \tag{36}$$

$$\boldsymbol{R} = \boldsymbol{G}\,\varrho^t\,\boldsymbol{Q} + \boldsymbol{Q}\,\varrho^t\,\boldsymbol{G}\,. \tag{37}$$

The elements of the matrices are defined by

$$H_{ij} = (\eta_i \mid \hat{h} \mid \eta_j) = \int \eta_i^*(1)\, \hat{h}(1)\, \eta_j(1)\, dv_1 \tag{38}$$

where $\hat{h}$ is the one-electron operator, and by

$$J_{ij}^\sigma = \sum_{k=1}^{N} \sum_{l=1}^{N} \varrho_{kl}^\sigma (\eta_i\, \eta_j \mid \eta_k\, \eta_l) \tag{39}$$

$$K_{ij}^\sigma = \sum_{k=1}^{N} \sum_{l=1}^{N} \varrho_{kl}^\sigma (\eta_i\, \eta_k \mid \eta_j\, \eta_l) \tag{40}$$

with σ taking the symbols t or o. The two electron integral $(\eta_i\, \eta_j \mid \eta_k\, \eta_l)$ is defined by (17) in Appendix 5.1 (i).

The "density matrices" ϱ^t and ϱ^o are given by

$$\varrho_k^t = \sum_{\substack{r \\ \text{closed}}}^{\text{occupied}} Y_{rk} \cdot Y_{rl} + f \sum_{\substack{r \\ \text{open}}}^{\text{occupied}} Y_{rk} \cdot Y_{rl} \tag{41}$$

$$\varrho_k^o = f \sum_{\substack{r \\ \text{open}}}^{\text{occupied}} Y_{rk} \cdot Y_{rl} \tag{42}$$

with the summations being over the open shell or closed shell orbitals only, and f being the fraction of the open-shell which is occupied. The constants α and β given above depend on the state being investigated. It is seen that when the state is a closed shell, then f is zero so ϱ^o, $\boldsymbol{Q}$, and $\boldsymbol{R}$ all are zero and the equation is greatly simplified. The total energy is given by

$$E = \text{trace}\,\{(\boldsymbol{H} + \boldsymbol{F})\,\varrho^t - \boldsymbol{Q}\,[\varrho^t + (f - 1)\,\varrho^o]\}\,. \tag{43}$$

The solution of the equation is usually accomplished by an iterative process, since the matrix $\boldsymbol{F}$ involves the values of Y_{ri}. An estimate is made for $\boldsymbol{Y}$ initially, and this is used to compute the two density matrices, and hence the two $\boldsymbol{J}$ and two $\boldsymbol{K}$ matrices. These are assembled to form $\boldsymbol{P}$ and $\boldsymbol{Q}$, and the latter one is used [*37*] with the overlap matrix $\boldsymbol{G}$ to form $\boldsymbol{R}$. The equation is solved to give a further estimate for $\boldsymbol{Y}$, and the process is repeated. For the simpler closed-shell case, this procedure often converges, but occasionally the solution is found to oscillate, and some extrapolation procedure [*34*] is necessary to force it to converge.

The most time consuming operation in the solution of SCF equations is usually the contraction of the two-electron integrals with the density matrix to form the $\boldsymbol{J}$ and $\boldsymbol{K}$ matrices. This time can be reduced if the two-electron integrals can be fitted in the high-speed memory simultaneously, or if they can be made available in a suitable order. Alternatively the computation can be done with symmetry orbitals as the η_i, which makes the equation separable, but this does not necessarily shorten the total computation time.

(iii) Electron Density Contours

The density matrix of the rth MO, in accordance with the definition given in Appendix 5.1 (ii) is,

$$\varrho_r(i, j) = \sum_{i=1}^{N} \sum_{j=1}^{N} Y_{ri} \, Y_{rj} = \boldsymbol{Y}_r^{\dagger} \, \boldsymbol{Y}_r \tag{44}$$

and the density value at a given point is

$$D_r(X, Y, Z) = f(r) \sum_{i=1}^{N} \sum_{j=1}^{N} \eta_i(X, Y, Z) \, \varrho_r(i, j) \, \eta_j(X, Y, Z) \tag{45}$$

where $f(r)$ is the integrated spin part of the orbital with 2 if the orbital is doubly occupied, 1 if it is singly occupied and 0 if it is empty. Consequently only occupied orbitals possess electron densities. Nevertheless if one wishes to see the shape of an empty orbital it can be formally treated as if it were doubly occupied.

The total electron density of the molecule is the sum of the M occupied orbital densities.

$$D(X, Y, Z) = \sum_{r=1}^{M} D_r(X, Y, Z) \, . \tag{46}$$

The problem is simply to calculate the individual orbital electron density values at every intersection of a given mesh around the molecule. In practice 1600 points, that is a 40 × 40 mesh provides a fine enough grid for a 10×10 a.u.^{2} area. Special purpose programs may be used to find electron density contours automatically from the available density values. The contours may be recorded photographically from the screen of an oscilloscope where the computer visually displays the contours of requested electron densities or a two dimensional (X, Y) plotter may be connected to the computer to obtain the electron density maps.

(iv) Population Analysis

Three quantities are calculated which to some extent reflect the one electron distribution in the system studied. These quantities are given in terms of the overlap matrix $\boldsymbol{G}$ and the one particle spinless density matrix $\boldsymbol{D}$. The density matrix $\boldsymbol{D}$ may be either $2\varrho^t$ where ϱ^t is defined in Appendix 5.1 (ii), or $\boldsymbol{P}^{\varkappa\lambda}$ or $\boldsymbol{R}^{pq}$. These last two matrices are defined in Appendix 5.1 (v).

It is convenient to discuss these quantities in terms of matrices referred to a re-ordered basis set of atomic functions. Let the atomic functions η_i be re-ordered so that the orbitals on a given atom occur consecutively in some list. Denote the functions on atoms R by η_i^R, $i = 1, m$ where there are m functions on centre R. The matrices referred to this re-ordered basis will assume block form and the relevant blocks will be denoted by $\boldsymbol{M}^R$ for the block involving only the orbitals of atom R and $\boldsymbol{M}^{RS}$ for the block involving the orbitals of atoms R and S.

The required quantities are then

$$X^{R,S} = 2 \sum_{ij} G_{ij}^{RS} \, D_{ij}^{RS} \tag{47}$$

$$Y^R = \sum_i D_{ii}^R + \sum_{ij}{}' \, G_{ij}^R \, D_{ij}^R \tag{48}$$

$$Z^R = Y^R + \sum_{R>S}{}' \, X^{RS} \, . \tag{49}$$

It is easy to show that

$$\sum_R Z^R = 2M \tag{50}$$

where $2M$ is the number of electrons.

The quantity Z^R, referred to as the gross atomic population of atom R, is to some extent a measure of the average charge (in electrons) on the atom R in the molecule. The gross atomic population becomes equal to the net atomic population (Y^R) if the orbitals on the different centres are orthogonal. The total overlap population X^{RS} can be thought of as a measure of the overlap charge density.

The relationship between these quantities and the actual one electron density can be seen most clearly by introducing the normalized orbital and overlap densities

$$\varrho_{ij}^R = \frac{\eta_i^R(1)\,\eta_j^R(1)}{G_{ij}^R} \text{ and } \varrho_{ij}^{R,S} = \frac{\eta_i^R(1)\,\eta_j^S(1)}{G_{ij}^{RS}} \tag{51}$$

respectively. Then the one electron density (normalized to $2M$) is

$$P_1(1) = 2\left\{\sum_R \left[\sum_i D_{ij}^R \, \varrho_{ij}^R(1) + \sum_{ij}{}' \, D_{ij}^R \, G_{ij}^R \, \varrho_{ij}^R(1)\right] + \sum_{S \neq R} \sum_{ij} G_{ij}^{RS} \, D_{ij}^{RS} \, \varrho_{ij}^{RS}(1)\right\} . \tag{52}$$

(v) Configuration Interaction

No attempt will be made to explain in detail the theoretical basis of the configuration interaction procedure as this is the subject of other papers [*37, 51*]. A brief outline will, however, be given.

It is assumed that the co-detors of equation (3) may be written as single bonded functions composed of SCF molecular orbitals

$$\Phi_p = \mathscr{A} \, (\phi_1 \, \phi_2) \ldots (\phi_{2p-1} \, \phi_{2p}) \, (\phi_{2p+1} \ldots \phi_N) \tag{53}$$

where $\mathscr{A}$ is the antisymmetry operator and

$$(\phi_i \, \phi_j) = \begin{cases} \phi_i(i) \, \phi_j(j) \, [\alpha(i) \, \beta(j) - \beta(i) \, \alpha(j)] & \text{if } \phi_i \neq \phi_j \\ \phi_i(i) \, \phi_j(j) \, [\alpha(i) \, \beta(j)] & \text{if } \phi_i = \phi_j \end{cases} \tag{54}$$

$$(\phi_i) \quad = \quad \phi_i(i) \, \alpha(i) \, . \tag{55}$$

A single bonded function may be chosen to transform like any one dimensional irreducible representation of the point group of the molecule. As any bonded function is an eigenfunction of S^2 and S_z. Single bonded functions can satisfy the restrictions placed on co-detors in Section 2.1 and hence serve as suitable expansion functions, for the ground states of almost all molecules. Clearly the single determinant of simple closed shell SCF theory is just a special case of a bonded function in which each spin coupled pair $(\phi_i \, \phi_j)$ is composed of identical orbitals.

In the CI procedure the dominant co-detor or root function Φ_0, is taken to be the SCF wave function. From this function and the given molecular orbitals a limited set of co-detors is built up as described in section 2.1. Each co-detor formed by substitution is examined to see if any linearly independent co-detors of the same form can be made up from its constituent orbitals. As many as can be formed are formed, and such a set of co-detors is referred to as a canonical set. From the final list of co-detors (5) required to solve the secular problem (6). These formulae express the matrix elements symbolically in terms of one and two electron integrals over the molecular orbitals. The matrix elements are evaluated by substituting numerical values for the integrals in the formulae. The secular problem can now be solved to yield the required eigen-values E, and vectors C_p such that

$$\Psi_\varkappa = \sum_p C_p^\varkappa \Phi_p \tag{56}$$

and

$$(\Psi_\varkappa \mid \mathscr{H} \mid \Psi_\varkappa) = E_\varkappa \, . \tag{57}$$

The vectors are used to calculate spinless one particle density and transition density matrices $\boldsymbol{P}^{\varkappa\lambda}$, defined so that

$$(\Psi_\varkappa \mid \mathscr{K} \mid \Psi_\lambda) = \sum_{ij} P_{ij}^{\varkappa\lambda} \, (\eta_i \mid k \mid \eta_j) \tag{58}$$

where k is any spinless one electron operator, such that

$$\mathscr{K}\,(1, \ldots, 2M) = \sum_{i=1}^{2M} k(i) \, . \tag{59}$$

The density matrix $\boldsymbol{P}^{\varkappa\lambda}$ is composed of density matrices for the individual co-detors Φ_p thus

$$P_{ij}^{\varkappa\lambda} = \sum_{p,q} C_p^{*\lambda} \, C_p^\varkappa \, R_{ij}^{pq} \tag{60}$$

with $\boldsymbol{R}^{pq}$ defined so that

$$(\Phi_p \mid \mathscr{K} \mid \Phi_q) = \sum_{ij} R_{ij}^{pq} \, (\eta_i \mid k \mid \eta_j) \, . \tag{61}$$

Using formula (58) moments and transition moments may be calculated for the polydetor wavefunctions, while using formula (61) moments and transition moments may be calculated for any pair of co-detors.

5.2 Computational Details

The POLYATOM System has been written in the form of a number of Technical Notes [*18, 45, 50*]. The programs as developed will be continuously submitted in the future to the Quantum Chemistry Program Exchange (Dr. Franklin Prosser, Department of Chemistry, Indiana University, Bloomington, Indiana, USA 47405).

(i) *List of Programs*

The system at present contains the following programs:

1. PA20: A program to write a tape containing the minimum list of integrals required to be calculated from specifications of the symmetry properties of the constituent functions.
2. PA30: A program to evaluate the one and two-electron integrals as specified by the above tape, and to write their values, with labels, on a second tape. The functions are restricted to be of the form

$$\eta = N(C_s + C_x X + C_y Y + C_z Z)\, e^{-\alpha r^2} \tag{62}$$

   (i.e., s and p symmetry type). There may be up to 50 functions and 20 centres.

3. PA31: A program to continue PA30 if it stopped during the evaluation of two electron integrals due to machine failure.
4. PA33: A program to evaluate one electron integrals over the basis functions of s, p and d symmetry type.
5. PA36: A program to evaluate two electron integrals over the basis functions of s, p and d symmetry type.

$$\eta = N(C_s + C_x X + C_y Y + C_z Z + C_{xx} X^2 + C_{yy} Y^2 + C_{zz} Z_2 + C_{xy} XY + \\ + C_{xz} XZ + C_{yz} YZ)\, e^{-\alpha r^2}\,. \tag{63}$$

6. PA39: A program analogous to PA30 but capable of using some previously evaluated integrals supplied by an additional tape.
7. PA40: A closed-shell SCF program which uses the tape of integrals in the form produced by PA30. There is no restriction on spatial symmetry, and there may be up to 50 functions.
8. PA41: An open shell SCF program, similar to PA40, using Roothaans procedure.
9. PA45: A dipole moment program, with the restrictions of PA20.
10. PA47: A program to perform Mulliken's population analysis.
11. PA48: A program to calculate radial functions and radial electron density for atoms.
12. PA50: A program to construct a starting coefficient matrix for PA40 and PA41.
13. PA60: A program to calculate electron density values on given mesh points around the molecule.
14. PA65: A program to plot electron density contours from data evaluated from PA60.
15. PA80: A program to construct canonical sets for CI.
16. PA81: A program to construct electronic configurations by single and double substitution.
17. PA82: A program to calculate symbolic matric elements for CI.
18. PA83: A program to evaluate the matrix elements H_{pq}, S_{pq} for CI.
19. PA84: A program to perform integral transformations.
20. PA85: A program to solve secular problem using Householder's method.
21. PA851: A program to solve secular problem using Boys' method.
22. PA86: A program to form one particle density matrix from the results of PA85.
23. PA861: A program to form one particle density matrix from the results of PA851.

24. PA87: Program to compute one electron matrix elements.
25. PA88: Program to edit numerical matrix elements from the results of PA851.
26. PA881: Program to edit electronic configurations from PA81.
27. PA89: Program to calculate energy using perturbation theory.

All the above programs are working, and are being continually improved and supplemented. Special purpose STO integral programs have also been used within the system.

The method used to select the programs to be used for a particular job is to include in the data cards which specify the programs to be entered. All the programs are compiled permanently on one tape as a "chain job", and input data cards select which link of the chain is to be executed next. This has made the operation of the system very convenient, with the exception of the book-keeping necessary for any large system. However, it is at present quite simple for anyone to prepare data to run any calculation which is within the capability of the system.

(ii) Orbital Exponents

The present method follows that of Reeves and Harrison [*47*], and consists of scaling the near-optimum exponents for neon by a factor related to the Slater rules for STO's to obtain values for F, O, ... etc. The nitrogen [*35*], and neon [*19*], parameters were restricted to be in geometric progression so that the ratio (C) between adjacent exponents was constant. In the optimization procedure two parameters, the exponent of the "centre gaussian" (β) and the ratio (C) of adjacent exponents were varied. The optimum values (β_0 and C_0) were taken at the minimal total energy according to a parabolic surface –

$$E = E_0 + P(\beta - \beta_0)^2 + Q(C - C_0)^2 . \tag{64}$$

The actual orbital exponents (α) were calculated from the optimal parameters (β_0 and C_0) as follows –

Odd Number of GTF's	Even number of GTF's
$\alpha_{-2} = \left(\frac{1}{C_0}\right)^2 \beta_0$	$\alpha_{-2} = \left(\frac{1}{C_0\sqrt{C_0}}\right)\beta_0$
$\alpha_{-1} = \frac{1}{C_0}\beta_0$	$\alpha_{-1} = \frac{1}{\sqrt{C_0}}\beta_0$
$\alpha_0 = \beta_0$	(hypothetical central gaussian)
$\alpha_1 = C_0\beta_0$	$\alpha_1 = \sqrt{C_0}\beta_0$
$\alpha_2 = C_0^2\beta_0$	$\alpha_2 = C_0\sqrt{C_0}\beta_0$.

Some empirical method similar to Slater's rule has to be devised for scaling the optimum orbital exponents obtained for nitrogen [*36*] and neon [*19*] from atom of Z_1 to atom Z_2 nuclear charge. The multiplying factors (f) of s and p type functions given below were chosen on intuitive grounds –

$$f_s = \tfrac{1}{2}\left\{\left(\frac{Z_2 - 0.3}{Z_1 - 0.3}\right)^2 + \left(\frac{Z_2 - 1.0}{Z_1 - 1.0}\right)^1\right\} \tag{65}$$

$$f_p = \left(\frac{Z_2 - 1.0}{Z_1 - 1.0}\right)^2 . \tag{66}$$

Table 6. *Orbital Exponents*[a] *of GTF's for Elements of the Second Period*

	Li	Be	B	C	N	O	F	Ne
3s	0.114	0.249	0.419	0.634	0.894	1.20	1.55	1.94
	0.902	1.96	3.31	5.00	7.05	9.45	12.5	15.3
	7.13	15.5	26.2	39.6	55.8	74.7	96.5	121.
5s	0.0543	0.118	0.199	0.302	0.425	0.570	0.735	0.922
	0.276	0.600	1.01	1.53	2.16	2.89	3.73	4.68
	1.40	3.05	5.14	7.77	11.0	14.7	19.0	23.8
	7.13	15.5	26.2	39.6	55.8	74.7	96.5	121.
	36.1	78.7	133.	200.	282.	378.	488.	613.
7s	0.0278	0.0604	0.101	0.154	0.217	0.291	0.376	0.471
	0.110	0.239	0.402	0.608	0.857	1.15	1.48	1.86
	0.431	0.938	1.58	2.39	3.37	4.51	5.83	7.31
	1.70	3.70	6.23	9.42	13.3	17.8	23.0	28.8
	6.72	14.6	24.6	37.3	52.5	70.4	90.9	114.
	26.3	57.4	96.6	146.	206.	276.	356.	447.
	104.	226.	380.	575.	811.	1090.	1400.	1760.
1p	0.00679	0.1375	0.244	0.382	0.550	0.749	0.978	1.24
2p	0.0403	0.0908	0.161	0.252	0.363	0.494	0.646	0.817
	0.237	0.533	0.948	1.48	2.13	2.90	3.79	4.80
3p	0.0285	0.0642	0.114	0.178	0.257	0.350	0.457	0.578
	0.148	0.332	0.591	0.923	1.33	1.81	2.36	2.99
	0.765	1.72	3.06	4.78	6.89	9.38	12.2	15.5

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[a] Orbital exponents were scaled from optimized exponents of Ne [*79*].
The only exception is 1p for which N is taken as standard [*36*].
The appropriate scaling factors were derived by Eqs. (65) and (66) and are summarized in Tab. 7.

Because GTF's do not possess principal quantum numbers the scaling factor of *s* type orbital exponents were taken as the arithmetic mean of the 1*s* and 2*s* scaling factors used for STO's. The multiplying scaling factors as well as the actual orbital exponents for atoms from lithium to neon are tabulated (Tab. 6 — 7). All

Table 7. *Scaling Factors for Orbital Exponents of* GTF's

Atom	Li	Be	B	C	N	O	F	Ne
$3^s, 5^s, 7^s$	0.05893	0.12831	0.21616	0.32698	0.46077	0.61754	0.79728	1.00000
1^p	0.12346	0.25000	0.44444	0.69444	1.00000	1.36111	1.77778	2.25000
$2^p, 3^p$	0.04938	0.11111	0.19753	0.30864	0.44444	0.60494	0.79012	1.00000

orbital exponents were scaled from neon except 1- for which nitrogen was used as basis.

This choice is made as a compromise between simplicity and accuracy. While the authors feel that it is reasonably adequate for their present purposes, they also realize that a much firmer basis for the choice of exponents will soon become necessary, and except that an accurate, systematic optimization of atomic parameters will be important in this respect. They would hope that rules analogous to the Slater rules might emerge, not only for atoms, but also for molecules.

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