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CURRENT METHODS IN MO THEORY FOR INORGANIC SYSTEMS AND THEIR FUTURE DEVELOPMENT – AN INTERPRETATIVE REVIEW

P.G. BURTON*

Research School of Chemistry, Australian National University, Canberra (Australia)

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A. INTRODUCTION

The continuing task of the chemist is the characterization and classification of inter- and intra-molecular chemical reactions, with the ultimate aim of formulation of rules for chemical reactivity having some predictive capability. Such rules are inevitably the subject

* Present address: Chemistry Department, Wollongong University, Wollongong, N.S.W. 2500, Australia.

of fundamental interpretation by theoretical chemists in terms of detailed characteristics of the electron distribution at various sites in molecules. With the aid of modern computational and mathematical techniques and sophisticated digital computers, enormous progress has been made in the investigation of molecular electronic structure from first principles, using the fundamental equations of quantum mechanics. These studies have provided an invaluable aid in the interpretation of experimental observations when providing knowledge of calculated electron distributions in various reactants typical of different reaction types[1].

The laboratory chemist continues to be interested, however, in molecules and molecular interactions far too complex in nature to be handled by accurate ab initio techniques of electronic structure calculation, (i.e. those involving no approximations other than the "one-electron orbital" approximation, and those associated with the choice of basis set; of course the use of a very restricted MO expansion basis can preclude the production of *realistic* ab initio wavefunctions). Their desire for some theoretical insight into the electronic structure of their molecules remains compelling. The phenomenal success of some semi-empirical schemes of approximate molecular orbital calculations of electronic structure serves as an illustration of this interest amongst chemists dealing with molecules containing the lighter first and second row atoms, and of their willingness sometimes to accept highly approximate calculated wavefunctions when no reliable ab initio information is available.

For the inorganic chemist dealing routinely with heavy atoms and complex metal–metal and metal–ligand interactions, the same desire for theoretical insight is frustrated on one hand by the prohibitive complexity of ab initio studies. Ab initio calculations on large inorganic systems are still the province of those fortunate few with access to immense computational power, as for such systems, the sheer number of multicentre integrals which arise causes serious problems of storage, quite apart from those of time and effort which must be expended in their exact evaluation and manipulation. On the other hand, the very diversity of bonding situations encountered in inorganic chemistry makes sufficiently general parametrization of existing semi-empirical and semi-quantitative[2] approximate (non-ab initio) MO schemes well-nigh impossible.

With these two limitations in mind, this review is aimed towards the elucidation of some essential requirements of design and specification of any MO scheme which is claimed to provide the inorganic chemist with a reliable predictive and interpretative tool of electronic structure calculations. Furthermore, it is hoped to illustrate that definite scope exists for further development of approximate MO schemes of what may be called intermediate mathematical complexity.

In view of the relatively early stage of development of theoretical inorganic chemistry at present, where no really cohesive theory of bonding *with a predictive capability* is yet available, this article will concentrate almost entirely on investigations of individual electronic state wavefunctions, and leaves any consideration of the calculation of properties depending on *the differences between states* until a later stage. As a background to the investigation of individual states (notably *ground* electronic states) we proceed by briefly re-

viewing some of the basic assumptions and tools of the application of quantum mechanics to the interpretation of molecular electronic structure. We begin with a discussion of techniques used within, and appropriate variants of, the Hartree–Fock (HF) theory of approximate solution of the molecular Schrödinger equation. After some preliminary general comments on current applied theoretical inorganic studies, a number of currently available approximate molecular orbital methods applicable to this area will be critically examined. They will be discussed in terms of the algebraic, computational and chemical significance of various key simplifications frequently used with the aim of bringing out their relation to ab initio and near ab initio techniques.

While particular attention will be paid to MO schemes suitable for tackling larger systems encountered in inorganic chemistry, most criticism of simplifications introduced into such schemes is general in nature, and in no way specific to, for instance, the transition metal area. In the main any such criticism is designed to generate strong scepticism about the general reliability of a number of MO schemes whose almost only asset lies in their ready computational adaptability to larger systems through great simplification. However, any criticism is also hoped to be constructive in pointing out the avenues seeming most likely to lead to development and testing of methods capable of really restoring inorganic chemists' faith in the usefulness of MO theory itself.

B. "SINGLE DETERMINANT" HARTREE–FOCK FORMALISMS USEFUL IN "OPEN SHELL" CASES

It is not possible to solve the time-independent molecular Schrödinger equation[3] exactly. For its application in the theoretical determination of the electronic structure of molecules, it is necessary to adopt simplifying assumptions, and employ simplified models of the actual molecular situation.

The best model to date for systems of more than 10 or 20 electrons is the one "one-electron orbital" representation or approximation of Hartree–Fock (HF) theory[4], where the spatial distribution wave function or *orbital* of each electron is obtained by ignoring the instantaneous correlation of electronic motions. Each orbital is determined by the attraction of nuclear centres along with the *time-averaged* repulsive effect of all other electrons of the molecule. Molecular vibration is normally ignored in the HF theory so that orbitals are obtained in the field of fixed nuclei. This approximation is the Born–Oppenheimer[5] or adiabatic approximation, where it is assumed that the electronic distribution can adjust to any particular nuclear configuration instantaneously during a molecular vibration.

In dealing with inorganic and more particularly transition metal systems, the additional complication arises of having to deal with open shell systems where all electrons are no longer in "pairs", of opposite spin. This means that a variant on conventional HF theory of closed shell molecules should be employed which can accommodate both open and closed shell electronic states with equal ease.

Even though investigation of excited electronic states inevitably demands *consideration*

of configuration interaction (CI) techniques, when only ground states are of immediate concern there are a great many cases where this complexity may be ignored due to the distance in energy of any configurations liable to interact with the ground state. There is strong reason from the point of view of computational economy to limit consideration to HF methods based on the use of a single determinant, and in practice ground state calculations (which may form the basis of subsequent excited state CI studies) are often carried out in a single determinant formalism, even when open shells are encountered in a particular molecular system. With a "single determinant" representation, the total electronic wavefunction corresponds to an antisymmetrized product of one-electron spin orbitals defining a particular configuration of electrons, where a spin orbital is the total one-electron wavefunction. Each spin orbital is written as a simple product of a spatial function or orbital, ϕ, with another function (either α or β) denoting the electronic spin, since the normal absence of spin-dependent operators in the molecular Hamiltonian ensures separability of the spatial and spin variables of motion. The determinantal notation of the total wavefunction, due to Slater[6], for N electrons

$$\Psi_N = \det\{\phi_1\alpha,\phi_2\beta,\phi_3\alpha,\ldots.\} \tag{1}$$

has the advantage of at once allowing for the indistinguishability of individual electrons and the demands of the Pauli principle[7].

Two commonly used variants of conventional HF theory[8] applicable to open shell systems which are based on the use of a single variationally determined determinant are those due to Roothaan[9] and to Pople and Nesbet[10]. In both cases, the normal variational procedure is employed, whereby variation of the functional form of all orbitals is carried out simultaneously, subject to an orthonormality constraint, until an energy minimum is reached. This minimum corresponds to the situation where each orbital determines, and is determined by, the other orbitals, and the orbitals are self-consistent and no further variation in them will further lower the total energy, within the variational subspace chosen. This concept, known as the Self-Consistent Field (SCF), is central to all Hartree–Fock theories.

For the closed shell case, these two "open shell" HF theories coincide, so discussion of their differing characteristics need only consider the open shell case. The two theories differ basically in the degree to which the concept of "perfect pairing" of opposite spin electrons is retained. Because of the fairly high incidence of MO studies based on either formalism, it may well be worthwhile illustrating some of the consequences of adopting one of these approaches rather than the other.

(i) Roothaan's open shell method ("RHF")

Roothaan's[9] extension of the conventional restricted[8] HF theory, which will be denoted the RHF approach in the present context, adopts the approach of demanding "perfect pairing" within all filled MO subshells, so that the distribution of unpaired electron spin density throughout the molecule is given *entirely* by the spatial characteristics of the mol-

ecular orbital(s) containing the unpaired electrons. The RHF approach therefore allows for the delocalization of unpaired electronic spin (spin delocalization, SD), and is characterized by the prediction of excess majority spin density (positive spin density) throughout the molecule.

The restriction on the functional form of the one-electron functions produced by the RHF approach guarantees that the predicted molecular wavefunction retains the full spatial and spin symmetry of the electronic state under consideration (cf. the "UHF" method below).

An advantage of this approach is adaptability to states not describable by a single determinant, by determining the orbitals appropriate to the *average* of the configurations contributing to the electronic state description, by adjusting the relative weights of the coulomb and exchange operators in the total energy Hamiltonian to correspond to this "average of configurations". This approach is necessary to tackle molecular systems with other than empty, full, or half filled (with like-spin electrons) degenerate molecular orbital subshells. However, it must be emphasized that only the number of orbitals appropriate to a single determinant is explicitly considered, the "averaging" being only over spin functions, so the effort required to attain self-consistency of these spatial orbitals is only that of a "single determinant" scheme (see Note added in proof, p. 71).

(ii) Spin-unrestricted HF method ("UHF")

The alternative approach of "single determinant" complexity is the spin-unrestricted, or just unrestricted, HF theory (SUHF or UHF) of Pople and Nesbet[10] (1954).

This approach retains the intuitive simplicity of the orbital description of atoms and molecules, with each spin orbital being a simple product of a spatial or orbital part with a simple spin function (α or β), as in the RHF approach. However, here the constraint of "perfect pairing" of pairs of electrons is relaxed, so that now the individual electrons of opposite spin of each so-called pair no longer *must* have identical spatial characteristics. The orbitals of each spin are considered separately, using two different Hamiltonians appropriate to the differing numbers of electrons of either spin. The effects of the differing overall exchange interaction conveyed by these Hamiltonians is reflected in the fact that when the orbitals of either spin type are aligned in order of energy, there is no longer a perfect coincidence of MO energy levels in the inner orbitals. For those orbitals normally considered to be "paired", the spatial characteristics of the orbitals of either spin are no longer identical (different orbitals for different spin, dods), and so the concept of "perfect pairing" is destroyed. Even so, it is still readily possible to identify the electrons of either spin which *would* be paired in the "perfect pairing" situation.

In addition to the spin delocalization (SD) given by the spatial characteristics of the open shell orbitals, in allowing the unpaired electrons to polarize the inner shells through differing exchange interaction, a new mechanism of distributing electronic spin is introduced in the UHF approach. This spin polarization (SP) of inner shells is necessary in fact to explain the well documented experimental observations of regions of excess *minority*

spin (negative spin) density in some molecules, and the existence of both mechanisms (SD and SP) in the UHF approach ensures that more realistic predictions of electron spin distribution are obtained by this approach than RHF methods.

Discarding the constraint of perfect pairing of the RHF approach allows greater variational freedom, and therefore better total energies are produced with the greater variational subspace of the UHF approach. Analogy with the closed shell case allows us to call the discrepancy in total energy, between the best RHF prediction and experiment, the correlation error for an open shell system. The UHF approach in part overcomes this discrepancy, which may amount to 0.5–1.5% of the total non-relativistic, non-magnetic energy for atoms and small molecules.

Unfortunately, this benefit of the UHF approach is only achieved at the expense of a partial loss of the overall spin symmetry S of the wavefunction. (The UHF wavefunction maintains the correct spatial (Γ), and projected spin (S_z) symmetry however, *by construction*.) In fact the UHF wavefunction contains small admixtures of higher spin multiplet states than the one sought, and the UHF approach may be thought of as incorporating a limited and specialized *configuration interaction* (CI) of the ground state $|S, S_z>$, with related states $|S+1, S_z>$, $|S+2, S_z>$ etc. This admixture, or contamination, results in the UHF wavefunction no longer being an exact eigenfunction of the total spin operator $\hat{S}^2$. However, by now this contamination by higher multiplets, $|\Gamma, S+n, S_z>$, of the state under consideration $|\Gamma, S, S_z>$, has been studied enough for its nature to have become clear[11], and the contamination is seen to arise almost entirely (for the ground state, near the equilibrium geometry) from the next highest multiplet. Annihilation[12] of this contribution usually results in the prediction of wavefunctions having eigenvalues very close to the correct eigenvalue of $\hat{S}^2$.

The effects of removal of the spin contaminants from the UHF wavefunction, on the predicted electronic distribution, have been studied from a theoretical standpoint, along with the nature of the UHF wavefunction itself[13]. In this study the relative roles of the SD and SP spin distributing mechanisms have been analyzed. It was shown that while the predictions of *spin distribution* of the UHF wavefunction are modified by annihilation, the overall electronic *charge distribution* remains unaffected. There is some evidence[14] that the predictions of electronic spin distribution by the untreated UHF wavefunctions are closer than the annihilated function to the predictions of the theoretically more precise spin extended Hartree–Fock approach.

(iii) An RHF vs. UHF comparison

To compare the two approaches, firstly for the RHF method one needs to weigh the absence of the SP spin distribution mechanism against the exact preservation of spin symmetry and wider applicability compared with the UHF method. For the UHF method, its limitation to electronic states having any *degenerate* MO subshells empty, full or "half-filled" is probably not unduly restrictive within the scope of inorganic chemistry, especially in early states of investigations into the capabilities of MO methods. As to the loss of to-

tal spin symmetry in UHF wavefunctions, contaminating spin components are generally readily identifiable, and accordingly this may not be a serious drawback when balanced against superior predictions of electron spin distribution through the SP mechanism of this method, particularly in the lower valence, and inner MO subshells.

In addition, in favour of the UHF formation is its generally wider applicability in following the paths of various chemical reactions. The absence of the perfect pairing constraint in the UHF approach allows the prediction of more realistic and energetically favourable products from some reactions such as chemical dissociations, involving open shell products or reactants. For instance, the lowest energy dissociation products of F_2 predicted by the RHF approach would be ($F_2 \rightarrow F^+ + F^-$), compared to the correct UHF prediction of ($F_2 \rightarrow F^{\cdot} + F^{\cdot}$). Furthermore, by using well known means of evaluating $\langle S^2 \rangle$ for UHF wavefunctions[12], it is possible to monitor changes in $\langle S^2 \rangle_{UHF}$ as a chemical reaction path is followed theoretically, as for example in the process $F_2(S = 0, S_z = 0) \rightarrow 2F^{\cdot}(S = 1, S_z = 0)$, where the predicted value of $\langle S^2 \rangle_{UHF}$ would change continuously from 0 for F_2 at equilibrium, to a value slightly greater (the effect of contaminants) than that for the triplet system, $2F^{\cdot}\langle S^2 \rangle = \bar{2}$. In other words, the lack of preservation of total spin symmetry in the UHF formalism has the potentiality of being used predictively, to anticipate the changes in total spin in particular chemical reactions, which can be a guide to the actual products formed if these are not known experimentally.

(iv) The role of Koopmans' theorem

Koopmans' theorem[15], which in closed shell HF theory provides a central link between calculated molecular orbital energy levels and observed ionization potentials (IP's), no longer has a clearcut application in the open shell oriented schemes discussed here, and must be considered as part of any general comparison of the RHF and UHF methods.

For closed shell molecules where the two methods coincide, molecular IP's are determined using Koopman's theorem according to which the energy required to remove an electron from the ith orbital of the molecule, leaving nuclei fixed and orbitals unaltered, is given by the negative of the molecular orbital energy or eigenvalue, if the molecular and ionic wavefunctions satisfy the Hartree–Fock or Roothaan[16] equations.

It should be noted that this latter condition is not precisely satisfied with approximate (non-ab initio) schemes[17], and also that the practical success of Koopmans' theorem relies in fact on a cancellation of the energy of relaxation of the *ion* molecular orbitals from their original form, with the change in correlation energy on loss of an electron, which latter quantity cannot be estimated within the HF formalism. Furthermore it is fairly well documented that when "soft", readily polarized molecular orbitals are involved, as in the case of the aromatic hydrocarbons[18], this cancellation no longer operates effectively. A similar lack of success of Koopmans' theorem has also been suggested to occur for some transition metal complexes[19].

However, even apart from the normal caution which evidently must be exercised in using this route to calculate ionization potentials of molecules, with open shell systems the rela-

tion of calculated molecular orbital energy levels to physically meaningful quantities becomes less clear, as extra complications characteristic of the particular open shell formulation (RHF or UHF) adopted arise.

With the RHF open shell formalism, for instance, examples exist of wavefunctions which have calculated properties disconcertingly at variance with the intuitively satisfying AUFBAU principle, which dictates that electron configurations of lowest energy are those which have the most stable orbitals occupied preferentially. One such example is the RHF wavefunction of Carlson and Moser[20] for the state of VO, the calculated ground state, where the $^4\Sigma^-$ configuration $\{\ldots 2\pi^4 1\delta^2 7\sigma^2 3\pi^4 8\sigma^2 9\sigma\}$ is predicted. This means that the *partly filled* 1δ subshell is predicted to lie at lower energy than three *filled* molecular orbital subshells in this molecule.

For UHF wavefunctions of open shell systems, where different molecular orbital forms and energy levels occur for electrons of either spin, there is a difficulty in choosing which calculated molecular quantity should be associated with ionization energies. However, in this case Boyd and Whitehead[21] have suggested that the "splitting" of open shell state orbital levels should be treated like the observed splitting of degenerate levels by spin orbit coupling, and that the experimental ionization potentials are best compared, therefore, with the *mean* of the calculated orbital energies associated with the corresponding levels of either spin of each "pair".

(v) Routes to excited state properties

The adoption of one or other of the RHF or UHF formalisms as the basis for MO investigations of ground states has a bearing on the precise path that any subsequent investigation of excited state properties will take. At present, fairly sophisticated techniques which hold promise of yielding both accurate and reliable spectral predictions, are in use or are available for investigations of excited states within either formalism.

Within the RHF formalism, the studies of Richardson et al.[22] on hexafluoride complexes have shown that excellent correlation with experiment may be obtained by obtaining firstly RHF SCF wavefunctions for individual configurations, and subsequently allowing these to *interact* to yield predictions for excited *states*. This procedure is obviously most suited to the situation where it is reasonably straightforward to decide which individual configurations must be included to generate an adequate description of particular states, as is the case in the "*d*–*d* only" spectral transitions investigated by these workers for the hexafluorides.

In using the UHF formulation, it is also possible to calculate the SCF energies of some excited states even when degeneracies are involved, providing one component of the state can be found which corresponds to a single configuration (determinant). In that instance transition energies may be calculated by taking the difference in SCF energies for the ground and excited states, but when configuration interaction can be anticipated as being important, the "different orbitals for different spins" characteristics of individual configuration wavefunctions considerably complicates the mathematics of the CI. However, a means has

been proposed[23] to circumvent this difficulty, in which the Dewar "half-electron" method[24] is extended to obtain an approximate representation of the ground state which is a suitable basis for CI studies, and this appears to offer a general economical route to states of all multiplicities originating from this "ground state".

To conclude this section, there is no a priori means of deciding the supremacy of excited state predictions based on methods appropriate to one or other of the RHF or UHF formalisms. The device of determining non-physical "average of configuration" wavefunctions is normally employed in either procedure, and accordingly only future numerical comparisons will enable a reasoned choice of the better general method to choose for investigating excited state properties.

C. LCAO–SCF SOLUTIONS TO THE HF EQUATIONS

From the previous discussion, it is apparent that each of the "single determinant" open shell HF formalisms is possibly more appropriate in some instances than in others, and the best choice between the RHF and UHF approaches in a given situation very much depends on the precise system and properties which are of interest. However, having discussed some of the factors by which the "appropriateness" of a particular formalism in each case may be judged, we now move on to discussion of the means available by which either *formalism* may be translated into a mathematically solvable problem.

The expansion technique described by Roothaan[16], where each MO is written as a linear combination of some known set of basis functions, with coefficients of the linear combinations being determined variationally, is most commonly used to transform the coupled set of integro-differential equations of a "single determinant" HF theory into essentially a readily solvable iterative pseudo-eigenvalue problem of matrix algebra.

If the MO expansion is over a complete set of functions, then the HF equations (themselves approximate) are solved exactly. This situation is known as the Hartree–Fock limit. In practice, however, a smaller, more convenient and economical basis must be chosen than a mathematically complete set of functions, and the choice of a tractably small set, capable of spanning the most important elements of a complete set, remains a central problem of practical molecular HF theory.

Atomic-like orbitals, sited at the nuclear centres of the molecule, are normally chosen as a convenient set, and in this case the problem becomes primarily one of choosing sufficiently faithful representations for the orbitals of each atom, while bearing in mind the perturbing influence the molecular environment may have on these orbitals. Such a choice of basis functions results in the Linear Combination of Atomic Orbitals–Self Consistent Field–Molecular Orbital (LCAO–SCF–MO) technique of solving the molecular HF equations, due to Roothaan[16].

With the LCAO–SCF technique, the mathematical difficulty is associated with evaluating the *integrals* over the chosen basis set, contributing to the elements of the matrices of the pseudo-eigenvalue matrix equations[16], which in the UHF formalism, with $\sigma = \alpha$ or β, are denoted

$$\begin{cases} F^{\sigma}C^{\sigma} = S^{\sigma}C\epsilon^{\sigma} \\ \det|F^{\sigma} - S\epsilon^{\sigma}| = 0 \end{cases} \tag{2}$$

The composition and orbital energy of each set (α or β) of the molecular spin orbitals is contained in the coefficient matrix C^{σ}, and the eigenvalue matrix ϵ^{σ} respectively. In the UHF formalism, the eigenvectors and eigenvalues of either spin are determined separately, and for the open shell case $C^{\alpha} \neq C^{\beta}$, $\epsilon^{\alpha} \neq \epsilon^{\beta}$, while these do become identical in the closed shell case. C^{σ} and ϵ^{σ} are determined by the overlap matrix S of the chosen basis set, along with the Roothaan F^{σ} matrix. Since F^{σ} depends on C^{σ} ($\sigma = \alpha, \beta$) an iterative technique must be adopted to obtain the final self-consistent eigenvectors C^{σ}.

The integrals over atomic orbitals occurring in the F matrix elements represent the interactions that a charge distribution arising from the product of two AO functions may undergo. These interactions include nuclear attraction, coulomb repulsion by other electronic distributions, exchange interaction, and there is also a kinetic energy associated with each AO product distribution. The situation of AO's on various centres facilitates natural division in these integrals into those involving only AO's of the one centre (*monocentric*), and the other *multicentre* integrals.

The difficulty associated with the evaluation of each of these integral types occurring in the LCAO–SCF F matrix elements is bound up with the functional form chosen to represent the atomic orbitals in the basis set.

The reference for atomic orbital representations is the exact numerical Hartree–Fock solutions of the individual atoms. These Hartree–Fock atomic orbitals (HFAO's) are available for various electronic states and degrees of ionization of the atoms. Unlike the molecular case, the atomic HF problem is capable of exact solution, and the HFAO's consequently are to be considered "Hartree–Fock limit" solutions.

The obvious relation between simple exponential functions and the exact hydrogen atom orbitals[25] has led to their widespread use as basis functions in the *analytical* determination of HFAO's. The HFAO's are obtained as linear combinations of simple exponentials with optimized exponents and coefficients. The size of the linear combinations used determines the degree of correspondence observed between the analytic and exact numerical HFAO's, but it is found that the HFAO's are well represented[26] by quite small linear combinations of simple exponentials.

In this context the simple exponentials are called Slater-type functions (STF)[25], and in the most simplified case, where a single Slater-type function is used to represent each HFAO, the AO functions are called Slater-type orbitals (STO's).

The use of STF's in HFAO representations has significant repercussions in the evaluation of the required molecular integrals. While techniques are available for the evaluation of monatomic and diatomic molecular integrals[27,28], it has proved difficult to formulate a method to calculate three- and four-centre integrals over STF's sufficiently rapidly[29].

The use of alternative basis functions with better integration characteristics (Gaussian-type functions, GTF's) has helped to overcome this difficulty, but as these functions are

individually worse AO representations, larger linear combinations of GTF's are required for realistic AO representation.

In either case, the great numbers of multicentre integrals involved in investigation of even quite small molecules, has led to the formulation of a great many variously simplified approaches to the solution of the Roothaan LCAO–SCF equations, with the aim of circumventing the most difficult aspects of the complete ab initio solution of the equations. STF-type basis sets are usually chosen in the approximate MO schemes.

For large inorganic and transition metal systems, it is the numbers of multicentre molecular integrals over atomic orbitals which provides the forcing limitation on the scope of ab initio approaches. In this area, ab initio calculations in terms of STF-based AO representations are virtually out of the question. With GTF-based AO representations, when one is limited to facilities liable to be routinely available to chemists at present (e.g. CDC 6400, IBM 360/75, UNIVAC 1108), even for quite simple metal complexes, the realism or adequacy of individual AO representations must be compromised so severely to reduce the computational task to a reasonable level that it is not at all clear that the GTF-based ab initio approach can be packaged to provide a "universal" route to reliable wavefunctions of systems of this complexity. Accordingly, it seems that for this class of systems considerable emphasis will continue to be placed on (STF-based) approximate solutions to the HF equations, and methods of this type will provide the basis of discussion in the next sections of this review.

D. COMMON "CHEMICAL" SIMPLIFICATIONS IN THEORETICAL INORGANIC CHEMISTRY

General considerations of the internal quantum mechanical soundness of some available means of deriving molecular wavefunctions such as those touched on in the previous two sections certainly remain significant in the field of electronic structure investigation of large inorganic and transition metal systems. However in this field it is common to encounter the use of extra simplifying assumptions, in addition to those associated with the mathematical formalism of electronic structure investigation, which are based more on the peculiar chemical characteristics of some inorganic systems and which are introduced to provide for special economizations in otherwise exceedingly complex computations. Some of the more "intuitively" based extra simplifying assumptions encountered are not always altogether without significance in relation to the credibility of resulting wavefunctions produced.

(i) Use of atypical or uncharacterized test systems

It is the author's opinion that many existing approximate MO schemes oriented particularly towards transition metal complexes make a far too liberal use of special characteristics of these systems in the formulation of schemes of matrix element evaluation; in effect that prior knowledge or assumptions of the systems is either explicitly or implicitly used as input information in the MO schemes, and in interpretation of the resulting wavefunctions, insuffucient recognition is paid to the possible effects of these prior assumptions.

For example, the very high symmetry and the substantially ionic nature of the hexafluorides of the transition metals, which have been studied extensively theoretically[30], literally prejudice the predictions of even grossly approximate MO methods. The high symmetry of such systems often makes exact what would otherwise be severe integral approximation, and in addition in this case, the long bond lengths of the hexafluorides generate relatively small overlaps, and this makes overlap dependent physically or arithmetically based integral approximations *appear* quite acceptable. In this light, systems such as the hexafluorides would appear unsuitable as vehicles for testing approximate MO schemes, and the success of any scheme for such systems should not be taken as evidence for any claim of generality.

This is evidenced in the author's experience, where the application of a superficially quite acceptable approximate MO technique[11c] to these hexafluorides yielded quite satisfactory results. However, this success obscured the major inherent defects of the technique that were later revealed when more covalent, lower symmetry species were investigated[31].

This is not to imply, of course, that approximate MO schemes, which through their embodiment of quite severe approximations are suitable only for use in very restricted applications, cannot provide substantial insight *within those restricted areas*, just that they must be used with great caution *outside* those areas for which they were developed.

As an example of the fairly persistent use of insufficiently characterized inorganic systems for theoretical study, we may take the widely studied inorganic tetroxyanions, such as SO_4^{2-}, MnO_4^- and CrO_4^{2-} (see, for example, ref. 32). Studies of such systems have been made, aimed at spectral predictions, where the results obtained relating to *differences between states* are used to give indications of the effectiveness of different MO methods, without the assurance that each MO method concerned is capable of adequately describing at least one of the states concerned. Here the high molecular symmetry combines with closed shell, symmetric ground electronic states to afford little experimentally obtainable information on the electronic structure of even the ground state, so that it is impossible to measure the accuracy of the ground state wavefunction used as the basis of spectral predictions.

The need to attempt rationalization of electronic spectra of transition metal complexes, using simplified models and highly parametrized empirical MO techniques, is of course granted in the light of the vast array of experimental data to be correlated. However, where more sophisticated MO techniques are employed in the hope of achieving interpretation rather than just correlation it would seem elementary prudence to ensure that the technique is capable of producing a realistic ground state wavefunction, where predicted electronic properties of that state can be meaningfully compared with experimentally observable properties. Such prudence has not always been in evidence, and in the case of the permanganate ion, Davies and Webb[2] were led to state: "The assignment of the electronic spectrum of permanganate ion has been the subject of much experiment, discussion and controversy. Consequently it is not reasonable to claim a general success for a particular MO description on the basis of a prediction of the electronic spectrum of this ion".

(ii) Inadequate accounting for the "molecular environment"

One of the most common chemical simplifications encountered in theoretical inorganic chemistry is the neglect of the effect of the *environment* on the molecular system of interest. With small molecules containing say first and second row atoms, there is often no objection to calculating the wavefunction for the "isolated molecule". However, a great many metal complex systems which have been studied theoretically because of their experimental interest, do not in fact *ever* occur as isolated systems (perhaps because of their "charged" nature) and are found only in solution, with a number of associated solvation spheres, or in crystalline environments.

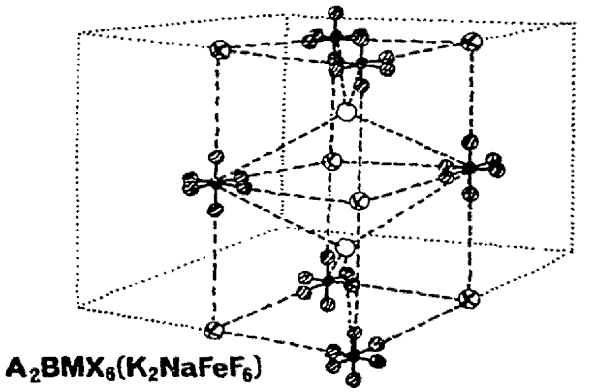
Taking the example of single metal complexes, experiments have shown that a great many observable properties are largely independent of the surrounding environment other than the "ligands" immediately coordinated to the metal, and this has led to the use in theoretical studies of the "cluster approximation". The "cluster" is the metal plus the directly coordinated ligands, and by the "cluster approximation" is meant that the environment of the *cluster* is assumed to have no effect on the electronic structure of the cluster. (This is equivalently stated as assuming that the environment contributes a constant, purely electrostatic potential over the dimensions of the cluster.)

The chemical significance of the cluster approximation is difficult to ascertain as far as complexes in solution are concerned, because of uncertainties not only in the structure of the cluster itself, but also in the precise nature of the environment (in this case the outer solvation sheaths) outside the cluster itself, but still intimately associated with it.

As regards the use of the cluster approximation in crystals, it is possible to discern two quite separate classes of crystal where the cluster approximation can be expected to operate with differing degrees of success. These two classes will be denoted as "shared-cluster" crystals, and "isolated-cluster" crystals respectively[11c]. The basis of this differentiation can be understood by reference to Fig.1, which illustrates examples of isolated- and shared-cluster octahedral transition metal hexafluoride complex systems.

In the first case of an isolated-cluster crystal, the clusters of octahedral hexafluoride anions are well separated from each other, and each is surrounded by a number of alkali metal ion nearest neighbours. On the other hand, in shared-cluster crystals such as the fluoroperovskite illustrated in Fig.1, the use of an octahedral cluster model to investigate the metal–fluorine interaction in these crystals causes a greatly distorted view to be taken of the bonding capabilities of the ligands. While in reality each ligand in this example interacts equally with two metal atoms, an octahedral cluster model would completely neglect the effect of *one* of these interactions.

It is unfortunate therefore that so little attention has been paid to this distinction in crystal types when theoretical studies of such systems have been embarked upon, and particularly unfortunate, for instance, that the archetype of the transition metal hexafluoride systems chosen for theoretical study should have been the NiF_6^{4-} cluster occurring in shared-cluster fluoroperovskite environments. In this case it would seem unreasonable to



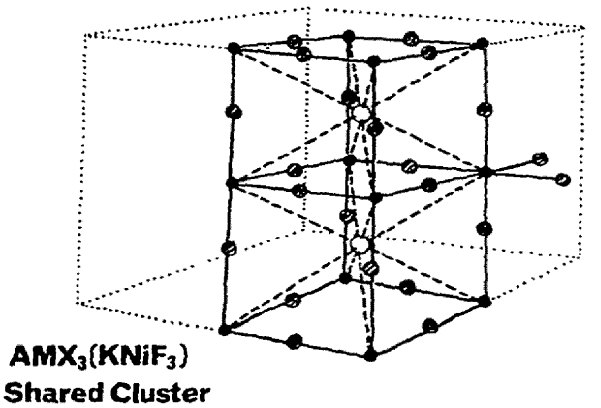


Fig. 1. Schematic representation of the qualitatively differing environments of hexafluoride clusters, MF_6^{n-}, occurring in an "isolated cluster" case, and a "shared cluster" case. Full circle – transition metal "ions"; shaded circle – fluoride "ions"; others – alkali metal ions.

assume that the environment of the cluster should *only* generate a constant electrostatic potential over the cluster dimensions. It is highly probable that the extra interaction of an extra-cluster transition metal ion with each fluoride "ligand" of the cluster would substantially alter the character of each metal fluorine bond, from the form of the bond as calculated by taking into account only intra-cluster interactions.

E. CURRENT METHODS IN MO THEORY FOR INORGANIC SYSTEMS

With the background of the previous three sections, we may proceed to indicate briefly the nature of a number of the approximate MO schemes currently used in application to inorganic systems. We adopt the Davies and Webb classifications[2] of MO techniques into

the categories *(i) semi-empirical* and *(ii) semi-quantitative*, while a third category would contain *ab initio* and *near-ab initio* calculations.

A *semi-empirical* approach is one where approximations are not listed explicity and some of the terms of the SCF operator in the LCAO–SCF F matrix are related directly to experimentally determined quantities.

If computational simplifications are introduced into the solution of the LCAO–SCF equations in a systematic manner using well defined approximations of reasonable accuracy, a *semi-quantitative* approach is evolved.

The *ab initio* approach consists of solving the LCAO–SCF equations exactly, in terms of a given Hartree–Fock formalism in terms of a chosen MO expansion basis, but this basis may or may not be sufficiently extensive to guarantee realistic wavefunctions.

In each of these classifications we aim to discuss various significantly different available approaches, and no attempt is made at exhaustive coverage of individual MO studies of transition element, or other, systems, especially in view of a number of relevant reviews that have recently appeared[2,32–34].

It is the supposition of this work that the most successful approximate MO calculations will result when the least departure from the full LCAO–SCF formalism is evident[34], and that new approximate MO approaches should be liable to the least possible criticism, and should be as generally applicable as possible through being as quantum mechanically sound as possible. In these terms there appears to exist a very real gap between on one hand, the fairly rapid semi-quantitative approaches where much information is lost by approximation, and on the other hand the ab initio or near-ab initio approaches where all or most information is painstakingly included.

This gap is apparent in the area of studies of transition metal systems, just as for smaller non-transition metal molecules, but in the former case it is accentuated by having to deal with heavy, many-electron atoms, any one of which may contain as many electrons as are involved in what are normally considered quite difficult ab initio calculations on smaller molecules (e.g. SO_2: 32 electrons, Cu: 29 electrons).

We will attempt to elucidate this gap that does exist in the extant MO techniques for the more demanding larger molecular systems, by discussing first the current semi-quantitative schemes, and then the ab initio schemes.

We may foreshadow the overall conclusions to be drawn from these discussions by the statement that for current semi-quantitative MO techniques there seems to have been an undue emphasis placed on approximating individual integrals. The neglect of, or approximation to, those integrals individually difficult to evaluate (in the STF-based approach) has tended to occur without due recognition being given to the accuracy of the crucial off-diagonal matrix elements of the (now) approximate LCAO–SCF F matrix (in the UHF formalism, F^{α} matrices). *It is these elements, particularly the two-centre* F *matrix elements containing the most difficult integrals to evaluate, which contain any information on covalency effects, and it is those which ultimately affect the accuracy of a predicted wavefunction.*

A discussion of the form of the Hamiltonian matrix, F, elements of the LCAO–SCF–MO procedure, their physical significance and the way individual contributions to them are treated in the various semi-quantitative MO schemes mentioned in the following, is given in Section H.

(i) Semi-quantitative MO techniques

The earliest applications of MO theory to transition metal systems, as opposed to attempts at quantification of the ionic crystal field theory model, was the adaptation of the extended Huckel MO (EHMO) formalism by Wolfsberg and Helmholz[36]. This very simple technique is unashamedly semi-empirical in nature, and while of little or no use in reliably predicting subtle chemical effects, it may be parametrized to correlate gross chemical effects in a series of related molecules.

A revision of the EHMO formalism by Ballhausen and Gray[37] made the scheme more responsive to the large variations in oxidation state occurring in transition metal complexes. Evaluating the leading terms of diagonal SCF F matrix elements as a function of the atomic charge predicted in each SCF iteration enabled this, but the practice of employing ionization potential data (VOIP's) for *free ions* of given charge *alone* to calibrate the complete diagonal elements remained a severe approximation in terms of the interatomic effects not accounted for. The scheme is known as the Self-Consistent Charge and Configuration (SCCC–MO) scheme.

Richardson and Rundle (RR)[38] suggested simplifying the full LCAO–SCF F matrix elements by applying the Mulliken approximation[57] to the two-electron parts of the Roothaan closed shell SCF operator[16]. When the Roothaan and RR–SCF operators are written in expanded form they become, respectively, for the closed shell case

$$\hat{F} = \hat{T} + \Sigma\, \hat{V}^{A} + \sum_{i}\sum_{\mu}\sum_{\nu} C_{i\mu}C_{i\nu}[2(\ /\mu\nu) - (\ \mu/\nu\ )] \tag{3}$$

and

$$\hat{F}_{RR} = \hat{T} + \Sigma\, \hat{V}^{A} + \sum_{i}\sum_{\mu}\sum_{\nu} C_{i\nu}C_{i\mu}S_{\mu\nu}[2(\ /\mu\mu) - (\ \mu/\mu\ )] \tag{4}$$

where

$$\sum_{\mu}\sum_{\nu} C_{i\mu}C_{i\nu}(\ /\mu\nu) \equiv \hat{J}_i \tag{5}$$

and

$$\sum_{\mu}\sum_{\nu} C_{i\mu}C_{i\nu}(\ \mu/\nu\ ) \equiv \hat{K}_i \tag{6}$$

The operators $\hat{F}$ and $\hat{F}_{RR}$ contain in operator notation the interactions which must be accounted for in evaluating the energy of electrons occupying a particular MO, and the energy of interaction between different MO's. When the MO's are expressed as a linear combination of atomic orbitals, the coulomb and exchange operators, $\hat{J}_i$ and $\hat{K}_i$, by which the cou-

lomb and exchange interaction of molecular orbital i with any other electron distribution (another MO, or itself) can be evaluated, can be expanded to the form shown above for either the exact, or the RR, formalism. For the first time in the application of simplified MO theory to large systems, the RR formalism attempted to cast the off-diagonal F matrix elements in a form amenable to ready evaluation by theoretical means and so replaced the somewhat arbitrary procedure of EHMO theory of using arithmetic or geometric means of diagonal elements for these elements.

The RR formalism formed the basis of a range of proposed MO schemes[39-47], and though these tended to retain a large element of the earlier EHMO simplifications, some of the more important additional interactions not accounted for by simple EHMO and SCCC–MO schemes were included.

Dahl and Ballhausen[32] criticized the RR formalism itself, however, for an inconsistent use of the Mulliken approximation. Theoretical evaluation of RR matrix elements results in inclusion of the effect of each electron interacting with itself.

More recently Basch[48] tested the RR formalism numerically over a range of molecules, against corresponding complete LCAO–SCF calculations. The generally poor agreement casts grave doubts on the usefulness of the RR scheme and tends to support criticism of it.

The WH–EHMO, SCCC–MO and RR-based schemes are all oriented towards essentially a ligand field theory level treatment of metal complexes, where emphasis on the electronic effects only on the central metal arose mainly from preoccupation with electronic spectra of the complexes.

The advent of the various neglect of differential overlap (NDO) schemes of Pople et al.[49] provided the possibility of studying more general systems other than simple (binary) complexes, since the unbiased treatment of all atoms of the molecule predicts detailed bonding effects equally well at each site. The straight molecular orbital approach, of which the NDO schemes represent simplified examples, takes covalency effects more completely into account than either the ligand field or ionic crystal field models, and so may be regarded as capable of yielding better bonding descriptions for a larger range of complexes (and other molecules) than those models.

While the least simplified scheme proposed by Pople et al.[49], the NDDO scheme, has been used in calculations on second-row fluorides[50], the tendency has been to use the much simpler CNDO scheme of parametrization of approximated F matrix elements for transition metal and large inorganic systems.

There are two distinct parts to the CNDO parametrization scheme. The first is the elimination of all integrals containing non-coincident product charge distributions by invoking a complete neglect of differential overlap approximation, so that only simple coulomb integrals remain to be evaluated. Secondly, it was found that to maintain desirable consistency of the CNDO approximation under rotation of local atomic axes, it was necessary to average integral values over all the orbitals of each atom, for each integral type considered. This causes the value used for each integral to depend only on the atoms involved, and contains no information, for example, on directional properties of the orbitals involved in the integral.

Averaging integrals in this way in a "valence electron" transition metal basis of $3d$, $4s$, $4p$ is very severe in view of the quite different nature of relatively compact $3d$, and very diffuse $4s$ and $4p$ functions – the "atom-averaged" CNDO one-centre coulomb integral will overestimate the $(4s4s/4s4s)$ integral and underestimate $(3d_i3d_i/3d_i3d_i)$ integrals for example, tending to lead to prediction of artificially high $4s$ and $4p$ populations.

Nevertheless, the CNDO formalism has been extended to apply to transition metal systems by several authors. Dahl and Ballhausen[32], and subsequently Allen et al.[51] implemented schemes of form virtually identical to the Pople parametrization. In both cases, complexes of high symmetry were investigated: MnO_4^-, and the hexafluorides MF_6^{n-} respectively. These systems probably represent particularly favourable systems for study at the CNDO level.

Aspects of CNDO type schemes which would tend to limit widespread extension to systems (of lower symmetry?) with more complex bonding effects apparent are primarily those arising from the great loss of detailed knowledge of those interactions not considered at the CNDO level. An obvious example here is the complete absence of exchange-type integrals, which are needed to account for differences in various open shell states abounding in the transition metal area. Since only gross interactions are included explicitly at the CNDO level, it is not reasonable to expect the CNDO wavefunction to respond to any but gross changes in the molecular systems considered.

More particular faults of the Pople parametrizations at the CNDO level are the rather inflexible formulation of the off-diagonal F matrix elements; and the disregard of the explicit effect of the overlap matrix in the LCAO–SCF equations (2), since the zero differential overlap (ZDO) approximation invoked replaces the overlap matrix with the unit matrix. This means that the CNDO scheme essentially evaluates interactions over an assumed completely orthogonal multicentre basis set by using a *non-orthogonal* AO basis. This is clearly inconsistent.

The many unsatisfactory aspects of the Pople et al. parametrization of CNDO-type schemes stimulated the search for ways of refining the parametrization so that some generality in application to a range of inorganic systems could be achieved. Thus, for example, Roby[53] re-examined the overall CNDO parametrization and concluded that a completely theoretically based scheme of parameter evaluation was necessary for extension to inorganic systems generally.In addition, Roby made the first attempt in the transition metal area to base the NDO approximations, in particular the ZDO approximation, on a much sounder theoretical footing by employing the symmetric orthogonalization of the AO basis set due to Lowdin[54]. This reparametrized scheme retained the cipher "CNDO" to indicate that most individual *interactions* are still eliminated by the complete neglect of differential overlap approximation.

As a further refinement, a scheme known as MCZDO was introduced[53], where the neglect of differential overlap approximation is only retained in evaluating multicentre two-electron integrals. This scheme consequently relaxed the requirement of complete "atom averaging" of the integral types included, and explicit individual values were given to all one-centre integrals.

One of the more important aspects of the MCZDO scheme was the complete theoretical, though still approximate, evaluation of the one electron integral part of the LCAO SCF matrix, the "core" matrix H^{core}. It was found that the evaluation of this matrix as accurately as possible in the AO basis, followed by symmetric orthogonalization, yielded a final wavefunction most in accord with more elaborate calculations on the SO_4^{2-} test system.

These schemes were originally applied to attempt interpretation of the UV spectra of some tetroxyanions; SO_4^{2-} (ref. 53), and later MnO_4^- and CrO_4^{2-} by James et al.[55]. Surprisingly, the supposedly more accurate MCZDO formulation produced worse results than the CNDO type formulation in the latter cases. The application of scaling to various molecular integrals in the CNDO scheme allowed the simultaneous production of satisfactory ground state electron distribution and UV spectral predictions, which was not the case in the MCZDO scheme.

The unsuitability of the tetroxyanions as a vehicle for testing approximate MO theories has already been reflected upon, and later application of the MCZDO scheme in an open shell modification (since MCZDO retains all one-centre exchange integrals, the use of the UHF formalism is meaningful at this level) to the ground state properties *alone* of transition metal hexafluorides indeed showed the scheme could quite adequately account for electronic spin and charge distributions in these systems[11c].

However, as previously mentioned, attempts by the author to extend the MCZDO scheme to more covalent, less symmetric systems revealed that irreconcilable defects existed within it. Efforts to trace the cause of the meaningless predictions of MCZDO for such simple systems as CO led to the adoption firstly of more accurate atomic orbital representations for the valence AO's included, and secondly the removal of significant approximation in the core matrix evaluation by exact evaluation of all one- and two-centre kinetic energy and nuclear attraction integrals, in each case to no avail.

The real origin of failure of the MCZDO scheme was ultimately recognized as stemming from poor nomenclature in the original parametrization of CNDO[49], INDO[52] and NDDO[49] schemes of Pople et al. Throughout the NDO-based schemes (CNDO, INDO, NDDO, and the "CNDO" and MCZDO schemes), the neglect of differential overlap approximation at the one-*and* two-centre level, or at the two-centre level, with only *bicentric* product distributions being neglected, provides substantial simplification in evaluation of the approximate *diagonal F* matrix elements, by retaining all the largest interactions contributing to those elements and eliminating smaller and more troublesome integrals from consideration. In addition, both the NDDO and MCZDO schemes can be seen to include the most important contributions to the one-centre off-diagonal F elements.

There is a different situation entirely, however, when the two-centre off-diagonal F matrix elements are considered. If the NDO approximations, where in every case integrals over bicentric distributions are neglected, were used in the evaluation of these elements, as they are for the one-centre F elements, every contributing molecular integral, except a single group, would be uniformly neglected, and a hopelessly unrealistic estimate of the off-diag-

onal F matrix elements would result (further discussion on this point is contained in Section H).

When the Pople parametrization is followed in the NDO schemes, where a parametrized "core resonance integral" taken directly from previous ab initio calculations on diatomics, is used[56], viz. $\{H_{\mu_A \nu_B}{}^{NDO} = S_{\mu\nu}(\beta^\circ_A + \beta^\circ_B)/2\}$, then at least the correct order of magnitude is obtained for the F elements in question. However, this procedure effectively obscures the real nature of the group of terms within the "resonance" integral, as a complex sum containing individually large contributions of opposite sign, from one-electron attractive and two-electron repulsive terms.

In the MCZDO scheme, the "core resonance integrals" are taken at face value, and accurate theoretical techniques were employed to evaluate each of the one-electron terms contributing to $H^{core}_{\mu_A \nu_B}$. Applying the NDO approximation to the two-electron terms involved in these two-centre off-diagonal elements eliminated all the *compensating* repulsive interactions generated by integrals of the form (AA/AB) and (CC/AB) which should contribute to these elements. Thus the MCZDO off-diagonal F elements are artificially large in magnitude, and on diagonalization of the MCZDO F matrix, this feature generates an unsatisfactory, artificially large, spread in MO energy levels, along with correspondingly unsatisfactory eigenvector form for the molecular orbitals contributing to the overall predicted wavefunction.

In summary, then, the MCZDO parametrization can be considered the most sophisticated of the NDO-type MO techniques. Many molecular interactions, and hence much more detailed information is included in the scheme, relative to say CNDO schemes, severe integral averaging is mainly avoided, and Lowdin orthogonalization is used to justify the ZDO ($S = 1$) assumption. However, the MCZDO formulation goes only halfway towards the introduction of a completely theoretical determination of the crucial off-diagonal two-centre F matrix elements. Consequently the aim that these elements may faithfully reflect the very real changes occurring in them as the molecular charge distribution changes in each iteration towards self-consistency is not realized even at the MCZDO level.

(ii) Critique of semi-quantitative methods

While the MCZDO scheme is obviously unsatisfactory from the point of view of evaluation of two-centre approximate F matrix elements, criticism on this score can certainly be levelled at the other semi-quantitative schemes, all of which use some special tool to overcome the problem of evaluating explicitly individual terms contributing to these elements.

For the RR-based methods, this means a simplification of the SCF operator by the Mulliken approximation. While we have already noted the RR formalism does not stand numerical testing against comparable ab initio calculations, the widespread use of the Mulliken approximation in simplifying problems of integral evaluation demands we look fairly closely at it.

Nicholson[34] and Ruttink[35] have both examined aspects of the Mulliken approximation. Ruttink has considered the rotational characteristics of the Mulliken approximation, and has concluded that for consistency under local rotation of axes, the Mulliken approximation should be combined with "atom averaging" of integrals, so that this approximation should only be employed in calculations aimed at the CNDO level of accuracy. Nicholson pointed out that the size of errors expected from the use of this approximation in off-diagonal elements may be very large ($\sim \frac{1}{2}$ a.u. or $\sim$ 13 eV), but also pointed to the very serious failing of the Mulliken approximation in evaluating "zero overlap" off-diagonal elements, which often occur in the one-centre part of the F matrix. These F elements between orthogonal orbitals on one centre are only identically zero if the two functions concerned transform as different representations of the molecular point group. For instance, in octahedral coordination complexes, metal orbitals spanning single subshells of s, p and d symmetry transform as different representations of the molecular point group, and so the off-diagonal one-centre metal F matrix elements are identically zero. So in this octahedral case (the tetrahedral case is the same for such a metal basis) the *approximation* of these elements as zero, by calculation at the CNDO level, or by invoking the Mulliken approximation, is obviously acceptable. However, this is not the case for lower symmetry systems, or where lower local symmetry is evident. This can be illustrated in the case of the ligand of an octahedral system. Here there is local cylindrical symmetry, so the sigma ligand ns and $np\sigma$ orbitals, though orthogonal, transform as the same representation, and the equating to zero of the connecting F matrix element would usually be a serious error. Similar arguments would apply to metal functions in a diatomic molecule, for example, where non-zero F elements should exist between all basis orbitals of σ, of π, or of δ symmetry etc. This is why claims concerning CNDO-type or RR-based schemes must be viewed with some caution when only high symmetry systems are considered. As has been previously stated, high molecular symmetry may in fact validate otherwise severe approximations, and for the purposes of *proving* generality of MO schemes, it is desirable to investigate systems of fairly low symmetry.

Alternatively to the Mulliken approximation, another widely used means of obtaining approximate values for off-diagonal two-centre F matrix elements, is by parametrizing the major part of these elements (i.e. the difficult to evaluate part) by direct comparison with exact ab initio calculations. This technique is employed in all the Pople NDO-based schemes NDDO[49], INDO[52] and CNDO[49] and derived versions, where the original parametrization technique is followed[2,51], along with a further scheme known as NEMO III[58]. NEMO III is the most developed of a series of schemes involving a bewildering array of approximations: along with the off-diagonal F matrix parametrization under discussion at the moment, a special approximation to obtain values for "zero overlap off-diagonal matrix elements" is employed, which restricts its present use to high symmetry molecules.

The use of this technique firstly requires that calculations of each diatomic fragment possible in the molecule be performed. This may involve many ab initio calculations on diatomic pairs of atoms over a range of internuclear distances. The effort involved in performing a large number of diatomic calculations, prior to the MO calculation, may cause the ne-

glect of some interactions between pairs of atoms arbitrarily considered not to be "bonded". Secondly, it is necessary to choose for reference calculation diatomic fragments with some arbitrarily chosen charge distribution *assumed* to be appropriate to the actual situation of the diatomic fragment as it occurs *in the molecule*. This assumed distribution may differ markedly from the isolated diatomic ground state distribution, and unless some constraint can be imposed on the possible distribution within the SCF procedure the results of the diatomic problem may not be appropriate. In either case *convergence difficulties* often occur in diatomic calculations well away from the ground state geometry of the isolated molecule, or in molecules with odd electron distributions such as transition metal carbide and nitride diatomics[2]. In other cases the proximity of a number of electronic states in a particular diatomic calculation may necessitate the use of multiconfiguration or CI studies.

So it can be seen that direct parametrization of off-diagonal F matrix elements is fraught with difficulties in performing calculations on the relevant molecule fragments alone.

However, even in cases where such calculations are available or feasible, to ascribe effectively the same *balance* between the large attractive and repulsive contributions previously referred to, in the off-diagonal F element in the molecular situation, as occurs in a particular reference calculation seems highly questionable. In fact such a procedure would seem to prejudice substantially the possible predictions of the MO scheme in view of the importance of these elements in determining bonding, and be particularly inappropriate in any situation which could involve unusual bonding effects.

One can perhaps sympathize with the Pople NDO schemes applied to related organic systems, as was the original aim, from this point of view. Here the transferability of parametrized elements may be reasonable because of the general similarity of particular bond types in different environments. On the other hand the composite nature of these parametrized F elements would seem to preclude their use transferably in a scheme aimed at quite general applicability, as inorganic systems tend to embrace quite large variations in bond polarities, and the consequent sizeable local deviations from neutrality would be expected to substantially alter the real balance of the off-diagonal F elements concerned.

A further criticism of the use of reference diatomic calculations to obtain values for these matrix elements is of course that it prejudges the importance of *three-centre* attractive and repulsive contributions to these elements in the full LCAO–SCF formulation, not to mention the *four-centre* two-electron terms.

In view of the unsatisfactory aspects related for the whole range of semi-quantitative MO methods available for the general inorganic/transition metal area, it seems almost superfluous to add mention of the tendency in such schemes to use minimal basis sets (typically 1STO/AO), having poor accuracy relative to exact HFAO functions and which usually necessitate empirical evaluation of one-centre interactions, when as is usual at the semi-quantitative level, only valence electrons are considered, because of the poor behaviour of 1STO/AO accuracy functions near the nucleus. The intricacies of combining a suitable AO basis set with a core/valence separation will, however, not be under discussion here.

(iii) An important ingredient for future semi-quantitative techniques

The overall comments on a representative range of semi quantitative MO schemes suitable for application to inorganic systems, discussed in the previous section, indicate strongly that a need exists for completely theoretically based MO formulations in this area. Such schemes must aim to avoid highly approximate or inadequately parametrized values of the all-important off-diagonal two-centre LCAO–SCF F matrix elements.

Allowing for the subtle effects of covalency by accurately computing these elements *in the actual molecular situation* every time in the iterative approach to self-consistency of the molecular wavefunction is the only approach capable of avoiding any prior assumptions about bonding and bonding effects in the molecule; only this approach could claim generality to unusual bonding situations. It would be hoped that in such a theoretically based scheme the only variable, the basis set chosen, could be varied at will without difficulty, according to the accuracy desired in the final wavefunction. The limitations of the wavefunction in this case should be traceable to either inadequacy of the basis set, or to inapplicability of the particular Hartree–Fock formalism used; in other words, that inadequacies of the predicted molecular wavefunction should not be due to insufficient care being taken in evaluation of the LCAO–SCF F matrix.

An MO formulation of this type is necessarily more complex than the semi-quantitative schemes discussed already. However, the essential point in considering any extension of semi-quantitative MO theories is that computational economy be maintained at a reasonable level.

In the only schemes of a completely theoretical type which are available, in the ab initio and near-ab initio categories, computational demands are high, and some more simplified approach is required for use as a general, reliable, laboratory tool to be used at will for large chemically interesting molecules where the ab initio approach would become prohibitively expensive.

It is obvious that ab initio calculations are necessary periodically to check the performance of more approximate MO calculations whenever a significantly different new bonding situation is encountered, but it is equally obvious, in view of the difficulty and computer time consumption involved, that no more ab initio calculations than necessary should be performed.

There is, therefore, a need to explore the possibilities of new simplified but completely theoretical MO schemes which do "check out" against comparable ab initio calculations, and which are capable of extended application with the expectation of realistic predicted wavefunctions even though no "reference" calculations exist in the immediate area concerned.

But just as it was necessary to pinpoint the inadequacies of currently available semi-quantitative MO schemes in order to determine the essential features to include in any new scheme, for the same purpose one must also examine available ab initio or near-ab initio schemes to see if anything can be learned about such calculations which may have a bearing on the development of new simplified MO schemes.

(iv) Ab initio MO techniques

The term "ab initio" implies exact evaluation of all molecular integrals of the LCAO–SCF formalism. Therefore, ab initio calculations differ only in the type and accuracy of the basis set employed.

In the case of diatomic molecules, high accuracy ab initio STF-based calculations are possible where results obtained are "near the Hartree–Fock limit"[59]. In these cases, a fixed linear combination of STF's is not used for each atomic orbital, but rather the functions found to contribute for example to *atomic* HFAO analytical representations are used individually as expansion functions of the Roothaan procedure ("extended basis calculations"), and the relevance of atomic orbitals as such is lost in the final wavefunction. However, the molecular orbital energy levels of these wavefunctions are obviously a very good reference point for other calculations employing a less flexible "fixed-AO"-type expansion basis.

There are a great number of examples of "fixed-AO" LCAO–SCF ab initio calculations on diatomics and small molecules which, though not necessarily, and probably not, near the Hartree–Fock limit, serve to indicate the importance of exact integral evaluation compared with some approximate scheme using the same basis. Alternatively such calculations serve to indicate the effect of using different accuracy "fixed-AO" representations for the various atomic orbitals of the molecule. Many examples of dramatic improvement in total energy (the criterion of "goodness" in variational Hartree–Fock calculations) predicted in calculations as the accuracy of AO representations is improved (1STF/AO to 2STF/AO to . . .) are readily observable in compendia of ab initio calculations on small molecules[60], and it is apparent that as the size of atoms involved in molecules increases, then greater complexity of AO representations is necessary.

From atomic calculations, where the total energies are compared in going from the best "single zeta" (1STF/AO), to double zeta (2STF/AO) orbital representations, through to accurate Hartree–Fock calculations, one notices an increasingly dramatic improvement in going from single- to double-zeta accuracy AO representations, while the discrepancy between the double zeta and the HF results remains very small. This is illustrated in Table 1.

TABLE 1

"*n*-zeta" and Hartree–Fock energies (a.u.)[a]

	Single-zeta[b]	Double-zeta[c]	Hartree–Fock[c]
C	−37.622	−37.687	−37.689
F	−98.942	−99.401	−99.409
Si	−288.090	−288.851	−288.854
Cl	−458.524	−459.480	−459.482

[a] 1 a.u. = 27.21 eV.
[b] Ref. 66.
[c] Ref. 61.

This sort of information has led to the idea of a "double zeta" accuracy AO representation being the best choice for molecular calculations, this being a compromise between high accuracy atomic orbital representation and economy of molecular wavefunction production.

For GTF-based ab initio calculations, the criterion of accuracy of the wavefunction is also described with reference to the accuracy of the atomic orbital GTF representations used as the basis set. The accuracy of GTF representations is often measured by comparison with STF representations, by saying a given GTF representation is equivalent to "Minimal Basis Slater Accuracy" (1 STF/AO), or "double zeta" accuracy (2STF/AO), etc.

In contrast to STF representations, GTF representations are designed for use in ab initio calculations on more complex molecules than diatomics. For the inorganic/transition metal area, there are quite a few GTF ab initio computations available[62].

However, in few of these cases do the GTF basis sets used approach the accuracy of, say, "double zeta" STF/AO representations. High quality basis set GTF calculations as do exist (e.g. the recent permanganate calculation[62e]) serve as (enormously expensive) landmarks in areas such as orbital energy level prediction, but one of the biggest problems with GTF basis sets is not so much connected with the actual size of the basis sets, but with the desire to untangle the chemistry involved by correlating the final wavefunction with contributions from individual atomic orbitals of the component atoms of the molecule investigated. The means employed to reduce the GTF calculations to manageable size often destroys the "atomic orbital" character of the basis set, so that there are no longer recognizable individual contributions to molecular orbitals from particular orbitals. This is not a serious drawback except that the very convenient "linear combination of atomic orbitals" molecular orbital description, readily obtained from STF-based LCAO calculations, is not available for comparison with these calculations. This simply means that it is very difficult to know or find out how best to *improve* a GTF basis set by the significant, but smallest possible increments in order to correct some deficiency of the wavefunction. It is very difficult to determine from GTF calculations, for instance, whether an improved 4*s* representation is desirable for a transition metal atom in a given molecule, and equally difficult to ascertain whether the "4*s* orbital is involved significantly in bonding", since the 4*s* orbital as such normally has little meaning per se in GTF calculations.

Such difficulties of interpretation are minimized when the wavefunction is transformed to some localized orbital representation, since then density contours may be compared directly without reference to the expansion basis, but this device is far from widely used to date for inorganic systems of any great complexity.

There is much to be said of course in favour of GTF calculations, "if the basis set is sufficiently flexible to span the most important elements of a complete set of expansion functions", so that the Roothaan expansion technique is accurate. Since there are so few cases where there is high confidence that this requirement is met even fairly well, in the larger inorganic systems, and since it is difficult to judge in fact how good a particular basis set is in relation to STF bases, especially with respect to outer valence orbitals whose variation has little effect on total energy, most GTF calculations are not of direct use as reference

calculations for comparison with approximate STF-based MO calculations. It is normally not possible to differentiate between the effects of matrix element and integral approximation on the one hand, and differences in the bases used in either case, on the other hand.

(v) Near-ab initio techniques

In view of the caution with which many GTF calculations apparently must be viewed when large inorganic systems are involved, it is of interest to examine attempts to extend STF-based ab initio techniques from diatomic to polyatomic molecules. Because of the difficulty of multicentre integral evaluation with a STF basis, some simplifications generally must be adopted in integral evaluation in this case, and such schemes will be denoted as "near-ab initio".

Near-ab initio calculations using STF-based AO representations, aimed at the inorganic/transition metal area, have been performed by several groups: Klimenko, Dyatkina et al.[63], Richardson, Soules et al.[64], Nieuwpoort[67], and Hillier and Saunders[68].

The Richardson, Soules et al.[64] calculations on transition metal complexes involve accurate evaluation of all one- and two-centre integrals, since means are readily available to obtain these. Of the multicentre integrals, some three-centre integrals are evaluated by either the simple, or a modified, Mulliken approximation; other three- and all four-centre integrals are approximated as zero by assuming negligible contribution of charge distributions arising from the product of AO's of different ligands in the octahedral systems investigated. These multicentre integral approximations are unfortunately designed with the octahedral coordination characteristics in mind, and there seems to be no recipe for handling other situations where this particular set of approximations may not be as appropriate.

These calculations are more seriously limited by the basis set chosen[65]. The basis for the hexafluorides consisted of, for the fluoride ligands, minimal basis STO's with Slater exponents, appropriate to the assumed completely ionic distribution, for F^-. For the metal ions, the "core" orbitals are represented by single STO's, while the valence $3d$ functions were represented by "double zeta" functions. The exponents for this STF basis were determined by a somewhat arbitrary "fitting" procedure to more accurate analytical HF AO's appropriate to the metal ion of the completely ionic model of bonding in the complex. Functions thought to be appropriate to metal $4s$ and $4p$ functions in this environment were also included.

The use of this particular basis set[65] can be criticized for its poor performance with regard to the intra-atomic core valence separation characteristics, arising from the simple Schmidt orthogonalization of the single zeta functions into orthogonalized orbital subshell representations. This procedure does not provide sufficiently accurate "blocking" of the core and valence sections of the full F matrix to ensure meaningful results will be obtained by explicit consideration of the valence electrons alone. The basis for this criticism will not be spelled out here, except that mention can be made of the general point that the use of "fitted" single STO's which most nearly mimic accurate functions only well out from the nucleus, to evaluate *all* of the large energetic contributions arising near the nucleus where

the fitted STO's are relatively poor, is not very satisfactory, particularly when combined with a core/valence separation.

In addition, the more specific criticism of lack of balance in the basis set may be levelled at these calculations; the important 3*d* orbitals are given "double zeta" accuracy and are "fitted" functions, while the ligand functions with which they interact are firstly single zeta accuracy, but more importantly involve variationally obtained exponents which emphasize the regions near the nucleus rather than at some distance from it.

In these calculations, finally, as with the very similar calculations of Nieuwpoort[67] on some tetracarbonyls ($Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$), the molecular symmetry of the systems studied may be high enough to obscure faults in the scheme more apparent in lower symmetry systems.

Klimenko, Dyatkina et al.[63] have approached MO calculation on inorganic systems with a similar aim as regards accuracy of the final wavefunction, but have avoided some unsatisfactory aspects of the Richardson series calculations. They have carefully considered the problems of core/valence separation, and have found the use of "natural" Hartree–Fock AO functions (which diagonalize the intra-atomic part of the *F* matrix) as definitely desirable from this viewpoint. Secondly, their calculations, while employing minimal basis accuracy functions to represent core orbitals for economy, use double zeta accuracy valence functions quite generally, rather than just for the metal valence orbitals as in the Richardson calculations.

The Klimenko, Dyatkina scheme is designed for quite general applicability in that it contains no assumptions obviously particular to the characteristics of transition metal complexes, but the major problem of the three- and four-centre integrals is not really simplified sufficiently for this scheme to be widely applicable in large molecules; the group has so far concentrated on relatively small systems.

The technique used for the multicentre integrals by this group, as in some instances of Richardson series calculations, involves an accurately calibrated expansion of bicentric product charge distributions into one centre distributions, so that ultimately all the multicentre integrals can be expressed as "accurate" expansions over two centre integrals. This procedure necessitates the exact evaluation of at least some of the difficult integrals containing these distributions, e.g. $(\mu_A \nu_B/\lambda_A \lambda_A)$, $(\mu_A \nu_B/\lambda_C \lambda_C)$ and calibrating the expansion *for each pair* $(\mu_A \nu_B)$ at each internuclear distance, prior to the SCF procedure. This is undoubtedly a very painstaking procedure, especially if variations of internuclear distances are of interest from the chemical point of view. It is probable that this procedure is not readily automated – an almost essential requirement for larger systems.

Finally, in discussing near ab initio techniques, mention must be made of the increasingly common device of using GTF expansions of the STF AO representations to evaluate multicentre integrals, as exemplified by Hillier and Saunders' calculation[68] on tetroxyanions CrO_4^{2-} and MnO_4^-.

(vi) Special MO techniques

There are several special techniques that have been used to simplify ab initio calculations which must also be mentioned for completeness. These involve extensions to the limit of otherwise more commonly restricted versions of expansion techniques.

The first, that of Ellis et al.[69], involves expansion of the normal multicentre atomic orbitals basis, *all onto one centre*, so that the only integrals to be considered are monocentric integrals and may be evaluated exactly. While the method is technically ab initio in that all integrals are evaluated, the feeling is of course, as so often with Gaussian (GTF) calculations, that the significance of the basis set in the direct chemical sense has been compromised. In this particular case a very limited expansion series was used to expand the AO functions onto the central atom.

Secondly, Roby[70] has derived some potentially very important relations concerned with common "Neglect of Differential Overlap" (NDO) approximate molecular orbital methods. A theorem is found which directly justifies the use of an NDDO[49] approximate molecular orbital method, unlike all other (less exact) NDO methods[49,52]. It is found that the NDDO method, formulated in terms of orthonormal subsets of basis functions on each atom, which are subsequently symmetrically orthogonalized, is in fact equivalent to a minimal basis version of an MO method which becomes exact as the Ruedenberg expansion[71] becomes exact when the sets of atomic orbitals on each centre approach completeness. The NDDO method using a symmetrically orthogonalized basis becomes identical to using the "Ruedenberg approximation" in the normal AO basis, where the basis for expansion in the Ruedenberg sense is of course far from complete. Roby's work clearly demonstrates that the NDDO level of integral approximation is the *lowest theoretically justifiable level of approximation* to be used if a direct identifiable relationship with exact ab initio techniques is desired, when, as is standard, nuclear-centred (e.g. atomic orbital) basis sets are employed.

Of the "Linear Combination of Orthogonal Atomic Orbitals, Ruedenberg Expansion" method itself, taken as a purely ab initio technique, its ultimate success depends of course on the use of a sufficiently large basis set on each atom for the Ruedenberg expansion to be sufficiently accurate, and a great deal of work is necessary before a general prescription for such a set becomes available.

Finally, a further special technique that has been applied to some inorganic systems should be mentioned; the self-consistent field scattered wave (SCF–SW) technique, which has been applied to some closed shell tetrahedral tetroxyanions[72]. This technique is not based on the Hartree–Fock molecular model, and in particular employs a statistically based, adjustable estimate of the effects of exchange interaction that occur in the HF approach. While it appears to offer an economical route to both models of the charge distribution and the lowest excited states of the systems so far considered, it is not yet clear whether or not the high symmetry tetroxyanions are particularly favourable substrates for testing the method, or indeed whether the parametrization of exchange effects can be couched in a form which will allow reliable prediction of magnetic properties simultaneously with realistic charge distribution and excited state properties, bearing in mind that magnetic effects are often of great interest in transition metal systems.

F. AN OVERVIEW

We may summarize the present state of MO theory of inorganic systems in the light of the discussions of the previous section by observing that there does not exist a technique which satisfactorily combines adequate accounting for all intramolecular interactions of the HF model, with expansion bases of sufficient quality that realism of the final wavefunction is assured, while at the same time offering economy in both computational space and time at the level where it is practicable for the technique to be routinely used with large, chemically interesting systems.

Accordingly there is strong stimulus for further advancement in simplified molecular orbital methods of complexity intermediate between the existing semi-quantitative and essentially ab initio techniques available. This stimulus centres around the hope that it will be possible to reduce the multicentre interaction problem by some means which will allow consequent time savings to be redirected into utilization of better basis sets so necessary to realistically evaluate the larger magnitude intra-molecular interactions. Since we are interested here in dealing with large inorganic systems containing heavy atoms, there is a very compelling stimulus to avoid having to evaluate all the three- and four-centre integrals of an ab initio computation, and it may well prove that the utilization of great care in the evaluation of the largest one- and two-centre interactions with sufficiently accurate, or flexible basis sets for such systems may actually outweigh the effects of simplification in, say, four-centre integral evaluation, in the quest for wavefunctions as realistic as possible.

In terms of the present discussion, we can set down some features which would be desirable in any new "intermediate" simplified MO scheme.

Firstly, for dealing with heavy atoms particularly, one important simplification would be to allow for the introduction of the chemically reasonable device of only dealing explicity with a *valence* subset of electrons of each molecule; those which are thought to be primarily responsible for bonding effects.

It would be desirable that any new technique contain readily identifiable approximations, so that extrapolation of the technique into new or unknown (hitherto) molecular situations may be judged from the point of view of those approximations. The degree of approximation should be as low as possible so that there could be high confidence in the scheme without continual recourse to empirical or ab initio data. Roby's work[70] tends to indicate that greater deviation from the matrix element formalism of the ab initio approach than that represented by the NDDO level of approximation (with conventional nuclear-centred basis sets) would destroy any such confidence.

To maintain a real predictive capability, any new technique should include completely theoretical evaluation from first principles of all the LCAO–SCF matrix elements, particularly those between orbitals on different centres, so that covalency predictions depending on the magnitude of those elements will adequately reflect the molecular environment by allowing for changes in the balance between attractive and repulsive terms in those elements.

Finally, as a general point, it can be said that if a great deal of effort is expended in the

production of more sophisticated molecular wavefunctions than those of the semiquantitative MO methods mentioned earlier, then it seems sensible to employ more sophisticated means of interpreting them than the normal somewhat arbitrary population analysis (e.g. the Mulliken analysis with the arbitrary equal division of overlap change between the contributing centres) such as localization procedures[73].

Though the abstract notion of localization cannot be deduced from first principles – and so there is a variety of methods available for the production of localized orbital descriptions of electron distribution in molecules – localized orbitals emphasize the linking of orbital descriptions with chemical concepts of additivity and separability of measurable chemical quantities[74]. Localized orbital descriptions of bonding in inorganic and transition metal systems will probably hold the key to development of any generalized bonding theory of such systems. Furthermore, the direct comparison of localized orbital contours facilitates meaningful comparison of different MO calculations where, for example, only the basis set differs. Accordingly some system for generating localized orbital descriptions of bonding would seem a very desirable part of any new MO technique.

G. A NEW MO TECHNIQUE

As we have shown elsewhere[31], detailed analysis of the form of the LCAO–SCF F matrix elements shows that it is possible to formulate new molecular orbital schemes of intermediate complexity between present semi-quantitative and ab initio techniques.

The derivation of these schemes was centred around obtaining good approximations to the LCAO–SCF F matrix elements themselves (see Section H). The importance of all the contributions to the F elements was investigated, and a new scheme of approximation of these elements was formulated which allows most of the multicentre repulsion integrals to be discarded. In contrast to previous semi-quantitative molecular orbital schemes, consistent, physically reasonable approximations to the F elements were obtained. In particular it was shown that the aim of consistent approximation to *molecular integrals* by neglect of differential overlap (NDO) techniques is not compatible with the reasonable approximation to the overall LCAO–SCF F matrix of the Hartree–Fock–Roothaan technique.

These schemes have been widely tested[75], and are currently being exploited by the author in the investigation of a range of inorganic systems, including a number of binuclear transition metal complexes. These investigations feature the use of double zeta 2STF/AO basis functions, and interpretation through localization procedures.

H. THE CRUCIAL TWO-CENTRE HAMILTONIAN F MATRIX ELEMENTS

The review of Davies and Webb[2] concluded with the hope that CNDO-type calculations would, in the absence of widespread ab initio calculations, find further application to transition metal complexes. The present author emphatically does not share that hope, because of a belief that the CNDO level of approximation is so severe that any genuine predictive capability has been "approximated away" at this level, that the parametrization of CNDO

methods does not contain the flexibility required to react adequately to the very different local balances between attractive and repulsive interactions occurring through the great diversity of bonding situations existing in inorganic systems.

To elucidate the origin of this belief, it is helpful to set down important individual contributions to the Hamiltonian F matrix elements of the LCAO–SCF–MO procedure.

The individual contributions to an element $F_{\mu\nu}$ of the F matrix in Roothaan's equations (2) comprise *(i)* the kinetic energy of the one-electron distribution defined by the product $(\mu\nu)$ of orbitals μ and ν, $<\mu|T|\nu>$; *(ii)* the attraction of various nuclei of the molecule for that one-electron distribution, $<\mu|\sum_{N} V^{N}|\nu>$, and *(iii)* the interaction of other one-electron distributions $(\lambda\sigma)$, occupied with $P_{\lambda\sigma}$ electrons, with the distribution $(\mu\nu)$. The bond order elements $P_{\lambda\sigma}$ are calculated from the fractional contribution of the orbitals λ and σ to the various occupied molecular orbitals. This *coulomb interaction* is always accompanied by an exchange term which reflects the fact that electrons of like spin ($\sigma = \alpha$ or β) in both the distributions $(\mu\nu)$ and $(\lambda\sigma)$ will tend to avoid each other, leading to an overall term $P_{\lambda\sigma}(\mu\nu|\lambda\sigma) - P^{\alpha}(\mu\sigma|\lambda\nu)$. The magnitude of the individual terms may be roughly judged from consideration of the *diffuseness* of individual one-electron orbital distributions, and the *distance* between the charge distributions involved in each interaction, and accordingly it is helpful to arrange the contributions to the F elements according to the number of nuclear centres involved in each interaction. Then in an AO or hybrid orbital nuclear-centred basis set $\{\chi\} = \mu, \nu, \lambda, \sigma \ldots$, we have, in the UHF formalism, for the α-electron set,

$$
\begin{aligned}
{}^{x}F^{\alpha}_{\mu_A\nu_A} = [&<\mu_A|T + V^A|\nu_A> + \sum_{\lambda,\sigma}^{A}(P_{\lambda\sigma}(\mu_A\nu_A|\lambda_A\sigma_A) - P^{\alpha}_{\lambda\sigma}(\mu_A\sigma_A|\lambda_A\nu_A))] \\
&+ [\sum^{B\neq A}<\mu_A|V^B|\nu_A> + \sum_{\lambda,\sigma}^{B\neq A} P_{\lambda\sigma}(\mu_A\nu_A|\lambda_B\sigma_B)] + {}^{x}D^{\alpha}_{\mu_A\nu_A} \qquad (7)
\end{aligned}
$$

and

$$
\begin{aligned}
{}^{x}F^{\alpha}_{\mu_A\nu_B} = [&<\mu_A|T + V^A + V^B|\nu_B> - \sum_{\lambda\sigma}^{B}\sum^{A} P^{\alpha}(\mu_A\sigma_A|\lambda_B\nu_B) \\
&+ \sum_{\lambda,\sigma}^{A}(P_{\lambda\sigma}(\mu_A\nu_B|\lambda_A\sigma_A) - P^{\alpha}_{\lambda\sigma}(\mu_A\sigma_A|\lambda_A\nu_B)) \\
&+ \sum_{\lambda,\sigma}^{B}(P_{\lambda\sigma}(\mu_A\nu_B|\lambda_B\sigma_B) - P^{\alpha}_{\lambda\sigma}(\mu_A\sigma_B|\lambda_B\nu_B))] \\
&+ [\sum^{C\neq A,B}<\mu_A|V^C|\nu_B> - \sum_{\lambda,\sigma}^{C\neq A,B} P_{\lambda\sigma}(\mu_A\nu_B|\lambda_C\sigma_C)] + {}^{x}D^{\alpha}_{\mu_A\nu_B} \qquad (8)
\end{aligned}
$$

Here the matrix D contains the interactions originating from the interaction of two or more bicentric distributions[31], which are neglected in all semi-quantitative MO schemes. (It is the explicit inclusion of interactions contained in the matrix D which differentiates the near-ab initio and ab initio treatments from the semi-quantitative schemes.)

Of the terms of F, the one-centre ${}^{X}F^{\alpha}$ elements, where $\mu_A = \nu_A$ (the *diagonal* ${}^{X}F^{\alpha}$ elements) can be seen to arise from a sum of terms equal to the kinetic energy and nuclear attraction of the distribution $(\mu_A\mu_A)$ to nucleus A, reduced by the repulsive interaction of $(\mu_A\mu_A)$ with other electrons on A. This first group of terms in the diagonal F element is often parametrized from ionization potential data (WH–EHMO, SCCC–MO, and the CNDO, INDO and NDDO formalisms of Pople et al.). The second group of terms in the diagonal element corresponds to the overall coulomb interaction (nuclear attraction reduced by electronic coulomb repulsion) of $(\mu_A\mu_A)$ with other atoms B of the molecule. This type of term corresponds to the "penetration integral" of pi-theory, and is often simplified by taking the interaction to be well represented by the interaction of $(\mu_A\mu_A)$ with the (point) charge on B. In other cases, notably the CNDO methods, the contributions to this second term of the diagonal elements of F are simplified by neglecting integrals containing non-coincident product distributions $(\lambda_B\sigma_B)$, $\lambda \neq \sigma$.

The off-diagonal one-centre elements of ${}^{X}F^{\alpha}$, where $\mu_A \neq \nu_A$, in ab initio calculations have magnitudes highly dependent on the atomic orbital basis used, and on the local symmetry of the atom A, and may assume quite large values, even when the two orbitals μ_A and ν_A are mutually orthogonal AO's. In the case of an orthogonal set of AO's on A, any method evaluating off-diagonal elements of F as some proportionality to the overlap integral ($S_{\mu_A\nu_A}$ here) of course equates these elements to zero, and this may be a severe approximation. The CNDO methods, through neglecting any integrals involving non-coincident orbital product one-electron distributions, neglect the influence of the ${}^{X}F^{\alpha}_{\mu_A\nu_A}$, $\mu \neq \nu$, elements, though this is not the case for the more sophisticated INDO and NDDO levels of approximation.

Since the determination of the coefficients of each AO $\mu, \nu, \lambda, \sigma \ldots$ in each molecular orbital of the system proceeds by a diagonalization of the F^{α} matrices (which may (e.g. ab initio methods) or may not (e.g. the NDO methods and others employing the ZDO approximation, $S = 1$) have been first transformed to correspond to an orthogonal atomic orbital $(OAO)^2$ basis), the degree of mixing the AO's (or OAO's) to form the MO's very much depends on the magnitude of the off-diagonal connecting F^{α} elements, and the off-diagonal one-centre ${}^{X}F^{\alpha}$ elements certainly play a part in this mixing.

However, it is the two-centre off-diagonal ${}^{X}F^{\alpha}$ elements, ${}^{X}F^{\alpha}_{\mu_A\nu_B}$, which play the greatest part in the mixing of AO's to form MO's (with OAO's, the corresponding *transformed* F^{α} elements . . . .). Consequently great care must be exercised in their evaluation. Inspection of the composition of these elements (8) shows that the magnitude of these elements depends on a complex interplay of positive and negative terms corresponding to repulsive and attractive terms respectively. In some highly simplified methods, these elements are evaluated simply through some proportionality to the geometric or arithmeric means of the diagonal elements, $F^{\alpha}_{\mu_A\mu_A}$ and $F^{\alpha}_{\nu_B\nu_B}$, and in other methods, notably all the NDO methods, CNDO, INDO and NDDO, these two-centre F^{α} elements are parametrized directly from ab initio calculations on the appropriate diatomic, AB. This latter situation is demanded by the fact that the NDO two-electron integral approximations themselves would eliminate all but one minor two-electron contribution to these elements; it of course neglects any contribution from the last two three-centre terms of eqn. (8).

Since the balance between attractive and repulsive terms in these elements will vary particularly widely through inorganic systems where even the qualitative bonding existing between any given pair of atoms can vary greatly from compound to compound, it would appear important to allow for the consequent changes in the degree and nature of covalency from compound to compound by accurately determining the balance of contributions to the ${}^{X}F^{\alpha}_{\mu_A \nu_B}$ elements in each case. To maintain any real predictive capability in an approximate MO method at the semi-quantitative level, therefore, it would appear necessary[31] to evaluate explicitly the terms given in eqn. (8). As the CNDO (and most other semi-quantitative methods) schemes fail to do this, the author believes that they should not be treated as an in any way general means of obtaining reliable wave functions in this area.

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NOTE ADDED IN PROOF

The flexibility of the RHF scheme does not extend to cover more than one open shell of a given symmetry. It was recently noted that a number of attempted extensions of the RHF formalism for this purpose have proved unsatisfactory (see; R. Albat and N. Gruen, *Chem. Phys. Lett.*, 18 (1973) 572).