

A Re-Examination of the Justification of Neglect of Differential Overlap Approximations in Terms of a Power Series Expansion in S

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Neglect of differential overlap methods are treated as approximations to calculations in a symmetrically orthogonalized basis. The accuracy of this approximation is investigated in terms of a power series expansion of the overlap matrix. The S -matrix can be transformed into a matrix which will give a convergent series, and this series is used in the examination. The only approximation having any justification from this point of view is the NDDO method and even this neglects certain important three-electron integrals. Corrected expressions for the repulsion integral scaling factors introduced by Chandrasekhar *et al.* are also derived.

Key words: Neglect of differential overlap methods

1. Introduction

Semi-empirical calculations based on the neglect of differential overlap (NDO) approximations and explicitly treating only valence electrons have become widely used through the ready availability of programs using the complete neglect of differential overlap (CNDO) methods or modifications of them.

These methods derive from the zero differential overlap approximation (ZDO), first applied to π -electron systems, which can be summarized as follows:

$$(\mu\nu | \lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu | \lambda\lambda) \quad (1)$$

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where $\delta_{\alpha\beta}$ is the Kronecker delta, and

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

$$S_{\mu\nu} = \int \phi_\mu(1)\phi_\nu(1) d\tau_1 = \delta_{\mu\nu}. \quad (2)$$

However, core integrals,

$$H_{\mu\nu} = \int \phi_\mu(1)\mathcal{H}^{\text{core}}\phi_\nu(1) d\tau_1 \quad (3)$$

with

$$\mathcal{H}^{\text{core}} = \sum_p \left[-\frac{1}{2}\nabla_p^2 - \sum_A Z_A r_{pA}^{-1} \right],$$

are not neglected.

CNDO methods [1] incorporate the ZDO approximations, making adjustments so that all integrals are invariant to rotations of axes by having any surviving two-electron integrals depend only on the nature of the atoms A and B to which the orbitals belong and not on the type of the orbital. CNDO calculations cannot adequately differentiate between spin states. The intermediate neglect of differential overlap methods (INDO) [2] perform this task better by including one-centre integrals with differential overlap, so that

$$(\mu_A\nu_B | \lambda_A\sigma_B) = \delta_{AB}(\mu_A\nu_A | \lambda_A\sigma_A) \quad (4)$$

is retained.

The most sophisticated NDO method which has been introduced is neglect of diatomic differential overlap (NDDO) [2]. It is invariant to rotations without forcing any equivalences or averaging between integrals. Here, two-electron integrals are neglected only if the differential overlap occurs between atomic orbitals on different atoms,

$$(\mu_A\nu_B | \lambda_C\sigma_D) = \delta_{AB}\delta_{CD}(\mu_A\nu_A | \lambda_C\sigma_C) \quad (5)$$

Although several authors have sought a justification of these methods by treating them as approximations to a calculation in a symmetrically orthogonalized basis [3-5], it has been demonstrated by Gray and Stone that these approaches were not valid except for the special case of π -electron calculations [6], because the expansion in the overlap matrix S used in these studies can become divergent.

Using a different approach Roby [7, 8] demonstrated a theoretical foundation for NDDO methods. Beginning with a complete basis set on each atom, and using the Ruedenberg expansion [9], Roby showed

$$[M^0, S] = 0, \quad (6)$$

where M^0 has as elements the integrals in the chosen basis over a one-electron operator, but with all two-centre integrals being set equal to zero. S is the overlap matrix. Further consideration of the one-electron operator matrix elements after

transformation to a canonically orthogonalized basis [10] lead Roby to conclude that

$${}^{\lambda}M = M_p^0. \quad (7)$$

Here, ${}^{\lambda}M$ is the matrix over the orthogonalized basis. The matrix M_p^0 is the corresponding matrix in the non-orthogonal basis with all two-centre elements set to zero and reduced in order to correct for linear dependencies. Equation (7) leads to the important corollary that the canonically orthogonalized Coulomb repulsion integral matrix can be constructed from the integral array in the non-orthogonal basis containing only interactions between one-centre charge distributions, so that only

$$(\mu\nu | \lambda\sigma)^0 = \delta_{AB}\delta_{CD}(\mu_A\nu_B | \lambda_C\sigma_D) \quad (8)$$

need be considered. This is the NDDO approximation. A similar result is approximately true [8] for a symmetrically orthonormal basis set [10].

This work has been critically re-examined by King, Newton and Stanton [11, 12], who confirmed (7) but pointed out that M_p^0 need not necessarily be diagonal as assumed earlier. It then follows that Roby's corollary concerning the Coulomb repulsion integral matrix can only be correct when the orthogonal basis consists of three-dimensional delta functions, hence the practical applications of the work would seem to be severely limited. So, while a formal connection has been established between the NDDO assumptions and calculations in an orthogonal basis it still has not provided much insight into the practicalities of using a severely truncated basis. Even Roby's examination of an approximate theorem in a symmetrically orthogonalized basis does not provide much help, since his exposition depends on there being a large enough basis set to give Ruedenberg expansions which leave only a small error and yet do not introduce any linear dependencies. Though these very innovative investigations opened up new ways of thinking about NDO methods, nevertheless the earlier $S^{-1/2}$ expansion technique is valuable for examining practical applications using basis sets which are necessarily small when compared with complete basis sets.

It is the purpose of this paper to show that the $S^{-1/2}$ expansion can be transformed to make a convergent series. The consequence of this is that the conclusions arrived at by Brown and Roby [5] concerning the validity of the CNDO and NDDO approaches can be re-examined in a formally correct framework. Although their conclusions are not substantially altered, some recent attempts by Chandrasekhar *et al.* [13] to produce integral scaling factors from the Brown and Roby equations need to be completely revised.

2. The S -Expansion Technique

Let χ , a row vector be a non-orthogonal normalized set of atomic orbital functions with overlap matrix Δ ,

$$\Delta = \int \chi^\dagger \chi \, d\tau = \langle \chi | \chi \rangle \quad (9)$$

The basis χ is transformed into a symmetrically orthogonalized one,

$$\phi = \chi \Delta^{-1/2}. \quad (10)$$

We can assume that S will form a convergent power series and write

$$\begin{aligned} \Delta^{-1/2} &= (\mathbf{1} + S)^{-1/2} \\ &= \mathbf{1} - \frac{1}{2}S + \frac{3}{8}S^2 \dots \end{aligned} \quad (11)$$

with the intention of considering approximations to $\Delta^{-1/2}$ resulting from truncation of the series in S . Before doing this the convergence properties need to be examined.

If U is a matrix which diagonalizes S so that $S = U\Lambda U^{-1}$, with Λ a diagonal matrix whose diagonal elements are the eigenvalues λ_i of S , then obviously $S^n = U\Lambda^n U^{-1}$ and a power series in S will only converge if $\rho = \max\{|\lambda_i|\} < 1$. This condition is not met in general for molecular basis sets.

However, the overlap matrix (Δ) is Hermitian and positive definite which follows because for any

$$\lambda = \sum_i c_i \chi_i \quad (12)$$

$$\begin{aligned} \langle \lambda | \lambda \rangle &= \sum_{ij} c_i^* c_j \langle \chi_i | \chi_j \rangle \\ &= \mathbf{c}^\dagger \langle \chi | \chi \rangle \mathbf{c} = \langle \chi \mathbf{c} | \chi \mathbf{c} \rangle \geq 0. \end{aligned} \quad (13)$$

In order to get a convergent series (11) it is necessary to factorize $(\mathbf{1} + U\Lambda U^{-1})^{-1/2}$ so that $\max\{|\lambda_i|\} < 1$, which can be achieved by subtracting a constant diagonal matrix, $X = x\mathbf{1}$ from S so that

$$(\mathbf{1} + U\Lambda U^{-1})^{-1/2} = (\mathbf{1} + U\Lambda U^{-1} - X + X)^{-1/2}$$

with X a constant matrix having positive elements x . Then

$$\begin{aligned} (\mathbf{1} + U\Lambda U^{-1})^{-1/2} &= (\mathbf{1} + X + U\Lambda U^{-1} - UU^{-1}X)^{-1/2} \\ &= (\mathbf{1} + X + U(\Lambda - X)U^{-1})^{-1/2} \\ &= (\mathbf{1} + X)^{-1/2} (\mathbf{1} + (\mathbf{1} + X)^{-1} U(\Lambda - X)U^{-1})^{-1/2} \\ &= (\mathbf{1} + X)^{-1/2} [\mathbf{1} + (\mathbf{1} + X)^{-1} (S - X)]^{-1/2} \end{aligned} \quad (14)$$

The constant matrix is chosen so that $(\rho - x)/(1 + x) < 1$ and also so that if $\rho_m = \min\{\lambda_i\}$ then $|(\rho_m - x)/(1 + x)| < 1$. Since Δ is positive definite the smallest eigenvalue of S is greater than -1 and both conditions can be satisfied. Figure 1 shows a sketch of ρ and $|\rho_m|$ versus x . The optimum choice of x is obviously given by,

$$\frac{|\rho_m - x|}{1 + x} = \frac{\rho - x}{1 + x} \quad (15)$$

so that

$$x = \frac{\rho + \rho_m}{2} \quad (16)$$

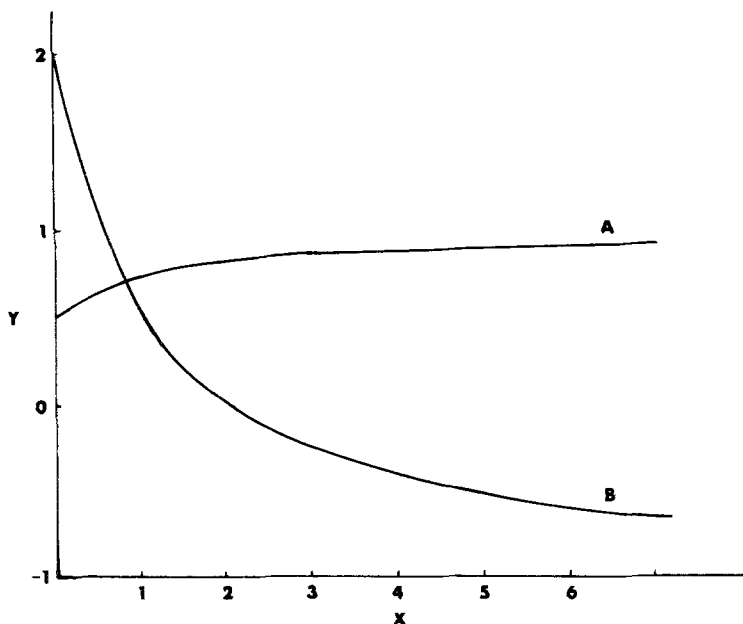


Fig. 1. Graphs of $y = (\rho - x)/(1 + x)$, curve B, and $y = |(\rho_m - x)/(1 + x)$, curve A, versus x for the case $\rho = 2$ and $\rho_m = -\frac{1}{2}$

Equation (14) can thus be expanded in the convergent power series of $(1 + X)^{-1}(S - X)$,

$$(1 + S)^{-1/2} = (1 + X)^{-1/2} \left[1 - \frac{1}{2} \{(1 + X)^{-1}(S - X)\} + \frac{3}{8} \{(1 + X)^{-1}(S - X)\}^2 \dots \right] \tag{17}$$

In order to simplify the following discussion we put

$$\mathfrak{P} = (1 + X)^{-1}(S - X) \tag{18}$$

with the elements of $\mathfrak{P} = \mathfrak{P}_{ij}$. This expansion will now be used to investigate how integrals in a non-orthogonal atomic basis are related to those in an orthogonal basis, and which integrals become small after the transformation, and hence can be neglected.

3. The S-Expansion Technique and NDO Approximations

To consider applications of (17) to the examination of neglect of differential overlap approximations it is convenient to partition the molecular Hamiltonian in the manner discussed by Brown and Roby [5]. A partitioning of the core Hamiltonian matrix into one-centre and two-centre terms is used:

$$H = H^{1c} + H^{2c}, \tag{19}$$

the elements of H^{1c} obeying the condition

$$H_{\mu\nu}^{1c} = 0$$

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

$$H_{\mu\nu}^{2c} = 0$$

unless χ_μ , and χ_ν are on different centres. For the two-electron repulsion terms of the Hamiltonian matrix it is useful to split them into one-centre and many-centre parts,

$$G = G^{1c} + G^{mc} \quad (20)$$

with

$$G_{\mu\nu}^{1c} = 0$$

for χ_μ and χ_ν on different centres, and

$$G_{\mu\nu}^{1c} = \sum_{\lambda\sigma}^A P_{\lambda\sigma}[(\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\sigma | \lambda\nu)] \quad (21)$$

for χ_μ and χ_ν on the same atom A. The summation is taken over all orbitals χ_λ and χ_σ on A. G^{mc} can be further broken up into two, three and four-centre terms:

$$G^{mc} = G_{BB}^{AA} + G_{AB}^{AA} + G_{AB}^{AB} + G_{BC}^{AA} + G_{AC}^{AB} + G_{CD}^{AB} \quad (22)$$

As an example the matrix G_{BB}^{AA} contains 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, so that in full the elements of G_{BB}^{AA} are:

$$(G_{BB}^{AA})_{\mu\nu} = \sum_{\lambda}^B \sum_{\sigma}^B P_{\lambda\sigma}(\mu\nu | \lambda\sigma). \quad (23)$$

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

$$(G_{BB}^{AA})_{\mu\lambda} = -\frac{1}{2} \sum_{\nu}^A \sum_{\sigma}^A P_{\nu\sigma}(\mu\nu | \lambda\sigma)$$

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

The importance of the various integrals neglected in approximate differential overlap methods can be assessed by considering only valence orbitals and then individually examining the elements of the Hamiltonian matrix. When a basis set which is Schmidt orthogonalized on each centre is subjected to a symmetric orthogonalization as in (10) matrix elements of one-electron operators are transformed so that

$${}^\lambda M = \Delta^{-1/2} M \Delta^{-1/2} \quad (24)$$

Substituting the binomial expansion (17) and (18) for $\Delta^{-1/2}$ to the second order in \mathfrak{P} into (24) gives

$$\begin{aligned} {}^\lambda M &= (1 + X)^{-1} [1 - \frac{1}{2}\mathfrak{P} + \frac{3}{8}\mathfrak{P}^2] M [1 - \frac{1}{2}\mathfrak{P} + \frac{3}{8}\mathfrak{P}^2] \\ &= (1 + X)^{-1} [M - \frac{1}{2}\{M\mathfrak{P} + \mathfrak{P}M\} + \frac{1}{4}\{\frac{3}{2}M\mathfrak{P}^2 + \mathfrak{P}M\mathfrak{P} + \frac{3}{2}\mathfrak{P}^2M\} \\ &\quad + O(\mathfrak{P}^3)]. \end{aligned} \quad (25)$$

Expanding this out into individual elements, yields

$$\begin{aligned}
 (1+x)^\lambda M_{\mu\mu} &= M_{\mu\mu} \left[1 - \mathfrak{P}_{\mu\mu} + \frac{3}{4} \sum_{\sigma} \mathfrak{P}_{\mu\sigma}^2 \right] - \sum_{\sigma \neq \mu} M_{\mu\sigma} \mathfrak{P}_{\sigma\mu} \\
 &+ \frac{1}{4} \sum_{\sigma} M_{\sigma\sigma} \mathfrak{P}_{\mu\sigma}^2 + \frac{3}{4} \sum_{\lambda \neq \mu} \sum_{\sigma} M_{\lambda\mu} \mathfrak{P}_{\mu\sigma} \mathfrak{P}_{\sigma\lambda} \\
 &+ \frac{1}{4} \sum_{\lambda \neq \sigma} \sum_{\sigma} M_{\lambda\sigma} \mathfrak{P}_{\mu\lambda} \mathfrak{P}_{\sigma\mu} + O(\mathfrak{P}^3)
 \end{aligned} \tag{26}$$

$$\begin{aligned}
 (1+x)^\lambda M_{\mu\nu}^{AA} &= M_{\mu\nu} (1 - \mathfrak{P}_{\mu\mu}) - \frac{1}{2} \sum_{\lambda \neq \mu, \nu} [M_{\mu\lambda} \mathfrak{P}_{\lambda\nu} + M_{\lambda\nu} \mathfrak{P}_{\mu\lambda}] \\
 &+ \frac{3}{8} \sum_{\sigma} M_{\mu\nu} [\mathfrak{P}_{\nu\sigma}^2 + \mathfrak{P}_{\mu\sigma}^2] \\
 &+ \frac{1}{4} \sum_{\sigma}^{B \neq A} \sum_{\sigma} \left\{ \frac{3}{2} (M_{\nu\nu} + M_{\mu\mu}) \mathfrak{P}_{\mu\sigma} \mathfrak{P}_{\sigma\nu} + M_{\sigma\sigma} \mathfrak{P}_{\mu\sigma} \mathfrak{P}_{\sigma\nu} \right\} \\
 &+ \frac{3}{8} \sum_{\lambda \neq \nu, \mu}^A \sum_{\sigma} [M_{\lambda\nu} \mathfrak{P}_{\mu\sigma} \mathfrak{P}_{\sigma\lambda} + M_{\mu\lambda} \mathfrak{P}_{\lambda\sigma} \mathfrak{P}_{\sigma\nu}] \\
 &+ \frac{1}{4} \sum_{\lambda \neq \sigma} \sum_{\sigma}^{\text{both on } B \neq A} M_{\lambda\sigma} \mathfrak{P}_{\mu\lambda} \mathfrak{P}_{\sigma\nu} + O(\mathfrak{P}^3)
 \end{aligned} \tag{27}$$

where $\sum^{B \neq A}$ means that the summation is to be carried out over all orbitals on atoms other than A, and

$$\begin{aligned}
 (1+x)^\lambda M_{\mu\lambda}^{AB} &= M_{\mu\lambda} (1 - \mathfrak{P}_{\mu\mu}) - \frac{1}{2} \mathfrak{P}_{\mu\lambda} [M_{\lambda\lambda} + M_{\mu\mu}] \\
 &- \frac{1}{2} \sum_{\sigma \neq \lambda}^{C \neq A} M_{\sigma\lambda} \mathfrak{P}_{\mu\sigma} - \frac{1}{2} \sum_{\sigma \neq \mu}^{C \neq B} M_{\mu\sigma} \mathfrak{P}_{\sigma\lambda} \\
 &+ \frac{1}{4} \sum_{\sigma} \left\{ \frac{3}{2} [M_{\lambda\lambda} + M_{\mu\mu}] \mathfrak{P}_{\mu\sigma} \mathfrak{P}_{\sigma\lambda} + M_{\sigma\sigma} \mathfrak{P}_{\mu\sigma} \mathfrak{P}_{\sigma\lambda} \right\} \\
 &+ \frac{3}{8} \sum_{\sigma} \left\{ \sum_{\omega \neq \lambda}^{\text{on B only}} M_{\omega\lambda} \mathfrak{P}_{\mu\sigma} \mathfrak{P}_{\sigma\omega} + \sum_{\omega \neq \mu}^{\text{A only}} M_{\mu\omega} \mathfrak{P}_{\omega\sigma} \mathfrak{P}_{\sigma\lambda} \right\} \\
 &+ \frac{1}{4} \sum_{\sigma} \sum_{\omega \neq \sigma}^{\text{both on C}} M_{\omega\sigma} \mathfrak{P}_{\mu\omega} \mathfrak{P}_{\sigma\omega} + O(\mathfrak{P}^3)
 \end{aligned} \tag{28}$$

where $\sum^{\text{A only}}$ means the summation only goes over orbitals on A.

In these expressions the Mulliken approximation [14] for a one-electron operator

$$\langle \mu_A | \hat{M} | \lambda_B \rangle = S_{\mu\lambda} / 2 [M_{AA} + M_{BB}] \tag{29}$$

has been invoked to eliminate terms which become of $O(\mathfrak{P}^3)$ after its application. Subscripts are used in the last term of (28) to emphasize that the term is only included if both ω and σ are on the same atom. Expressions (26–28) apply directly to the calculation of the following integrals which are used in ZDO approaches

$$\alpha_\mu = \langle \mu_A | -\frac{1}{2} \nabla^2 + V_A + \sum_{B \neq A} V_B | \mu_A \rangle \tag{30}$$

where V_A is the potential due to the nucleus and inner shells of atom A,

$$\beta_{\mu\nu}^{AA} = \langle \mu_A | \sum_B V_B | \nu_A \rangle, \quad (31)$$

$$\beta_{\mu\lambda}^{AB} = \langle \mu_A | -\frac{1}{2}\nabla^2 + V_A + V_B | \lambda_B \rangle, \quad (32)$$

and to the charge distributions ${}^\wedge\Omega_{\mu\mu}^{AA}$, ${}^\wedge\Omega_{\mu\nu}^{AA}$ and ${}^\wedge\Omega_{\mu\lambda}^{AB}$ which arise when the electron repulsion integrals are written

$${}^\wedge(\mu\nu | \lambda\sigma) = ({}^\wedge\Omega_{\mu\nu} | {}^\wedge\Omega_{\lambda\sigma}) \quad (33)$$

Equations (26–28) reinforce the conclusions of Brown and Roby [5], concerning core integrals, that

$${}^\wedge\alpha_\mu \not\approx \alpha_\mu \quad (34)$$

$${}^\wedge\beta_{\mu\nu} \not\approx \beta_{\mu\nu} \quad (35)$$

Further consideration of the electron repulsion integrals requires products of the expressions (26–28) which are then simplified using the Mulliken approximation, and by recognizing that $(\mu_A\mu_A | \lambda_B\sigma_B) \approx O(S) \times (\mu_A\mu_A | \sigma_B\sigma_B)$ when $\lambda_B \neq \sigma_B$. In the present instance this is more complicated than in Brown and Roby's treatment since there is no longer equality between the elements ($\mathfrak{P}_{\mu\nu}$) appearing in the $S^{-1/2}$ expansion and the overlap ($S_{\mu\nu}$) from the Mulliken approximation, but they are still of the same order of magnitude. In particular, terms in integrals belonging to G_{AB}^{AB} , G_{AC}^{AB} and G_{CB}^{AB} do not cancel identically to second order in overlap so that for G_{AB}^{AB}

$$(1+x)^2 {}^\wedge(\mu_A\nu_B | \lambda_A\sigma_B) = \frac{1}{4}[S_{\mu\nu}S_{\lambda\sigma} - \mathfrak{P}_{\lambda\sigma}S_{\mu\nu} - \mathfrak{P}_{\mu\nu}S_{\lambda\sigma} + \mathfrak{P}_{\mu\nu}\mathfrak{P}_{\lambda\sigma}][(\mu\mu | \lambda\lambda) + (\nu\nu | \lambda\lambda) + (\mu\mu | \sigma\sigma) + (\nu\nu | \sigma\sigma)] \quad (36)$$

and there are terms identical in form for G_{AC}^{AB} and G_{CB}^{AB} . However, the multiplying factor in (36) will be of the order of \mathfrak{P}^3 for all circumstances, so that integrals of G_{CB}^{AB} , G_{AC}^{AB} and G_{AB}^{AB} may be neglected to the second order in overlap.

The remaining three-centre terms G_{BC}^{AA} give

$$\begin{aligned} (1+x)^2 {}^\wedge(\mu_A\nu_A | \lambda_B\sigma_C) &= \frac{1}{2}[S_{\lambda\sigma} - \mathfrak{P}_{\lambda\sigma}][(\mu\nu | \lambda\lambda) + (\mu\nu | \sigma\sigma)] \\ &+ \frac{1}{2}[\mathfrak{P}_{\mu\mu}\mathfrak{P}_{\lambda\sigma} - 2\mathfrak{P}_{\mu\mu}S_{\lambda\sigma}][(\mu\nu | \lambda\lambda) + (\mu\nu | \sigma\sigma)] \\ &+ \sum_a^A \{ [\frac{3}{8}\mathfrak{P}_{\lambda a}\mathfrak{P}_{a\sigma} - \frac{1}{4}S_{\lambda a}\mathfrak{P}_{a\sigma}](\mu\nu | \lambda\lambda) \\ &\quad + [\frac{3}{8}\mathfrak{P}_{\lambda a}\mathfrak{P}_{a\sigma} - \frac{1}{4}S_{a\sigma}\mathfrak{P}_{\lambda a}](\mu\nu | \sigma\sigma) \\ &\quad + [\frac{1}{4}\mathfrak{P}_{\lambda a}\mathfrak{P}_{a\sigma} - \frac{1}{4}S_{a\sigma}\mathfrak{P}_{\lambda a} - \frac{1}{4}S_{\lambda a}\mathfrak{P}_{a\sigma}](\mu\nu | aa) \} \\ &+ \sum_a^{D \neq A, B, C} \{ [\frac{3}{8}\mathfrak{P}_{\lambda d}\mathfrak{P}_{d\sigma} - \frac{1}{4}S_{\lambda d}\mathfrak{P}_{d\sigma}](\mu\nu | \lambda\lambda) \\ &\quad + [\frac{3}{8}\mathfrak{P}_{\lambda d}\mathfrak{P}_{d\sigma} - \frac{1}{4}S_{d\sigma}\mathfrak{P}_{\lambda d}](\mu\nu | \sigma\sigma) \\ &\quad + [\frac{1}{4}\mathfrak{P}_{\lambda d}\mathfrak{P}_{d\sigma} - \frac{1}{4}S_{d\sigma}\mathfrak{P}_{\lambda d} - \frac{1}{4}S_{\lambda d}\mathfrak{P}_{d\sigma}](\mu\nu | dd) \} \\ &+ \frac{3}{4}\mathfrak{P}_{\mu\mu}\mathfrak{P}_{\lambda\sigma}[(\mu\nu | \lambda\lambda) + (\mu\nu | \sigma\sigma)] + \frac{1}{4}\mathfrak{P}_{\mu\mu}\mathfrak{P}_{\lambda\sigma}(\mu\nu | \lambda\lambda) \\ &+ \frac{1}{4}\mathfrak{P}_{\lambda\sigma}\mathfrak{P}_{\mu\mu}(\mu\nu | \sigma\sigma) - \frac{1}{2} \sum_c^{c \text{ only}} \mathfrak{P}_{\lambda c}(1 - \mathfrak{P}_{\mu\mu})(\mu\nu | c\sigma) \\ &- \frac{1}{2} \sum_b^{B \text{ only}} \mathfrak{P}_{b\sigma}(1 - \mathfrak{P}_{\mu\mu})(\mu\nu | b\lambda). \end{aligned} \quad (37)$$

While this is not of $O(\mathfrak{P}^3)$, under some circumstances it can be quite small. When the S matrix itself gives a convergent expansion the first and second terms, and all other terms containing the diagonal elements $\mathfrak{P}_{\mu\mu}$, disappear, and the summations over a and b simplify to the expressions given by Brown and Roby [5]. In this case the terms inside the summations over orbitals on A and B approximately cancel and are multiplied by a small factor $\frac{1}{4}S^2$; the final summations over c and b do not have cancellations but are expected to be small. As modifications to the S matrix become important and x , Eq. (16), becomes larger the overall contributions to (37) remain of $O(\mathfrak{P}^2)$. The first term enters with this order since

$$\mathfrak{P}_{\lambda\sigma} = \frac{1}{1+x} S_{\lambda\sigma} \tag{38}$$

$$\therefore \frac{1}{2}[S_{\lambda\sigma} - \mathfrak{P}_{\lambda\sigma}] = \frac{1}{2}\left[S_{\lambda\sigma} - \frac{1}{(1+x)} S_{\lambda\sigma}\right] = \frac{1}{2}S_{\lambda\sigma}\left(\frac{x}{1+x}\right) \tag{39}$$

which = $O(\mathfrak{P}^2)$ if the factor $(1+x)^2$ on the l.h.s. is included. Again, because of cancellation or multiplication by the factor $x/(1+x)^2$, the terms in the summation over a and d will be small. Other terms are clearly of $O(\mathfrak{P}^2)$.

The effect of orthogonalization on the remaining two-centre integrals G_{BB}^{AA} is given by

$$\begin{aligned} (1+x)^2 \lambda(\mu_A\nu_A | \lambda_B\sigma_B) &= \frac{(1+3x)}{1+x} (\mu\nu | \lambda\sigma) \\ &+ \frac{1}{8} \sum_{c \neq B} \sum_c \{ [3\mathfrak{P}_{\lambda c}\mathfrak{P}_{c\sigma} - 2\mathfrak{P}_{\lambda c}S_{c\sigma}](\mu\nu | \sigma\sigma) \\ &\quad + [3\mathfrak{P}_{\lambda c}\mathfrak{P}_{c\sigma} - 2\mathfrak{P}_{c\sigma}S_{\lambda c}](\mu\nu | \lambda\lambda) \\ &\quad + [2\mathfrak{P}_{\lambda c}\mathfrak{P}_{c\sigma} - 2\mathfrak{P}_{c\sigma}S_{\lambda c} - 2\mathfrak{P}_{\lambda c}S_{c\sigma}](\mu\nu | cc) \} \\ &+ \frac{1}{8} \sum_{c \neq A} \sum_c \{ [3\mathfrak{P}_{\mu c}\mathfrak{P}_{c\nu} - 2\mathfrak{P}_{\mu c}S_{c\nu}](\nu\nu | \lambda\sigma) \\ &\quad + [3\mathfrak{P}_{\mu c}\mathfrak{P}_{c\nu} - 2\mathfrak{P}_{c\nu}S_{\mu c}](\mu\mu | \lambda\sigma) \\ &\quad + [2\mathfrak{P}_{\mu c}\mathfrak{P}_{c\nu} - 2\mathfrak{P}_{c\nu}S_{\mu c} - 2\mathfrak{P}_{\mu c}S_{c\nu}] \\ &\quad \times (cc | \lambda\sigma) \}. \end{aligned} \tag{40}$$

The importance of modifications to the S matrix become evident in (40) where the change to the integral on orthogonalization depends on the parameter x , firstly through the contribution of the leading term $(\mu\nu | \lambda\sigma)$ which decreases as x increases and secondly through the remaining terms which show a more complicated dependence. This can be examined by substituting (38) into (40) to give

$$\begin{aligned} (1+x)^2 \lambda(\mu_A\nu_A | \lambda_B\sigma_B) &= (\mu\nu | \lambda\sigma) \left(\frac{1+3x}{1+x}\right) + \frac{1}{8} \sum_c \left\{ \frac{S_{\lambda c}S_{\sigma c}}{(1+x)^2} [(1-2x)(\mu\nu | \lambda\lambda) + (1-2x) \right. \\ &\quad (\mu\nu | \sigma\sigma - 2)(1+2x)(\mu\nu | cc)] + \frac{S_{\mu c}S_{c\nu}}{(1+x)^2} \\ &\quad \left. [(1-2x)(\mu\mu | \lambda\sigma) + (1-2x)(\nu\nu | \lambda\sigma) - 2(1+2x)(cc | \lambda\sigma)] \right\}. \end{aligned} \tag{41}$$

The terms within the summation which do not depend on x approximately cancel, and the terms involving x are of order \mathfrak{P}^3 , and become less important as x becomes larger, but they all contribute with the same sign.

Two-centre repulsion integrals are a special case of (40) and if we write $\gamma_{\mu\lambda}$ for $(\mu\mu | \lambda\lambda)$ then they are given by,

$$\begin{aligned}
 (1+x)^2 {}^\lambda(\mu_A\mu_A | \lambda_B\lambda_B) &= (1 + 2\mathfrak{P}_{\mu\mu}^2 - 2\mathfrak{P}_{\mu\mu})\gamma_{\mu\lambda} \\
 &+ \sum_a^A [(\frac{3}{4}\mathfrak{P}_{\lambda a}^2 - \frac{1}{2}\mathfrak{P}_{\lambda a}S_{\lambda a})\gamma_{\mu\lambda} - (\frac{1}{2}\mathfrak{P}_{\lambda a}S_{\lambda a} - \frac{1}{4}\mathfrak{P}_{\lambda a}^2)\gamma_{\mu a}] \\
 &+ \sum_b^B [(\frac{3}{4}\mathfrak{P}_{\mu b}^2 - \frac{1}{4}\mathfrak{P}_{\mu b}S_{\mu b})\gamma_{\mu\lambda} - (\frac{1}{2}\mathfrak{P}_{\mu b}S_{\mu b} - \frac{1}{4}\mathfrak{P}_{\mu b}^2)\gamma_{\lambda b}] \\
 &+ \sum_c^{C \neq A, B} [(\frac{3}{4}\mathfrak{P}_{\lambda c}^2 - \frac{1}{2}\mathfrak{P}_{\lambda c}S_{\lambda c})\gamma_{\mu\lambda} - (\frac{1}{2}\mathfrak{P}_{\lambda c}S_{\lambda c} - \frac{1}{4}\mathfrak{P}_{\lambda c}^2)\gamma_{\mu c} \\
 &\quad + (\frac{3}{4}\mathfrak{P}_{\mu c}^2 - \frac{1}{2}\mathfrak{P}_{\mu c}S_{\mu c})\gamma_{\mu\lambda} \\
 &\quad - (\frac{1}{2}\mathfrak{P}_{\mu c}S_{\mu c} - \frac{1}{4}\mathfrak{P}_{\mu c}^2)\gamma_{\lambda c}] \quad (42)
 \end{aligned}$$

Using (38) we can put this in the more useful form

$$\begin{aligned}
 (1+x)^2 {}^\lambda(\mu\mu | \lambda\lambda) &= \left(\frac{1+4x+5x^2}{(1+x)^2} \right) (\mu\mu | \lambda\lambda) + \frac{1}{4(1+x)^2} \\
 &\times \left\{ \sum_a^A S_{\lambda a}^2 [(1-2x)\gamma_{\mu\lambda} - (1+2x)\gamma_{\mu a}] \right. \\
 &\quad + \sum_b^B S_{\mu b}^2 [(1-2x)\gamma_{\mu\lambda} - (1+2x)\gamma_{\lambda b}] \\
 &\quad + \sum_c^{C \neq A, B} (S_{\lambda c}^2 [(1-2x)\gamma_{\mu\lambda} - (1+2x)\gamma_{\mu c}] \\
 &\quad \left. + S_{\mu c}^2 [(1-2x)\gamma_{\mu\lambda} - (1+2x)\gamma_{\lambda c}]) \right\} \quad (43)
 \end{aligned}$$

When $x = 0$ this converts to Brown and Roby's equation (52), and as they deduced ${}^\lambda\gamma_{\mu\lambda}^{AB}$ might be expected to be less than $\gamma_{\mu\lambda}^{AB}$. If $x \neq 0$ this conclusion should be unchanged.

Differences between the values of one-centre exchange integrals and Coulomb repulsion integrals in the orthogonal and non-orthogonal bases are small, provided x is kept small, and probably remain so even as x becomes larger, although the precise behaviour in these circumstances is not obvious.

$$\begin{aligned}
 (1+x)^2 \lambda(\mu_A \mu_A | \nu_A \nu_A) &= \left\{ 1 + \sum_{\lambda}^{B \neq A} \left[\frac{3}{4} \mathfrak{P}_{\mu\lambda}^2 - \frac{1}{2} \mathfrak{P}_{\mu\lambda} \mathcal{S}_{\mu\lambda} \right] \right. \\
 &\quad + \sum_{\lambda \neq \nu}^{B \neq A} \left[\frac{3}{4} \mathfrak{P}_{\nu\lambda}^2 - \frac{1}{2} \mathfrak{P}_{\lambda\nu} \mathcal{S}_{\lambda\nu} \right] + \frac{3}{2} \mathfrak{P}_{\mu\mu}^2 - 2 \mathfrak{P}_{\mu\mu} \left. \right\} (\mu\mu | \nu\nu) \\
 &\quad + \sum_{\lambda \neq \mu}^{B \neq A} \left[\frac{1}{4} \mathfrak{P}_{\mu\lambda}^2 - \frac{1}{2} \mathfrak{P}_{\mu\lambda} \mathcal{S}_{\mu\lambda} \right] (\nu\nu | \lambda\lambda) \\
 &\quad + \sum_{\lambda \neq \nu}^{B \neq A} \left[\frac{1}{4} \mathfrak{P}_{\nu\lambda}^2 - \frac{1}{2} \mathfrak{P}_{\lambda\nu} \mathcal{S}_{\lambda\nu} \right] (\mu\mu | \lambda\lambda) \tag{44}
 \end{aligned}$$

$$\begin{aligned}
 (1+x)^2 \lambda(\mu_A \nu_A | \mu_A \nu_A) &= [1 - 2 \mathfrak{P}_{\mu\mu}] (\mu\nu | \mu\nu) \\
 &\quad - \sum_{\lambda}^{B \neq A} [\mathfrak{P}_{\lambda\nu} \mathcal{S}_{\mu\lambda} - \frac{1}{2} \mathfrak{P}_{\lambda\nu} \mathfrak{P}_{\mu\lambda}] (\mu\nu | \lambda\lambda) \\
 &\quad + \sum_{\lambda}^{B \neq A} \left\{ \left[\frac{3}{4} \mathfrak{P}_{\mu\lambda} \mathfrak{P}_{\lambda\nu} - \frac{1}{2} \mathfrak{P}_{\lambda\nu} \mathcal{S}_{\mu\lambda} \right] (\mu\nu | \mu\mu) \right. \\
 &\quad \left. + \left[\frac{3}{4} \mathfrak{P}_{\mu\lambda} \mathfrak{P}_{\lambda\nu} - \frac{1}{2} \mathfrak{P}_{\lambda\mu} \mathcal{S}_{\lambda\nu} \right] (\mu\nu | \nu\nu) \right\} \tag{45}
 \end{aligned}$$

4. Conclusions

The conclusions resulting from this study are very similar to those made by Brown and Roby [5] but in the present case they are formally correct because of the convergent nature of the expansion used. As previously concluded the assumptions

$$\lambda \alpha_{\mu} \approx \alpha_{\mu} \tag{46}$$

$$\lambda \beta_{\mu\lambda} \approx \beta_{\mu\nu} \tag{47}$$

are not justified. But, the present work does confirm that the integral assumptions

$$\lambda(\mu_A \nu_B | \lambda_C \sigma_D) \approx 0, A \neq B, C \neq D \tag{48}$$

and

$$\lambda(\mu_A \nu_A | \lambda_B \sigma_B) \approx (\mu_A \nu_A | \lambda_B \sigma_B) \tag{49}$$

do have some justification. The exceptions to this statement are the integrals contained in G_{BC}^{AA} (Eq. (37)) which can still have terms of $O(\mathfrak{P}^2)$ contributing to the integral over the orthogonal basis. The problem created for the NDDO method by three-centre integrals has already been recognized by Brown and Burton [15] who have introduced what they call a balanced approximate SCF MO theory which includes, as well as the NDDO two-electron integrals, all interactions of the form

$$G_{BC}^{AA} = (\mu_A \nu_A | \lambda_B \sigma_C).$$

They showed that including these terms in an otherwise NDDO calculation led to a big improvement in the agreement of the calculated MO energies of FCN with those from a near Hartree–Fock limit *ab initio* calculation.

The modification of the S -expansion technique described here demonstrates that neglect of differential overlap methods can be derived and justified in a basis of orthogonal atomic orbitals, and confirms the following general conclusions [5]:

- 1) The zero-differential-overlap assumptions for repulsion integrals apply in an orthogonal basis, and non-zero integrals may be evaluated using normal rather than orthogonal orbitals.
- 2) If core elements are evaluated theoretically in a non-orthogonal basis to form the core matrix H it is necessary, because of (34) and (35) to transform H to a symmetrically orthogonalized basis,

$${}^{\lambda}H = S^{-1/2}HS^{-1/2}$$

- 3) Of the neglect of differential overlap approximations, the CNDO and INDO methods do not receive any justification because omission of two-centre integrals of the form $(\mu_A\nu_A | \lambda_B\lambda_B)$ and also in the former method, of some one-centre integrals, cannot be supported. The NDDO method, however, provided that the core elements have been calculated correctly, is correct to at best the second order in overlap, so that

$$F^{NDDO} = {}^{\lambda}F + O(\mathfrak{P}^3).$$

Diatomic molecules, which have no three-centre integrals, and in addition have overlap matrices forming convergent series in powers of S without adjustment, are the most favourable cases. Tables 1 and 2 present the overlap matrices for N_2 and HF, calculated from Schmidt orthogonalized single term Slater type orbitals with the following exponents

$$2s_N = 1.95, \quad 2p_N = 1.95, \quad 2s_F = 2.6, \quad 2p_F = 2.6, \quad 1s_H = 1.0$$

Direct diagonalization shows the largest eigenvalues as N_2 (0.820) and HF (0.558), thus the expansion (11) converges although in the case of N_2 this must be slow.

Errors rise as the number of ligands attached to a centre increase, more orbitals

Table 1. Overlap matrix for valence orbitals of N_2 . Slater type orbitals with exponents 1.95, internuclear distance = 109.4 pm

$2s(N1)$	$2p_z(N1)$	$2p_x(N1)$	$2p_y(N1)$	$2s(N2)$	$2p_z(N2)$	$2p_x(N2)$	$2p_y(N2)$
1.0	0	0	0	0.45	0.43	0	0
0	1.0	0	0	-0.43	-0.32	0	0
0	0	1.0	0	0	0	0.28	0
0	0	0	1.0	0	0	0	0.28
0.45	-0.43	0	0	1.0	0	0	0
0.43	-0.32	0	0	0	1.0	0	0
0	0	0.28	0	0	0	1.0	0
0	0	0	0.28	0	0	0	1.0

$2s(\text{F})$	$2p(\text{F})$	$1s(\text{H})$
1.0	0	0.47
0	1.0	-0.30
0.47	-0.30	1.0

Table 2. Overlap matrix for valence orbitals of HF. Slater type orbitals with exponents of 2.6 for fluorine and 1.0 for hydrogen, internuclear distance = 91.7 pm

per centre are included, and the overlap between participating orbitals increases, so that

$$\lambda G = G^{\text{NDDO}}$$

or

$$\lambda(\mu_A \nu_B | \sigma_C \lambda_D) = \delta_{AB} \delta_{CD} (\mu_A \nu_A | \sigma_C \lambda_C) \quad (50)$$

becomes more approximate. Already we have seen that three-centre integrals involving interactions between a one-centre distribution and a two-centre distribution may not satisfy (50) to $O(\mathfrak{P}^2)$. Equations (42–45) show also that two-centre Coulomb and one-centre Coulomb and exchange integrals may also fail to satisfy (50) to $O(\mathfrak{P}^2)$. Two approaches have been made to overcome this latter problem. Roby and Sinanoğlu [16] used a scheme which decreased all two-centre repulsion integrals and increased all one-centre repulsions by amounts between 9–14%. A more promising approach has been used by Chandrasekhar *et al.* [13] who have calculated the actual values of the transformed integrals correct to second order in overlap using expressions corresponding to Eqs. (42) and (44). Unfortunately, they used expressions derived from an unmodified S matrix which, as an examination of (41–45) shows, will give a result considerably in error especially in the ions they studied, PO_4^{3-} , SO_4^{2-} , and ClO_4^- where the spectral radius of the S matrix is high. Despite this Chandrasekhar *et al.* reported a good agreement with *ab initio* calculations. Considering this success use of the corrected expressions reported here should be investigated.

The foregoing analysis gives a rigorous examination of NDO methods in the framework of their relationship to calculations in an orthogonalized basis and the S expansion technique. It clearly shows that the CNDO and INDO methods and their modifications cannot be justified by this technique. NDDO methods have some justification. The analysis shows strengths and weaknesses of these and suggests areas where improvements can be sought.

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