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Approximate Molecular Orbital Theory for Inorganic Molecules

I. Analysis of Possible Integral Approximations

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As a first stage in the development of a suitable molecular orbital method for treating inorganic systems, we consider the possible integral approximations that may be made to reduce the complexity of the computation. The significance of invariance of the approximations to different transformations is discussed and the effect of various levels of neglect of differential overlap is analysed by the S-expansion technique. A method – the many-centre ZDO method – that is computationally feasible but contains more information than the widely used CNDO approximation is given particular consideration.

Als erste Stufe in der Entwicklung einer geeigneten Molekular-orbital-Methode für die Behandlung anorganischer Systeme untersuchen wir mögliche Integralnäherungen, die geeignet sind, die Berechnungen zu vereinfachen. Die Bedeutung der Invarianz der Näherungen unter verschiedenen Transformationen wird diskutiert und der Einfluß verschiedener Stufen der Vernachlässigung der differentiellen Überlappung wird mit der S-Entwicklungstechnik analysiert. Einer Methode, der Vielzentren-ZDO-Methode, die rechnerisch gut durchführbar ist, aber mehr an Information enthält als die meistens benutzte CNDO-Näherung, wird besondere Beachtung geschenkt.

Dans une première étape lors du développement d'une méthode d'orbitales moléculaires convenant aux systèmes inorganiques, nous envisageons les approximations possible pour les intégrales. On discute la signification de l'invariance des ces approximations par rapport à différentes transformations et l'on analyse par la technique du développement en S l'effet des différents niveaux d'approximation du recouvrement différentiel nul. On considère en particular une méthode – la méthode ZDO polycentrique – qui s'avère réalisable numériquement tout en contenant plus d'information que l'approximation CNDO couramment utilisée.

1. General Approach

Increasing attention has been paid by theoretical chemists in recent years to the possibilities and problems of devising reliable theoretical methods for use in the investigation of inorganic molecules. Recent calculations in our laboratory, the first of which have been published, [1, 2] have indicated that important difficulties remain in carrying out this task. These difficulties become especially apparent when molecules containing elements of the second row of the Periodic Table or transition metal complexes are considered, but apply also to first row molecules. In this and subsequent papers we attempt to clarify the situation in this field through a systematic analysis of the theoretical factors involved.

The aim is to develop a treatment that is reliable enough to give definitive answers to some of the current controversies – assignment of UV spectra, the role

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of d-orbitals in bonding, the influence of ligand properties on the properties of transition metal complexes, etc. – yet simplified by using a series of approximations. Only in this way can larger inorganic molecules be treated with our present computing facilities. For example, if no approximations are made, the number of unique electron repulsion integrals needed for an *ab initio* molecular orbital calculation of the sulphate anion would be 94,830 (and without including sulphur $3d$-orbitals)! How approximate the methods need to be so that they are at once manageable and give meaningful answers, remains an open question for the moment.

In the present paper we shall survey those methods that have been suggested hitherto – approximations for drastically reducing the number of two-electron integrals, such as neglecting differential overlap – and that might prove fruitful for application to systems where the valence orbitals include d-orbitals and the principal quantum number may range up to four. Although some form of each of these approximations has been described previously our purpose here is to scrutinise these again from first principles and particularly to set out approximations for the one-electron terms in the Hartree-Fock matrix elements that are theoretically compatible with the approximations invoked for the two-electron terms.

In Part II the various parameter schemes that have been suggested will be reviewed to decide which are most appropriate and consistent with the various approximate SCFMO schemes described in Part I. Part III will present exploratory calculations on the sulphate ion designed to test numerically the various approximations described in Part I and the various parameter schemes considered in Part II.

A review of previous comparable work and some commentary on it is given in the concluding section of the present paper.

2. The Basic Framework

The LCAOMO approach adopted here involves the Hartree-Fock approximation, whereby each electron is placed in an average field of the nuclei and other electrons. However if answers of chemical accuracy for energy quantities, such as binding energy and electronic spectra, are to be obtained, electron correlation has to be taken into account. In later papers, it is shown how the Sinanoğlu many-electron theory of atoms and molecules [3–5] provides a way of doing this for approximate methods. Accordingly we consider that the exact many-electron wave function Ψ may be divided into Hartree-Fock (Φ_{HF}) and electron correlation (Φ_{corr}) parts:

$$\Psi = \Phi_{\mathrm{HF}} + \Phi_{\mathrm{corr}} \tag{1}$$

and that each part for the moment may be treated separately.

Here we are concerned only with various approximations to Φ_{HF} and leave to subsequent discussion possible refinements to these approximations together with the treatment of Φ_{corr}.

The secular equation in the LCAOMO approximation, then is (Roothaan [6])

$$\boldsymbol{F}\boldsymbol{C}=\boldsymbol{S}\boldsymbol{C}\boldsymbol{\varepsilon} \tag{2}$$

which we designate "the secular equation in a full overlap basis", giving rise to "full overlap methods".

We also make use of the "secular equation in a Löwdin basis", of orthogonalized atomic orbitals, (Löwdin [7], Slater [8]) the transformation:

$$\boldsymbol{C}=\boldsymbol{S}^{-\frac{1}{2}}\,{}^{\lambda}\boldsymbol{C} \tag{3}$$

leading to the equation

$${}^{\lambda}\boldsymbol{F}\,{}^{\lambda}\boldsymbol{C}={}^{\lambda}\boldsymbol{C}\boldsymbol{\varepsilon} \tag{4}$$

where

$${}^{\lambda}\boldsymbol{F}=\boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{F}\boldsymbol{S}^{-\frac{1}{2}}. \tag{5}$$

As detailed below and in accord with the experience of π-electron theory for organic molecules [9], this gives rise to "zero differential overlap methods", whereby certain integrals involving differential overlap become small enough to be neglected.

General elements of the Hamiltonian matrix $\boldsymbol{F}$ over atomic orbitals χ_μ, χ_ν are given in terms of elements of the core Hamiltonian matrix $\boldsymbol{H}$ and repulsion integrals written in the usual way[1]:

$$F_{\mu\nu}=H_{\mu\nu}+\sum_{\lambda,\sigma} P_{\lambda\sigma}[(\mu\nu|\lambda\sigma)-\tfrac{1}{2}(\mu\sigma|\lambda\nu)] \tag{6}$$

In π-electron theory, the zero differential overlap (ZDO) approximations are applied:

$$S_{\mu\nu}=\delta_{\mu\nu}, \tag{7a}$$

$$(\mu\nu|\lambda\sigma)=0 \text{ unless } \mu=\nu \text{ and } \lambda=\sigma. \tag{7b}$$

Here $\delta_{\mu\nu}$ is the Kronecker δ. Fischer-Hjalmars [9] and others have pointed out that the Hamiltonian matrix formed under the ZDO approximations, $\boldsymbol{F}^{\mathrm{ZDO}}$, obeys the relation:

$$\boldsymbol{F}^{\mathrm{ZDO}}\approx{}^{\lambda}\boldsymbol{F} \tag{8}$$

3. The Development of all Valence Electron Methods

The invariance properties of the many-electron wave function in the LCAOMO approximation have been used recently by Pople, Santry, and Segal [10–12] in establishing criteria for approximate methods for molecules. From these criteria it is possible to develop a number of methods of varying complexity. We may consider these methods in terms of the difficulty of using them in practical calculations, the information that could be obtained from their results, and their degree of approximation. An $\boldsymbol{S}$-expansion technique, similar to the Fischer-Hjalmars expansion technique of π-electron theory [9], proves useful for the latter task.

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[1] Notation: $\iint \chi_\mu^*(1)\chi_\lambda^*(2)\hat{r}_{12}^{-1}\chi_\nu(1)\chi_\sigma(2)\,dv_1\,dv_2 \equiv (\mu\nu|\lambda\sigma) \equiv \langle\mu\lambda|\hat{r}_{12}^{-1}|\nu\sigma\rangle$; $(\mu\mu|\nu\nu)\equiv\gamma_{\mu\nu}$.

3.1 Invariance Criteria

Roothaan [6] has shown that the total energy and eigenvalues for the secular equation (2) are invariant both to an orthogonal transformation of the filled molecular orbitals ϕ among themselves, and to a similar transformation of the basic atomic orbitals χ among themselves.

Pople, Santry, and Segal [10] and Ruttink [13] discussed the latter orthogonal transformation

$$\chi' = \chi \boldsymbol{T}$$

in relation to integral approximations that might be made in approximate SCF calculations. They considered it essential that any approximations made should be such that the calculated total energy remained invariant with respect to rotations of local axes (i. e. transformations in which, for example, the set of three p-orbitals on an atom are mixed). Subsequently Dewar and Klopman [14] used an approximation that did not quite conform to this criterion and found negligible variation of calculated energy upon rotation of local axes. However a potentially more serious flaw is apt to arise if this rotational invariance criterion is neglected when calculating the energies of electronic states belonging to degenerate representations of the point group for highly symmetrical systems, namely [1] substantial deviations from the requisite degeneracies for such states.

Thus in view of this need to preserve an appropriate invariance to at least some categories of orthogonal transformations, the following appear to be the only acceptable alternatives on which to set up approximations for various integrals over the basis functions, χ:

i) The approximations may be developed relative to a standard set of axes. If a new set is chosen, or if hybrid or symmetry orbitals are used as a basis set, the approximations no longer apply.

ii) Approximations invariant to rotations of the local axes may be set up. If a new set of local axes is chosen, the same approximations still apply, but if a new basis set of hybrid or symmetry orbitals is used, they no longer apply.

iii) The approximations may be developed invariant to any local orthogonal transformation. In this case they would apply in a basis of atomic orbitals for any orientation of the local axes, and in a basis of hybrid orbitals, but not for a basis of symmetry orbitals. This is the criterion used by Pople, Santry, and Segal [10, 11].

iv) Approximations invariant to a general orthogonal transformation applicable for any choice of basis orbitals, may be considered, but would involve the inclusion of all integrals.

3.2. Partitioning of the Hamiltonian Matrix

If cases (i), (ii) or (iii) of the invariance criteria listed above apply, a further partitioning of the Hamiltonian matrix is useful, since any orbital χ'_m on a particular atom A is a function only of other orbitals in the original basis on that same atom:

$$\chi'_m = \sum_{\mu}^{\mathrm{A}} T_{m\mu} \chi_\mu \,. \tag{10}$$

Then monocentric integrals in the original basis remain monocentric integrals in the new basis, and similarly for two-centre integrals and for many-centre integrals.

For the core Hamiltonian matrix $\boldsymbol{H}$ the obvious partitioning into one-centre and two-centre terms is suggested:

$$\boldsymbol{H} = \boldsymbol{H}^{1c} + \boldsymbol{H}^{2c}, \tag{11}$$

the elements of $\boldsymbol{H}^{1c}$ obeying the condition

$$\boldsymbol{H}^{1c}_{\mu\nu} = 0$$

unless χ_μ and χ_ν are orbitals on the same centre, while for those of $\boldsymbol{H}^{2c}$

$$\boldsymbol{H}^{2c}_{\mu\nu} = 0$$

unless χ_μ and χ_ν are on different centres.

Partitioning of the electron repulsion part of the Hamiltonian matrix is somewhat arbitrary. The simplest approach would be to form one-centre and many-centre parts, the latter including two-centre integrals:

$$\boldsymbol{G} = \boldsymbol{G}^{1c} + \boldsymbol{G}^{mc} \tag{12}$$

with

$$\boldsymbol{G}^{1c}_{\mu\nu} = 0$$

for χ_μ and χ_ν on different centres, and

$$G^{1c}_{\mu\nu} = \sum_{\lambda\sigma}^{\mathrm{A}} P_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma) - \tfrac{1}{2}(\mu\sigma|\lambda\nu)\right]$$

for χ_μ and χ_ν on the same atom A and the summation being over all orbitals χ_λ and χ_σ on A. $\boldsymbol{G}^{mc}$ covers all other terms in $\boldsymbol{G}$, including the two- and three-centre parts of the elements $G_{\mu\nu}$ with χ_μ and χ_ν on the same atom.

The full partitioning of G^{mc} may be written:

$$\boldsymbol{G}^{mc} = \boldsymbol{G}^{\mathrm{AA}}_{\mathrm{BB}} + \boldsymbol{G}^{\mathrm{AA}}_{\mathrm{AB}} + \boldsymbol{G}^{\mathrm{AB}}_{\mathrm{AB}} + \boldsymbol{G}^{\mathrm{AA}}_{\mathrm{BC}} + \boldsymbol{G}^{\mathrm{AB}}_{\mathrm{AC}} + \boldsymbol{G}^{\mathrm{AB}}_{\mathrm{CD}} \tag{13}$$

in which for instance the matrix $\boldsymbol{G}^{\mathrm{AA}}_{\mathrm{BB}}$ collects all elements involving repulsion integrals $(\mu\nu|\lambda\sigma)$ with χ_μ and χ_ν both on atom A, χ_λ and χ_σ both on atom B, for all A and B except A = B. The other parts of $\boldsymbol{G}^{mc}$ may be defined similarly. In full, the elements of $\boldsymbol{G}^{\mathrm{AA}}_{\mathrm{BB}}$ are:

$$(G^{\mathrm{AA}}_{\mathrm{BB}})_{\mu\nu} = \sum_{\lambda}^{\mathrm{B}} \sum_{\sigma}^{\mathrm{B}} P_{\lambda\sigma}(\mu\nu|\lambda\sigma)$$

for χ_μ and χ_ν on the same centre A, different from B, and

$$(G^{\mathrm{AA}}_{\mathrm{BB}})_{\mu\lambda} = -\tfrac{1}{2} \sum_{\nu}^{\mathrm{A}} \sum_{\sigma}^{\mathrm{B}} P_{\lambda\sigma}(\mu\nu|\sigma\lambda)$$

for χ_μ and χ_λ on different centres, A and B, respectively.

On theoretical grounds, the two-centre terms involving only A and B, are likely to be the more important, and of these the $\boldsymbol{G}^{\mathrm{AA}}_{\mathrm{BB}}$ would make the largest contribution.

The invariance conditions apply equally to each part of the total $\boldsymbol{H}$ and $\boldsymbol{G}$ matrices in Eqs. (11), (12), and (13) for local orthogonal transformations. Therefore we can form approximations separately for each part, taking into account the magnitude of the contribution of that part to the whole. For example the neglect of a non-zero repulsion integral in G^{1c} is likely to be more drastic than the neglect of a corresponding integral in G^{mc}. The position is one of balancing up information lost against ease of computation gained as approximations are made subject to the invariance conditions.

3.3. Zero Differential Overlap Methods

If we orthogonalize the basis atomic orbitals by Löwdin's procedure, then the overlap matrix becomes a unit matrix, satisfying the first ZDO condition (7a), with no loss of accuracy. Evidence has been obtained in π-electron theory [9, 15], in all electron calculations on small molecules [16], and through the $\boldsymbol{S}$-expansion technique (Sect. 4), that electron repulsion integrals involving products of orbitals on different centres become very small in the Löwdin basis. Zero differential overlap methods usually begin with the neglect of such integrals, so that the Hamiltonian matrix is reduced to:

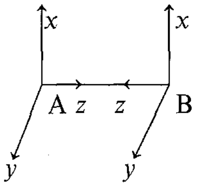
$$\boldsymbol{F} = \boldsymbol{H}^{1c} + \boldsymbol{H}^{2c} + \boldsymbol{G}^{1c} + \boldsymbol{G}^{\mathrm{AA}}_{\mathrm{BB}} \,. \tag{14}$$

There are now numerous ways of making further reductions, since each part of $\boldsymbol{F}$ of Eq. (14) may be treated quite separately, and may be subjected to any of the rotational invariance conditions (i) to (iii) of Sect. 3.1. We may decide to proceed with no further approximations, thus obtaining the "Neglect of Diatomic Differential Overlap" (NDDO) method [10], which automatically obeys the rotational invariance criterion (iii). We may decide to make approximations only in $\boldsymbol{G}^{\mathrm{AA}}_{\mathrm{BB}}$, which is the most difficult and time-consuming part of $\boldsymbol{F}$ to calculate. This is the basis of the diatomic approximate methods (Sect. 3.3) in which rotational invariance criterion (i) is applied, and the many-centre ZDO method (Sect. 3.5), in which rotational invariance criterion (ii) is applied. Or we may decide to apply the ZDO assumption (7b) rigorously to all integrals in $\boldsymbol{H}^{1c}, \boldsymbol{G}^{1c}$ and $\boldsymbol{G}^{\mathrm{AA}}_{\mathrm{BB}}$, eliminating integrals involving products of different orbitals on the same centre. Pople, Santry, and Segal [10] have shown that this necessitates averaging the remaining integrals in order that the approximations be invariant to local orthogonal transformations, criterion (iii). The number of parameters is reduced to an average Coulomb repulsion integral for each atom (denoted by γ_{A}) and each pair of atoms (γ_{AB}), and corresponding average nuclear attraction integrals ($V^{\mathrm{AA}}_{\mathrm{A}}$ and $V^{\mathrm{BB}}_{\mathrm{A}}$), where $V^{\mathrm{BB}}_{\mathrm{A}}$ measures the attraction of a unit positive charge at the nucleus of A for an electron on atom B. This is the "Complete Neglect of Differential Overlap" (CNDO) method. Since under the strict application of ZDO the elements of $\boldsymbol{H}^{2c}$ would become zero, $\boldsymbol{H}^{2c}$ is given special consideration here, an important matter to be considered in Part II of this series of papers.

Obviously we have not exhausted the number of methods which may be devised, but we have characterized "Zero differential overlap methods" in general as involving a basis of Löwdin orthogonalized atomic orbitals, the neglect of all parts of $\boldsymbol{G}^{mc}$ except $\boldsymbol{G}_{\mathrm{BB}}^{\mathrm{AA}}$, and the solution of the secular Eq. (4). We now consider the particular possibilities in more detail.

3.4. Diatomic Approximate Methods

The actual theoretical evaluation of two-centre integrals is generally carried out relative to the conventional diatomic axis set illustrated below:



consisting of a right-handed set of axes on centre A, and parallel left-handed set on B, the x axes in each case being along the internuclear axis.

Values of integrals found relative to this set are then transformed to the required axis set by the transformation (9), in which the basis χ now refers to the diatomic axes. Computationally, this is a fairly simple process.

Therefore, we may examine the magnitude of integrals relative to diatomic axes for the purpose of making approximations. Then all integrals in any other basis expressible in terms of non-zero diatomic integrals are calculated by the transformation. In the diatomic basis, two-centre Coulomb repulsion integrals $(\mu_{\mathrm{A}}\mu_{\mathrm{A}}|\lambda_{\mathrm{B}}\lambda_{\mathrm{B}})$ are an order of magnitude larger than any of the others, and fortunately are also the easiest to calculate. This leads to the Diatomic ZDO Method:

i) We adopt the ZDO approximations

$$S_{\mu\nu} = \delta_{\mu\nu}$$

$$\langle\mu_{\mathrm{A}}|\hat{M}|\lambda_{\mathrm{B}}\rangle = 0, \mathrm{A} \neq \mathrm{B}$$

relative to a diatomic axis set.

ii) All monocentric integrals are included.

iii) Relative to a diatomic axis set, only two-centre Coulomb-type integrals are included. These refer to nuclear attraction integrals $\langle\mu_{\mathrm{A}}|\hat{V}_{\mathrm{B}}|\mu_{\mathrm{A}}\rangle$ and Coulomb electron repulsion integrals $\langle\mu_{\mathrm{A}}\mu_{\mathrm{A}}|\lambda_{\mathrm{B}}\lambda_{\mathrm{B}}\rangle$.

iv) Integrals relative to any desired choice of local axes are then generated from the equation:

$$\langle m_{\mathrm{A}}|\hat{M}|n_{\mathrm{A}}\rangle = \sum_{\mu} T_{m\mu} T_{n\mu} \langle\mu_{\mathrm{A}}|\hat{M}|\mu_{\mathrm{A}}\rangle$$

Such a procedure is intermediate in complexity between the NDDO and CNDO approximations. It removes the more difficult integrals necessary for an NDDO calculation, while retaining directional qualities lost in the CNDO approach. It is an example of case (i) of the rotational invariance criteria, in which the approximations apply only for the standard set of diatomic axes.

3.5. *The* CNDO *and* NDDO *Approximations*

The invariance conditions for the CNDO approximation mean that only average nuclear attraction integrals, $V_{\mathrm{A}}^{\mathrm{AA}}$ and $V_{\mathrm{A}}^{\mathrm{BB}}$ and electron repulsion integrals γ_{A} and γ_{AB}, need be found for each atom and each pair of atoms present in the molecule. As mentioned in Sect. 3.3, special treatment is given to the non-zero elements of $\boldsymbol{H}^{2c}$, which are usually called resonance integrals and given the symbol $\beta_{\mu\lambda}^{\mathrm{AB}}$. If, as in Ref. [10, 12], direct proportionality of the resonance integral to the overlap integral prior to orthogonalization is assumed: i. e.:

$$H_{\mu\lambda}^{2c} \equiv \beta_{\mu\lambda}^{\mathrm{AB}} = k_{\mathrm{AB}} S_{\mu\lambda} \tag{15}$$

then the constant of proportionality k_{AB} should depend only on the atoms A and B themselves, and not upon the particular orbitals χ_μ and χ_λ involved. However, better theoretical formulae for the resonance integrals will be set out in Part II of this series, and examined in practice in Part III. The Hamiltonian matrix elements (6) become [10]:

$$F_{\mu\mu}^{\mathrm{AA}} = \alpha_\mu + (P_{\mathrm{AA}} - \tfrac{1}{2} P_{\mu\mu})\, \gamma_{\mathrm{A}} + \sum_{\mathrm{B} \neq \mathrm{A}} P_{\mathrm{BB}} \gamma_{\mathrm{AB}}\,, \tag{16}$$

$$F_{\mu\nu}^{\mathrm{AA}} = -\tfrac{1}{2} P_{\mu\nu} \gamma_{\mathrm{A}}\,, \tag{17}$$

$$F_{\mu\lambda}^{\mathrm{AB}} = \beta_{\mu\lambda} - \tfrac{1}{2} P_{\mu\lambda} \gamma_{\mathrm{AB}} \tag{18}$$

where, for simplicity, the particular centre A or B to which the orbitals belong is indicated on the left only, and $\boldsymbol{P}_{\mathrm{AA}}$ = total electron population on A $= \sum_{\mu}^{\mathrm{A}} P_{\mu\mu}$. In the above

$$\alpha_\mu \equiv H_{\mu\mu}^{1c} = \text{Coulomb integral for } \chi_\mu \text{ on atom A.}$$

Although the CNDO approximation may be extremely useful as a rapid way of obtaining semi-quantitative information, a number of limitations of the method are immediately apparent. The procedure of taking an average integral for each atom and each pair of atoms present leads to a loss of information content with respect to such matters as the relative importance of, say, *s*- and *p*-orbitals on the same centre. When *d*-orbitals are to be included, this problem becomes acute, since integrals involving these orbitals are quite different in magnitude from those involving *s*- and *p*-orbitals, and in using an average integral these differences are glossed over. Leaving out monocentric exchange-repulsion integrals $(\mu\nu|\nu\mu)$ means leaving out quantities of up to 4–5 eV and the failure of CNDO in some cases to give singlet-triplet splitting in the calculated electronic spectra. There are, then, deficiencies inherent in the method, which may be overcome to some extent by a judicious choice of parameters, but which mean that the limitations of the method and even qualitative conclusions drawn from it have to be carefully considered.

Some of these deficiencies may be corrected by requiring invariance of the approximations to rotations of local axes only (invariance criterion (ii)), rather than to general local orthogonal transformations, and using the separation of the $\boldsymbol{G}$ matrix in Eq. (12). We maintain the average two centre integrals γ_{AB} and $V_{\mathrm{A}}^{\mathrm{BB}}$, an approximation that is not too drastic, even when *d*-orbitals are included, in the cases studied. Under a rotation of the local axes on atom A, say, the *s*-orbitals remain unaffected, while the three *p*-orbitals transform among themselves, as do the five *d*-orbitals. Invariance requirements are met if we use an average integral for each set of orbitals, M_s, $M_{\bar{p}}$ and $M_{\bar{d}}$. Then, taking the example of *p*-orbitals only, we may put

$$\langle p|\hat{M}|p'\rangle = M_{\bar{p}}\delta_{pp'} \tag{19}$$

and we have for instance an average Coulomb repulsion integral per set of orbitals and pair of sets on each centre, $\gamma_{ss}, \gamma_{\bar{p}\bar{p}}, \gamma_{\bar{d}\bar{d}}, \gamma_{sp}, \gamma_{sd}$ and $\gamma_{\bar{p}\bar{d}}$. The bar indicates that an average integral is required, while in the other cases there is only one such integral (as for γ_{ss}) or the integrals have equal values (e. g. $\gamma_{sp_x} = \gamma_{sp_y} = \gamma_{sp_z}$). If a new basis of hybrid orbitals is chosen, all monocentric integrals with contributions from the integrals given here would have to be included. The significance of this modification of the CNDO approximation is that important distinctions between *s*-, *p*- and *d*-orbitals on the one centre are maintained in the calculations. It will be called the "rotational invariance only CNDO method".

In the NDDO approximation [10], the distinction between overlap charge densities $\mu_A\nu_A$ and $\mu_A\lambda_B$ is recognised, all integrals containing the former being included while those containing the latter are neglected. For repulsion integrals this means that all $(\mu\nu|\lambda\sigma) = 0$ unless χ_μ and χ_ν are on the same centre A and χ_λ and χ_σ are the same centre B, which may equal A. Then the Hamiltonian matrix elements become:

$$F_{\mu\mu}^{AA} = \alpha_\mu + \tfrac{1}{2}P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\nu\neq\mu}^{A} P_{\nu\nu}[(\mu\mu|\nu\nu) - \tfrac{1}{2}(\mu\nu|\nu\mu)] + \sum_{B}\sum_{\lambda,\sigma}^{B} P_{\lambda\sigma}(\mu\mu|\lambda\sigma)\,, \tag{20}$$

$$F_{\mu\nu}^{AA} = \beta_{\mu\nu} + P_{\mu\nu}[\tfrac{3}{2}(\mu\nu|\nu\mu) - \tfrac{1}{2}(\mu\mu|\nu\nu)] + \sum_{B}\sum_{\lambda,\sigma}^{B} P_{\lambda\sigma}(\mu\nu|\lambda\sigma)\,, \tag{21}$$

$$F_{\mu\lambda}^{AB} = \beta_{\mu\lambda} - \tfrac{1}{2}\sum_{\nu}^{A}\sum_{\sigma}^{B} P_{\sigma\nu}(\mu\nu|\lambda\sigma)\,. \tag{22}$$

The NDDO approximation seems to overcome all of the more serious deficiencies inherent in the CNDO approach. In practice it is still quite complex and time-consuming. Some idea of the advantages and problems of the method follow from a consideration of the number of unique repulsion integrals for an all valence electron calculation on tetrahedral oxyanions, in which *s*-, *p*- and *d*-orbitals on the central atom, and *p*-orbitals only on the oxygen atoms are used:

No. of unique repulsion integrals in full calculation = 26,796,
No. of unique repulsion integrals in NDDO calculation = 2,415,
No. of unique repulsion integrals in CNDO calculation = 15.

There is a dramatic reduction to be gained in doing an NDDO calculation rather than a full calculation. However, the number remaining is still considerable, especially when compared with the CNDO total. Admittedly some of these will be zero by symmetry, depending upon the particular case. Nevertheless, the calculation of all of the non-zero integrals is time consuming, and the size of the system that can be treated by an NDDO method becomes limited by the computer store available.

3.6. The Many-Centre Z. D. O. *Method*

By recognizing the difference in transformation properties between one-centre and two-centre repulsion integrals, a considerable simplification of the NDDO method becomes possible. After the NDDO approximation, the full Hamiltonian may be written:

$$\boldsymbol{F} = \boldsymbol{H} + \boldsymbol{G}^{1c} + \boldsymbol{G}^{AA}_{BB} \tag{23}$$

each part of which may be examined separately. All integrals in the matrices $\boldsymbol{H}$ and $\boldsymbol{G}^{1c}$ are fairly readily evaluated theoretically, while those in $\boldsymbol{G}^{AA}_{BB}$ present the most difficulty. The many-centre ZDO method results if the ZDO approximations are applied to all many-centre, including two-centre, repulsion integrals, while core elements and one-centre repulsion integrals are calculated without using a ZDO approximation. Then the conditions for invariance to local orthogonal transformations are automatically satisfied for $\boldsymbol{H}$ and $\boldsymbol{G}^{1c}$, and we may stipulate invariance to rotations of local axes (criterion (ii)) for approximations of $\boldsymbol{G}^{AA}_{BB}$ as being the most useful case having least loss of information in practice. Thus the many-centre ZDO method consists of:

i) No ZDO approximations are made for core elements (apart from core-valence electron separability), or for monocentric repulsion integrals. By symmetry, only monocentric Coulomb $(\mu\mu|\nu\nu)$ and exchange $(\mu\nu|\nu\mu)$ repulsion integrals are non-zero.

ii) The ZDO approximation is rigorously applied to all many-centre repulsion integrals, including two centre repulsion integrals.

$$\text{i. e. } (\mu\nu|\lambda\sigma) = 0 \quad \text{unless } \mu = \nu,\ \lambda = \sigma .$$

iii) In order to satisfy the conditions of invariance of (ii) to rotations of local axes, the remaining two-centre Coulomb repulsion integrals are averaged per set of orbitals on each centre. That is we have the average Coulomb repulsion-integrals between two-centres: $\gamma^{AB}_{ss}, \gamma^{AB}_{s\bar{p}}, \gamma^{AB}_{\bar{p}s}, \gamma^{AB}_{\bar{p}\bar{p}}$, etc. (For invariance to any local transformation, this procedure would be replaced by taking an average repulsion integral per pair of centre, γ_{AB}.)

The Hamiltonian matrix elements become

$$F^{AA}_{\mu\mu} = H_{\mu\mu} + \tfrac{1}{2}P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\nu\neq\mu}^{A} P_{\nu\nu}[(\mu\mu|\nu\nu) - \tfrac{1}{2}(\mu\nu|\nu\mu)] + \sum_{B\neq A}\sum_{\lambda}^{B} P_{\lambda\lambda}\gamma_{\bar{\mu}\bar{\lambda}}\,, \tag{24}$$

$$F^{AA}_{\mu\nu} = H_{\mu\nu} + P_{\mu\nu}[\tfrac{3}{2}(\mu\nu|\nu\mu) - \tfrac{1}{2}(\mu\mu|\nu\nu)]\,, \tag{25}$$

$$F^{AB}_{\mu\lambda} = H_{\mu\lambda} - \tfrac{1}{2}P_{\mu\lambda}\gamma_{\bar{\mu}\bar{\lambda}} \tag{26}$$

where $\gamma_{\bar{\mu}\bar{\lambda}}$ is the average Coulomb repulsion integral over all orbitals χ_ν and χ_σ having the same l quantum numbers as χ_μ and χ_λ, and being on the same respective centres.

The advantages of the many-centre ZDO method are that it eliminates the more difficult integrals of the NDDO approximation while promising results of the same order of accuracy, provided that two-centre repulsion integrals $(\mu_A\nu_A|\lambda_B\sigma_B)$ are small, as seems to be the case. The savings of computer time and space are considerable for larger systems. Failures of the CNDO approximation in distinguishing properly between orbitals on the one centre and in neglecting one-centre exchange repulsion integrals are eliminated. In addition the core element $H_{\mu\nu}^{AA}$, which turns out to have non-negligible values, is included, and there is the possibility of calculating all core elements purely theoretically.

One of the main ideas of the many-centre ZDO method, that of including one-centre exchange integrals, has been independently proposed in recent papers by Dixon [17] and by Pople, Beveridge, and Dobosh [18]. However the many-centre ZDO method differs from the methods of these authors in the full evaluation of core Hamiltonian elements, in the use of average two-centre Coulomb repulsion integrals per set of orbitals of the same type on each centre, and in the way the parameters are obtained (see Part II of this series of papers).

The many-centre ZDO method has grown out of extensive attempts to apply the CNDO and NDDO approximations to systems having *d*-orbitals on at least one atom. It is here that the CNDO method breaks down in many ways, while the NDDO method is most difficult to apply. We would expect the many-centre ZDO method to find most of its application in systems too large to be treated by the NDDO method, either because *d*-orbitals are included or the molecule contains too many atoms. It is particularly appropriate for transition metal-complexes and for all-valence electron calculations on larger organic molecules.

3.7. Approximate Full Overlap Methods

Full overlap methods are those in which the overlap integral, and integrals involving two-centre charge distributions, are included, the secular determinant

$$|\boldsymbol{F}-\boldsymbol{S}\varepsilon|=0$$

having to be solved. Ways of handling the difficult many-centre integrals are now required.

One way is to use the Mulliken approximation [17], in which each two-centre charge distribution is replaced as follows:

$$\chi_\mu^A \chi_\lambda^B = \frac{S_{\mu\lambda}}{2}(\chi_\mu\chi_\mu + \chi_\lambda\chi_\lambda). \tag{27}$$

Ruttink [13] and Manné [18] have shown that the Mulliken approximation is invariant to local orthogonal transformations only when average one- and two-centre integrals are used, i. e.

$$\langle\mu_A|\hat{M}|\lambda_B\rangle = \frac{S_{\mu\lambda}}{2}[M_{AA}+M_{BB}], \tag{28}$$

$$(\mu_A\nu_B|\lambda_C\sigma_D) = \frac{S_{\mu\nu}S_{\lambda\sigma}}{4}[\gamma_{AC}+\gamma_{AD}+\gamma_{BC}+\gamma_{BD}]. \tag{29}$$

Since these are also the CNDO conditions, the Mulliken method consists of the CNDO integrals as already discussed, plus many-centre integrals calculated via the Mulliken approximation. Repulsion integrals that contain the product $\mu_A\nu_A$, χ_μ and χ_ν being different orbitals, are neglected.

From the fact that atomic orbitals on one centre may be expanded without approximation in terms of a complete set of atomic orbitals on another centre, Ruedenberg [19] in 1951 derived the exact expansion:

$$\langle \mu_A | \hat{M} | \lambda_B \rangle = \tfrac{1}{2}\left\{ \sum_{\nu}^{A} S_{\nu\lambda} \langle \mu | \hat{M} | \nu \rangle + \sum_{\sigma}^{B} S_{\sigma\mu} \langle \lambda | \hat{M} | \sigma \rangle \right\} \tag{30}$$

expressing two centre charge distributions in terms of one-centre distributions. For truncated sets of orbitals, as used here, this expansion is an approximation, and has the required invariance properties, provided that all integrals containing $\mu_A \nu_A$ products are included [13, 19]. Since these are also the NDDO conditions the Ruedenberg method consists of the NDDO integrals as already discussed, together with the addition of all other integrals via the Ruedenberg approximation.

3.8. Relationship of Approximate Methods

The relationship of the all-valence-electron methods described in this paper is illustrated in the Table. The zero differential overlap methods are assumed to be in a Löwdin basis of atomic orbitals, while the Mulliken and Ruedenberg methods are assumed to be in a full overlap basis, and the secular determinants to be solved are

$$|{}^{\lambda}F - \varepsilon| = 0 \tag{31}$$

in the first case, and

$$|F - S\varepsilon| = 0$$

which may be rewritten

$$|S^{-\frac{1}{2}} F S^{-\frac{1}{2}} - \varepsilon| = 0 \tag{32}$$

in the second case.

In the second part of the table the methods are considered from the point of view of their inclusion or otherwise of electron repulsion integrals.

Table. *Relationship of all valence methods*

The Hamiltonian Matrix

$F^{\text{CNDO}} \doteq F^{\text{Many-centre ZDO}} \doteq F^{\text{NDDO}} \doteq {}^{\lambda}F$ (Löwdin Basis)

$F^{\text{Mulliken}} \doteq F^{\text{Ruedenberg}} \doteq F^{\text{ Full overlap basis}}$

Inclusion of repulsion integrals

Method	CNDO	⟶	Mulliken
Electron	Average		γ_A, γ_{AB} +
Repulsion	γ_A, γ_{AB}		Many-centre
	↓		│
Integrals	Many-centre ZDO all monocentric + orbital average two centre		│
	↓		↓
	NDDO	⟶	Ruedenberg
	all with one centre charge distributions		all integrals

If some appropriate averaging of Coulomb electron repulsion integrals is explicitly for each atom and each pair of atoms present, then the conventional CNDO method or the "rotational invariance only" CNDO method is obtained (Sect. 3.5).

We may now proceed in either of two ways. On relaxing the condition of average Coulomb repulsion integrals by including all one-centre integrals and two-centre Coulomb integrals averaged per set of orbitals, we have the many-centre ZDO method. By further including all two-centre integrals involving monatomic charge distributions, we have the NDDO method.

On the other hand the Mulliken method is reached from CNDO by allowing many-centre integrals not involving $\mu_A \nu_A$ with $\mu_A \neq \nu_A$ to be included.

Finally the Ruedenberg method includes all other repulsion integrals not evaluated in the NDDO method on the one hand, and in the Mulliken method on the other.

Because of these relationships, some important questions may be answered by a comparison of results obtained with the different methods:

i) What are the limitations of the zero differential overlap type methods in their various forms? Are such methods good enough for the predictions of experimental properties?

ii) Which of the types of electron repulsion integrals are important in all-valence-electron calculations? Is it reasonable to neglect any or all of many-centre integrals involving $\mu_A \nu_B, A \neq B$; many-centre integrals involving $\mu_A \nu_A$, $\mu_A \neq \nu_A$; one-centre exchange integrals?

iii) What is the effect of various approximations to ZDO core elements?

In Part III, we present some comparative calculations on the sulphate anion which attempt to answer these questions. Meanwhile we may utilize an S-expansion technique to evaluate the possible accuracy of the approximate methods so far described.

4. Evaluation of Approximate Methods: S-Expansion Technique

To examine the significance of neglecting various integrals according to the NDDO, many-centre ZDO and CNDO methods it is expedient to use the S-expansion technique developed by Fischer-Hjalmars for π-electron systems [9], [22]. The technique is based on earlier work by Löwdin [23]. Here we generalize the technique for the case where all of the *valence* electrons and more than one orbital per centre in a molecular system are to be specifically treated, and we obtain a justification of the ZDO approximations made in section 3, together with estimates of the likely accuracy of each of the ZDO methods and further information on their relationship to the full overlap methods. Some of the formulae derived may be used directly in the estimation of elements of the Fock Hamiltonian matrix ${}^{\lambda}\boldsymbol{F}$. This analysis starts with the Löwdin transformation for one-electron operators:

$$ {}^{\lambda}\boldsymbol{M} = \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{M} \boldsymbol{S}^{-\frac{1}{2}} \tag{33} $$

and the binomial expansion of $\boldsymbol{S}^{-\frac{1}{2}}$:

$$ \boldsymbol{S}^{-\frac{1}{2}} = (\boldsymbol{1} + \boldsymbol{d})^{-\frac{1}{2}} = \boldsymbol{1} - \tfrac{1}{2}\boldsymbol{d} + \tfrac{3}{8}\boldsymbol{d}^2 - \tfrac{5}{16}\boldsymbol{d}^3 + \cdots \tag{34} $$

where $\mathbf{1}$ is the unit matrix and $\boldsymbol{d}$ is the overlap matrix but with zero diagonal elements.

We may now proceed to examine the elements of the Hartree-Fock Hamiltonian ${}^{\lambda}\boldsymbol{F}$ by following the $\boldsymbol{S}$-expansion to the first order and then to the second order in $\boldsymbol{d}$.

4.1. Expansion to the First Order in Overlap

To the first order in the overlap integral

$$\begin{aligned} {}^{\lambda}\boldsymbol{M} &= \boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{M}\boldsymbol{S}^{-\frac{1}{2}} \\ &= (\mathbf{1}-\tfrac{1}{2}\boldsymbol{d})\,\boldsymbol{M}(\mathbf{1}-\tfrac{1}{2}\boldsymbol{d}) + O(S^2) \\ &= \boldsymbol{M} - \tfrac{1}{2}\boldsymbol{M}\boldsymbol{d} - \tfrac{1}{2}\boldsymbol{d}\boldsymbol{M} + O(S^2)\,. \end{aligned} \tag{35}$$

This will hold for core elements ${}^{\lambda}\boldsymbol{M}_{\mu\nu}$, and for one-electron charge distributions ${}^{\lambda}\Omega_{\mu\nu}$, where the repulsion integrals may be written:

$${}^{\lambda}(\mu\nu\,|\,\lambda\sigma) = ({}^{\lambda}\Omega_{\mu\nu}\,|\,{}^{\lambda}\Omega_{\lambda\sigma}) \tag{36}$$

The elements of the matrix ${}^{\lambda}\boldsymbol{M}$ in terms of those in the full overlap basis $\boldsymbol{M}$, are:

$${}^{\lambda}M^{\mathrm{AA}}_{\mu\mu} = M_{\mu\mu} - \sum_{\mathrm{B}\neq\mathrm{A}}\sum_{\lambda}^{\mathrm{B}} S_{\mu\lambda}M_{\mu\lambda} + O(\boldsymbol{S}^2)\,, \tag{37}$$

$${}^{\lambda}M^{\mathrm{AA}}_{\mu\nu} = M_{\mu\nu} - \tfrac{1}{2}\sum_{\mathrm{B}\neq\mathrm{A}}\sum_{\lambda}^{\mathrm{B}} [M_{\mu\lambda}S_{\lambda\nu} + S_{\mu\lambda}M_{\lambda\nu}] + O(\boldsymbol{S}^2)\,, \tag{38}$$

$${}^{\lambda}M^{\mathrm{AB}}_{\mu\lambda} = M_{\mu\lambda} - \frac{S_{\mu\lambda}}{2}(M_{\mu\mu} + M_{\lambda\lambda}) - \tfrac{1}{2}\sum_{\mathrm{C}}\sum_{\sigma\neq\mu,\lambda}^{\mathrm{C}} [M_{\mu\sigma}S_{\sigma\lambda} + S_{\mu\sigma}M_{\sigma\lambda}] + O(S^2) \tag{39}$$

noting that $d_{\mu\mu} = 0$ and $d_{\mu\nu} = S_{\mu\nu}$.

In the Löwdin basis, then, the core elements ${}^{\lambda}\alpha_{\mu}$ and ${}^{\lambda}\beta_{\mu\nu}$ become:

$${}^{\lambda}\alpha_{\mu} = \alpha_{\mu} - \sum_{\mathrm{B}\neq\mathrm{A}}\sum_{\lambda} S_{\mu\lambda}\beta_{\mu\lambda} + O(S^2)\,, \tag{40}$$

$${}^{\lambda}\beta^{\mathrm{AA}}_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2}\sum_{\mathrm{B}\neq\mathrm{A}}\sum_{\lambda}^{\mathrm{B}} [\beta_{\mu\lambda}S_{\lambda\nu} + S_{\mu\nu}\beta_{\lambda\nu}] + O(S^2)\,, \tag{41}$$

$${}^{\lambda}\beta^{\mathrm{AB}}_{\mu\lambda} = \beta_{\mu\lambda} - \frac{S_{\mu\lambda}}{2}[\alpha_{\mu} + \alpha_{\lambda}] - \tfrac{1}{2}\sum_{\mathrm{C}}\sum_{\sigma\neq\mu,\lambda}^{\mathrm{C}} [\beta_{\mu\sigma}S_{\sigma\lambda} + S_{\mu\sigma}\beta_{\sigma\lambda}] + O(\boldsymbol{S}^2)\,. \tag{42}$$

Usually both α_{μ} and $\beta_{\mu\lambda}$ are negative, and therefore the following relationships are to be expected:

$$\begin{aligned} |{}^{\lambda}\alpha_{\mu}| &< |\alpha_{\mu}|\,, \\ |{}^{\lambda}\beta^{\mathrm{AA}}_{\mu\nu}| &< |\beta^{\mathrm{AA}}_{\mu\nu}|\,, \\ |{}^{\lambda}\beta^{\mathrm{AB}}_{\mu\lambda}| &< |\beta^{\mathrm{AB}}_{\mu\lambda}|\,. \end{aligned} \tag{43}$$

In each case, the magnitude of the core element in the Löwdin basis is expected to be less than that in the full overlap basis.

Interesting results appear in the case of the repulsion integrals assuming expansion in the overlap integral to the first order and approximate validity of the Mulliken expression (28). Using the different classes of these integrals defined in Eqs. (12) and (13), it is readily shown that only the elements of G^{AA}_{AA} and G^{AA}_{BB} are non-zero to the first order in S and further:

$$\text{For } G^{AA}_{AA},\quad {}^{\lambda}(\mu_A\nu_A|\lambda_A\sigma_A) = (\mu_A\nu_A|\lambda_A\sigma_A) + O(S^2)\,, \tag{44}$$

$$\text{for } G^{AA}_{BB},\quad {}^{\lambda}(\mu_A\nu_A|\lambda_B\sigma_B) = (\mu_A\nu_A|\lambda_B\sigma_B) + O(S^2)\,. \tag{45}$$

The non-zero integrals here are those included in the NDDO approach, and partially included in the many-centre ZDO approach and CNDO approaches.

Special factors that now need to be taken into account are that the overlap integral may be comparatively large in inorganic systems, that the core elements will be large because of large core charges on the atoms, and that sums over atoms and orbitals are likely to be large because each atom contributes a number of valence orbitals to the system.

An expansion to only the first order in S may therefore involve some major approximations. For instance if $S_{\mu\lambda}$ has a value of 0.3, $\beta_{\mu\lambda}$ a not uncommon value of -30 eV, then terms of the size $\beta_{\mu\lambda}S^2_{\mu\lambda}$, 2–3 eV, are being neglected, and if included, would arise as part of a sum of a number of terms of this size. The errors become larger the larger the core charges on the atoms, the more atoms there are in the molecule, the more orbitals each atom contributes to the molecule and the larger the overlap integrals.

This suggests the need to examine terms to the second order in overlap and the need to take special care in calculating core elements. The procedure of finding the core matrix in a full overlap basis and transforming to the Löwdin basis for use with the repulsion integral approximations of the differential overlap methods may prove to be a necessary step.

But even the repulsion integral approximations bear examination. Coulomb repulsion integrals may have values of around 10 eV, and for an overlap integral of 0.3, terms of about 1 eV are being left out to the first order in overlap. Hence the importance of comparing the differential overlap methods with those in which all integrals are included in some way, such as via the Ruedenberg approximation.

4.2. *Expansion to the Second Order in Overlap*

Complex expressions are obtained if the expansion is carried out to the second order in the overlap integral S, where now:

$$\begin{aligned} {}^{\lambda}\boldsymbol{M} &= [\boldsymbol{1} - \tfrac{1}{2}\boldsymbol{d} + \tfrac{3}{8}\boldsymbol{d}^2]\boldsymbol{M}[\boldsymbol{1} - \tfrac{1}{2}\boldsymbol{d} + \tfrac{3}{8}\boldsymbol{d}^2] \\ &= \boldsymbol{M} - \tfrac{1}{2}[\boldsymbol{M}\boldsymbol{d} + \boldsymbol{d}\boldsymbol{M}] + \tfrac{1}{4}[\tfrac{3}{2}\boldsymbol{M}\boldsymbol{d}^2 + \boldsymbol{d}\boldsymbol{M}\boldsymbol{d} + \tfrac{3}{2}\boldsymbol{d}^2\boldsymbol{M}] + O(S^3). \end{aligned} \tag{46}$$

Individual elements then take the forms

$$\begin{aligned} {}^{\lambda}M_{\mu\mu} = M_{\mu\mu}\Big[1 + \tfrac{3}{4}\sum_{\lambda\neq\mu} S^2_{\mu\lambda}\Big] - \sum_{\sigma\neq\mu} M_{\mu\sigma}S_{\sigma\mu} + \tfrac{1}{4}\sum_{\lambda\neq\mu} S^2_{\mu\lambda}M_{\lambda\lambda} \\ + \tfrac{1}{4}\sum_{\lambda\neq\mu}\sum_{\sigma\neq\mu,\lambda}[\tfrac{3}{2}M_{\mu\lambda}S_{\lambda\sigma}S_{\sigma\mu} + S_{\mu\lambda}M_{\lambda\sigma}S_{\sigma\mu} + \tfrac{3}{2}S_{\mu\lambda}S_{\lambda\sigma}M_{\sigma\mu}] + O(S^3)\,, \end{aligned} \tag{47}$$

$$\begin{aligned} {}^{\lambda}M^{AA}_{\mu\nu} = M_{\mu\nu} - \tfrac{1}{2}\sum_{\sigma\neq\mu,\nu}[M_{\mu\sigma}S_{\sigma\nu} + S_{\mu\sigma}M_{\sigma\nu}] + \tfrac{1}{4}[\tfrac{3}{2}S_{\mu\sigma}S_{\sigma\nu}(M_{\mu\mu} + M_{\nu\nu}) \\ + S_{\mu\sigma}S_{\sigma\nu}M_{\sigma\sigma}] + O(S^3)\,, \end{aligned} \tag{48}$$

$$\begin{aligned}{}^{\lambda}M_{\mu\lambda}^{\mathrm{AB}} = M_{\mu\lambda} - \tfrac{1}{2}S_{\mu\lambda}[M_{\mu\mu} + M_{\lambda\lambda}] + \tfrac{1}{2} \sum_{\sigma \neq \mu,\lambda} \tfrac{3}{2}S_{\mu\sigma}S_{\sigma\lambda}(M_{\mu\mu} + M_{\lambda\lambda}) \\ + \tfrac{1}{2}S_{\mu\sigma}S_{\sigma\lambda}M_{\sigma\sigma} - (M_{\mu\sigma}S_{\sigma\lambda} + S_{\mu\sigma}M_{\sigma\lambda}) + O(S^3)\,. \end{aligned} \tag{49}$$

These expressions apply to the core elements ${}^{\lambda}\alpha_{\mu}$, ${}^{\lambda}\beta_{\mu\nu}^{\mathrm{AA}}$, and ${}^{\lambda}\beta_{\mu\lambda}^{\mathrm{AB}}$ respectively, and to the charge distributions ${}^{\lambda}\Omega_{\mu\mu}$, ${}^{\lambda}\Omega_{\mu\nu}$, ${}^{\lambda}\Omega_{\mu\lambda}$. When the various repulsion integrals are formed from these charge distributions, complex expressions are obtained, and may be simplified by using the Ruedenberg and Mulliken approximations.

Under these conditions integrals belonging to $G_{\mathrm{CD}}^{\mathrm{AB}}$, $G_{\mathrm{AC}}^{\mathrm{AB}}$ and $G_{\mathrm{AB}}^{\mathrm{AB}}$ may be neglected to the second order in overlap. However other repulsion integrals, involving one-centre charge distributions, are non-zero:
Three centre, $G_{\mathrm{BC}}^{\mathrm{AA}}$:

$$\begin{aligned}{}^{\lambda}(\mu_{\mathrm{A}}\nu_{\mathrm{A}} | \lambda_{\mathrm{B}}\sigma_{\mathrm{C}}) = -(\mu\nu | \lambda\sigma) + \tfrac{1}{4} \sum_{a}^{\mathrm{A}} S_{\lambda a}S_{a\sigma}[\tfrac{3}{2}(\mu\nu | \lambda\lambda) + \tfrac{3}{2}(\mu\nu | \sigma\sigma) + (\mu\nu | aa)] \\ + \tfrac{1}{2} \sum_{\mathrm{D} \neq \mathrm{A,B,C}} \sum_{d}^{\mathrm{D}} \tfrac{1}{8}S_{\lambda d}\, S_{d\sigma}[(\mu\nu | \lambda\lambda) + (\mu\nu | \sigma\sigma) - 2(\mu\nu | dd)]\,. \end{aligned} \tag{50}$$

Involving only small differences between the first and second terms, and within the third term, these integrals are likely to be very small in magnitude, and to take much smaller values than they would in a full overlap basis.

On the other hand, two-centre integrals are given by:

$$\begin{aligned} G_{\mathrm{BB}}^{\mathrm{AA}}: {}^{\lambda}(\mu_{\mathrm{A}}\nu_{\mathrm{A}} | \lambda_{\mathrm{B}}\sigma_{\mathrm{B}}) = (\mu\nu | \lambda\sigma) + \tfrac{1}{8} \sum_{\mathrm{C}} \sum_{c}^{\mathrm{C}} \{S_{\lambda c}S_{\sigma c}[(\mu\nu | \lambda\lambda) + (\mu\nu | \sigma\sigma) \\ - 2(\mu\nu | cc)] + S_{\mu c}S_{c\nu}[(\mu\mu | \lambda\sigma) + (\nu\nu | \lambda\sigma) - 2(cc | \lambda\sigma)]\} + O(S^3) \end{aligned} \tag{51}$$

where the sum is over all atoms in the molecule, including A and B themselves. Again the terms in the square brackets will approximately cancel, and anyway are multiplied by very small numbers ($\frac{1}{8}S^2$). If we write $(\mu\mu | \lambda\lambda)$ as $\gamma_{\mu\lambda}$ for convenience, two centre Coulomb repulsion integrals become:

$$\begin{aligned}{}^{\lambda}(\mu_{\mathrm{A}}\mu_{\mathrm{A}} | \lambda_{\mathrm{B}}\lambda_{\mathrm{B}}) = \gamma_{\mu\lambda} + \sum_{a}^{\mathrm{A}} \tfrac{1}{4}S_{\lambda a}^2[\gamma_{\mu\lambda} - \gamma_{\mu a}] + \sum_{b}^{\mathrm{B}} \tfrac{1}{4}S_{\mu b}^2[\gamma_{\mu\lambda} - \gamma_{\lambda b}] \\ + \sum_{\mathrm{C} \neq \mathrm{A,B}} \sum_{c}^{\mathrm{C}} \tfrac{1}{4}[S_{\lambda c}^2(\gamma_{\mu\lambda} - \gamma_{\mu c}) + S_{\mu c}^2(\gamma_{\mu\lambda} - \gamma_{\lambda c})] + O(S^3)\,. \end{aligned} \tag{52}$$

Since one centre Coulomb repulsion integrals ($\gamma_{\mu a}$, $\gamma_{\lambda b}$) are in general greater than two-centre Coulomb repulsion integrals, and since in many cases the contribution from the last sum, which involves only differences between two-centre integrals, will be small, we might expect ${}^{\lambda}\gamma_{\mu\lambda}^{\mathrm{AB}}$ to be less than $\gamma_{\mu\lambda}^{\mathrm{AB}}$, as found in the cases studied by McWeeny [15].

Again differences between the values of one-centre exchange repulsion integrals in the Löwdin and full overlap bases are small:

$${}^{\lambda}(\mu_{\mathrm{A}}\nu_{\mathrm{A}} | \nu_{\mathrm{A}}\mu_{\mathrm{A}}) = (\mu\nu | \nu\mu) - \sum_{\mathrm{B} \neq \mathrm{A}} \sum_{\lambda}^{\mathrm{B}} \tfrac{1}{2}S_{\mu\lambda}S_{\lambda\nu}(\mu\nu | \lambda\lambda) + O(S^3) \tag{53}$$

indicating that ${}^{\lambda}(\mu_{\mathrm{A}}\nu_{\mathrm{A}} | \nu_{\mathrm{A}}\mu_{\mathrm{A}})$ will be smaller than $(\mu\nu | \nu\mu)$. The reverse is the case for one-centre Coulomb repulsion integrals:

$${}^{\lambda}(\mu_{\mathrm{A}}\mu_{\mathrm{A}} | \nu_{\mathrm{A}}\nu_{\mathrm{A}}) = \gamma_{\mu\nu} + \sum_{\mathrm{B} \neq \mathrm{A}} \sum_{\lambda}^{\mathrm{B}} \tfrac{1}{4}[S_{\mu\lambda}^2(\gamma_{\mu\nu} - \gamma_{\nu\lambda}) + S_{\nu\lambda}^2(\gamma_{\mu\nu} - \gamma_{\mu\lambda})] + O(S^3) \tag{54}$$

and

$$^{\lambda}(\mu_{\mathrm{A}}\mu_{\mathrm{A}}|\mu_{\mathrm{A}}\mu_{\mathrm{A}}) = \gamma_{\mu\mu} + \sum_{\mathrm{B}\neq\mathrm{A}}\sum_{\lambda}^{\mathrm{B}} \tfrac{1}{2} S_{\mu\lambda}^{2}(\gamma_{\mu\mu} - \gamma_{\mu\lambda}) \,. \tag{55}$$

In each case the second term will be positive and $^{\lambda}\gamma_{\mu\nu} > \gamma_{\mu\nu}$ in general, also agreeing with the results of McWeeny [15].

The conclusions drawn in the expansion to the first order in overlap are reinforced when the expansion is carried out to the second order. In particular the care necessary in the evaluation of core elements is emphasized by the Eqs. (47)–(49). *The assumptions*

$$^{\lambda}\alpha_{\mu} \approx \alpha_{\mu} \,, \tag{56}$$

$$^{\lambda}\beta_{\mu\nu} \approx \beta_{\mu\nu} \tag{57}$$

do not seem justified. However the repulsion integral assumptions:

$$^{\lambda}(\mu_{\mathrm{A}}\nu_{\mathrm{B}}|\lambda_{\mathrm{C}}\sigma_{\mathrm{D}}) \approx 0, \mathrm{A}\neq\mathrm{B},\ \mathrm{C}\neq\mathrm{D} \tag{58}$$

and

$$^{\lambda}(\mu_{\mathrm{A}}\nu_{\mathrm{A}}|\lambda_{\mathrm{B}}\sigma_{\mathrm{B}}) \approx (\mu_{\mathrm{A}}\nu_{\mathrm{A}}|\lambda_{\mathrm{B}}\sigma_{\mathrm{B}}) \tag{59}$$

do receive some justification (see Refs. [16] and [27] for further discussion of this point). For the latter case, other terms in the expansion in general are of the order of S^2, and involve small differences.

4.3. *Equivalence of* ZDO *and Full Overlap Methods in Terms of Overlap*

We have already shown (Sect. 3.7) the equivalence in terms of the invariance criteria of the CNDO and Mulliken methods on the one hand, and the NDDO and Ruedenberg methods on the other. An equivalence in terms of overlap may now be readily derived from Eqs. (39) and (49) respectively. Thus, applying Eq. (39) to charge distributions, taking averages as required by the invariance criteria, and making the CNDO approximation ($^{\lambda}M_{\mu\lambda}^{\mathrm{AB}} = 0$) we obtain:

$$M_{\mu\lambda}^{\mathrm{AB}} = \frac{S_{\mu\lambda}}{2}(M_{\bar{\mu}\bar{\mu}} + M_{\bar{\lambda}\bar{\lambda}}) - \tfrac{1}{2}\sum_{\mathrm{C}\neq\mathrm{A,B}}\sum_{\sigma}[M_{\mu\sigma}S_{\sigma\lambda} + S_{\mu\sigma}M_{\sigma\lambda}] + O(S^2) \tag{60}$$

This equation shows, however, that both terms in the final sum are of the order S^2 (since $\mathrm{C}\neq\mathrm{A,B}$), and hence we obtain the Mulliken approximation, Eq. (28), to the first order in overlap.

Similarly, beginning with Eq. (49) [or Eq. (39)] and making the NDDO approximation, one finds that the NDDO and Ruedenberg approximations for charge distributions are equivalent to the first order in overlap. If Eq. (49) is used, one may further show that the NDDO and Ruedenberg approximation *as applied to repulsion integrals* (products of two charge distributions) are equivalent to the second order in overlap.

4.4. *Conclusions and Discussion*

The S-expansion technique has shown how the CNDO, many-centre ZDO and NDDO methods may be derived and justified in a basis of orthogonal atomic orbitals. The following general results have been found:

i) The zero-differential-overlap assumptions for repulsion integrals apply in a Löwdin basis, and non-zero integrals may be evaluated using normal, rather than Löwdin, atomic orbitals.

ii) Core elements may be evaluated theoretically to form the core matrix $\boldsymbol{H}$, followed by a transformation of $\boldsymbol{H}$ to the Löwdin basis for use with the above repulsion integral approximations:

$$ {}^{\lambda}\boldsymbol{H} = \boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{H}\boldsymbol{S}^{-\frac{1}{2}} \tag{61}$$

iii) Alternatively the expressions (40–42) or (47–49) may be used to evaluate core elements theoretically in the Löwdin basis to the first or second order in overlap, respectively.

iv) Provided that the core elements have been calculated correctly, the NDDO method is at best correct to the second order in overlap while the many-centre ZDO and CNDO methods are at best correct to the first order in overlap. That is

$$\boldsymbol{F}^{\text{NDDO}} = {}^{\lambda}\boldsymbol{F} + O(S^3)\,, \tag{62}$$

$$\boldsymbol{F}^{\text{Many-centre ZDO}} \approx \boldsymbol{F}^{\text{CNDO}} \approx {}^{\lambda}\boldsymbol{F} + O(S^2)\,. \tag{63}$$

Errors are likely to increase the larger the molecule, the more orbitals per centre that are included, and the greater the overlap between participating orbitals.

Note that the CNDO method involves approximations in addition to those necessary for its derivation correct to the first order in overlap, namely, the neglect of one-centre exchange repulsion integrals and the averaging of the remaining integrals. *Hence, the Many Centre* ZDO *method is the true first-order-in-overlap method.*

It should also be noted that we have not, in the present paper, attempted to justify the additional assumption of valence electron core electron separability. Preliminary investigations in this direction using the approach of Manné [20], have been set out elsewhere [3].

The general results found here are in substantial agreement with the conclusions of Cook, Hollis, and McWeeny [16, 24], based on their numerical comparisons, and in some respects, with those of Dahl [25], based on an analysis of the CNDO method. Numerical comparisons of the various methods obtained in our own laboratory will be presented in Part III of this series of papers, and provide further support of the conclusions derived in this paper. Initial applications of the NDDO method to inorganic systems by Brown and Peel [26], Brown and Roby [3], and Roby and Sinanoğlu [27] confirm the promise of this type of approach.

The invariance criteria and the S-expansion technique may be used to investigate the theoretical basis of other approximate molecular orbital methods [14, 28–38] presently in the literature. Such a critique has been given elsewhere [3]. In other papers of this series, (Parts II, III, and IV) we develop other criteria for the reliability and limitations of approximate methods and parameter schemes.

All valence electron calculations are very sensitive to the way in which the parameters of the particular method used are determined. The next main facet (Part II) of the molecular orbital theory for inorganic molecules is, then, the development of general schemes for parameter determination within the scope of the theoretical framework and the all-valence-electron methods outlined here.

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