Theoret. Chim. Acta (Berl.) 58, 233–244 (1981)

THEORETICA CHIMICA ACTA

The *Ab initio* Neglect of Differential Diatomic Overlap Method

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The *ab initio* Neglect of Differential Diatomic Overlap (N.D.D.O.) method of Roby is tested numerically for an extensive series of molecules. Agreement with the full *ab initio* molecular orbital method is poor. Total energies are more negative and dipole moments are overestimated. The failings of the N.D.D.O. method are accounted for using multipole-multipole expansions.

Key words: Neglect of differential diatomic overlap (N.D.D.O.) method – *Ab initio* molecular orbitals.

1. Introduction

There has been considerable recent interest in developing a theoretical framework for an *ab initio* Neglect of Differential Diatomic Overlap (N.D.D.O.) method, notably by K. R. Roby [1]. This has had, as a companion, the development of essentially parametric N.D.D.O. techniques, such as the "M.N.D.O." method of Dewar and co-workers [2]. These latter methods have apparently enjoyed considerable numerical success.

This paper presents what appears to be the first exhaustive account of an *ab initio* N.D.D.O. method, and attempts to analyse the results of the model used in a simple-minded manner. Previous studies [3, 4] have *implied* that this is a potentially valuable technique. But these studies have been performed on a rather limited range of molecules, exclusively at their equilibrium geometries.

2. The Roby N.D.D.O. Method

Roby [1] has given a limiting case justification of N.D.D.O. This might be summarized as follows. Given a complete basis set on each nucleus A, $B\ldots$ of a

0040–5744/81/0058/0233/$02.40

polyatomic molecule $\{\chi_A, \chi_B, \ldots\}$ he shows that for any one-electron operator $\hat{0}$

$$\langle \xi | \hat{0} | \xi \rangle = \langle 0 \rangle = \langle 0^{\circ} \rangle \tag{2.1}$$

where $\{\xi\}$ is an orthonormal canonical basis related to $\{\chi\}$ via a Löwdin transformation [5]:

$$\boldsymbol{\xi} = \chi S^{-1/2} \tag{2.2}$$

where $\boldsymbol{S}$ is the overlap matrix. The respective Fock, $\boldsymbol{F}$, and eigenvector, $\boldsymbol{C}$, matrices are equated:

$$\boldsymbol{F}^{\xi} = \boldsymbol{S}^{-1/2} \boldsymbol{F}^{\chi} \boldsymbol{S}^{-1/2} \tag{2.3}$$

$$\boldsymbol{C}^{\xi} = \boldsymbol{S}^{1/2} \boldsymbol{C}^{\chi}. \tag{2.4}$$

$\langle 0^{\circ} \rangle$ in Eq. (2.1) is $\langle 0 \rangle$ with the two-centre elements set equal to zero, i.e. by applying directly the zero differential overlap (Z.D.O.) N.D.D.O. restriction. A direct consequence of this is:

$$\boldsymbol{F}^{\xi} \text{ (exact)} = \boldsymbol{F}^{\chi} \text{ (evaluated using N.D.D.O.).} \tag{2.4}$$

Numerically precedents have been set to justify this contention. Fischer–Hjalmers [6] found that for π-systems

$$\boldsymbol{F}^{\xi} = \boldsymbol{F}^{\mathrm{ZDO}} \text{ (for the P.P.P. model)}$$

providing that diatomic overlap did not exceed 0.4.

However, King et al. [7] have pointed out certain flaws in Roby's "lemma". The χ-basis is overcomplete; Lowdin's orthogonalisation breaks down for $\boldsymbol{S}$ becomes non-positive definite. Thus the initial χ-basis must be arbitrarily incomplete. Given this, Roby's central equations are not universally valid. King et al. have shown that the only basis to fulfill Rob's requirements are the set of three-dimensional δ-functions. But they add as a "rider" to their conclusions the following remarks:

"We conclude that while Roby has erred in the interpretation of his results his equation . . . has some significance for computation with a finite basis set."

However, they add no numerical justifications to endorse this assertion. The fundamental motivation for this work was to assess this "sentiment", i.e. that limited basis N.D.D.O. is potentially useful, which we feel to be an inherent, or implicit, assumption of many workers.

An alternative approach to analysing Z.D.O. methods is the series expansion of $\boldsymbol{S}^{-1/2}$ originally used by Brown and Roby

$$\boldsymbol{S}^{-1/2} = (\mathbf{1} + \boldsymbol{Z})^{-1/2} = \mathbf{1} - \tfrac{1}{2}\boldsymbol{Z} + \tfrac{3}{8}\boldsymbol{Z}^2 \ldots . \tag{2.5}$$

This series however does not always converge and a modified series expansion has recently been used by Chandler and Grader [9]

$$(\mathbf{1} + \boldsymbol{Z})^{-1/2} = (\mathbf{1} + \boldsymbol{X})^{-1/2} [1 - \tfrac{1}{2}\boldsymbol{\beta} + \tfrac{3}{8}\boldsymbol{\beta}^2 \ldots] \tag{2.6}$$

where

$$\boldsymbol{\beta} = (\mathbf{1}+\boldsymbol{X})^{-1}(\boldsymbol{Z}-\boldsymbol{X}) \tag{2.7}$$

$$\boldsymbol{X} = x\mathbf{1} \qquad x \geq 0. \tag{2.8}$$

This series is identical to one earlier used by one of us [10] and implemented as a computational procedure [11] for $\boldsymbol{S}^{-1/2}$ and, in a modified way [12], for $\boldsymbol{S}^{1/2}$. This identity follows with the replacement

$$(\mathbf{1}+\boldsymbol{X})^{-1/2} = (1+x)^{-1/2}\mathbf{1} = \left(\frac{2}{r}\right)^{1/2} \tag{2.9}$$

$$\boldsymbol{\beta} = \frac{2}{r}\boldsymbol{S} - \mathbf{1}. \tag{2.10}$$

Chandler and Grader use Eq. (2.6) truncated to second-order to give some justification to the N.D.D.O. scheme. Even to second-order however not all non-N.D.D.O. terms disappear. Diatomic molecules are likely to be most favoured cases and close clusters of atoms the least favourable. Experience shows that the expansion (2.6) converges rather slowly in many cases of interest and thus truncation to second-order may have a limited validity.

3. Computational details

The scheme adopted was essentially the "Simplified *Ab Initio*" (N.D.D.O.) method of Roby et al. [4iv] which has been adapted by several others. It retained the minimal basis framework but evaluated integrals using contracted Gaussian Type Orbitals (cGTO's).

1. All the subsets, $\chi_A \ldots$, were orthonormal. The bases employed were either the orthogonal Hornback-Whitman [13] $5s/3p$ cGTO basis, or Schmidt orthogonalized STO-3G expansions [14].
2. The χ-basis was transformed to the orthonormal canonical ξ-basis by the $\boldsymbol{S}^{-1/2}$ symmetric transform (Eq. (2.2)).
3. The one-electron matrix $\boldsymbol{H}$ was evaluated fully in this basis.
4. The two-electron terms of the $\boldsymbol{G}$ ("repulsion") matrix were computed according to the N.D.D.O. restriction.
5. The symmetrically orthogonalized Fock matrix $\boldsymbol{F}$ was formed:

   $$\boldsymbol{F}^{\xi} = \boldsymbol{H}^{\xi} + \boldsymbol{G}^{x}.$$

   This was iteratively constructed in the normal self-consistent way, repeatedly diagonalizing $\boldsymbol{F}^{\xi}$ until a self-consistent electronic energy was obtained. (Note: it might be pointed out that others have optimised N.D.D.O. molecular orbitals, subjecting these to constraints other than energy minimization [3ii]. Minimal basis N.D.D.O. is not variational.)

Table 1. Summary of NDDO and *ab-initio* results for ~30 ground-state wavefunctions (N is the number of electrons in the molecule)

	N	ΔE (a.u.) ($E_{ab\text{-}initio} - E_{\mathrm{NDDO}}$)	$\Delta E/E$ ×100	dipole moment, μ	
				NDDO	*ab-initio*
Diatomics					
H_2	2	0.0102	0.09		—
LiH	4	0.0603	0.06	0.96	1.13
Li_2	4	0.0646	0.42		—
Be_2	6	0.1665	0.58		—
BH	6	−0.0478	−0.52	1.42	0.44
CH^+	6	0.1914	0.51	2.56	1.02
NH	8	0.3880		1.72	0.80
OH	10	0.0402	0.05	2.60	0.13
FH	10	0.3656	0.61	2.00	0.85
BeO	10	0.8065	1.01	2.88	1.48
LiF	12	0.4325	0.41	2.46	2.37
CO	14	0.7294	0.62	0.43	0.21
Triatomics					
BeH_2	6	−0.0707	−0.46		—
NH_2^-	12	0.3000	1.05	2.39	0.22
OH_2	12	1.0301	1.41	6.32	2.28
FH_2^+	12	1.2383	1.34	1.82	1.25
LiOH	12	0.6966	0.86	4.95	1.83
Tetra- and polyatomics					
BH_3	8	0.1152	0.56		—
NH_3	10	1.0161	1.02	5.91	0.82
OH_3	10	1.8810	1.80	6.54	1.03
CH_4	10	0.7975	2.06		—
NH_4^+	10	1.5298	2.56		—
BH_5	10	0.1169	1.53		—
CH_5^+	10	0.8216	2.26		—
C_2H_4	16	2.8859	3.79		—
B_2H_6	16	2.9894	5.70		—
Polymers					
$(LiH)_2$	8	0.2027	0.98		—
$(BeH_2)_4$	24	0.8897	0.95		—
H_8F_8	80	6.5001	0.81	13.45	8.93

All energies in atomic units $\approx 4.3598 \times 10^{-18}$ J.
All dipole moments in Debye $\approx 3.3356 \times 10^{-30}$ Cm.

4. Results (i)

Tables 1 and 2 present a summary of energetic, structural and dipolar data for nearly 30 molecules contrasted against results obtained from full scale *ab initio* studies using identical basis sets. A number of trends are apparent. Firstly, in nearly every instance N.D.D.O. overestimates (i.e. makes more negative) the total molecular energy compared with *ab initio* computations. This over-

Table 2. Summary of NDDO and *ab-initio* structural investigations on ~25 simple molecules. McConkey's values (10) in parentheses

	Structure NDDO (R_0)	Structure *ab-initio* (R_0)	Experiment
Diatomics			
H_2	1.35	1.38	1.40
LiH	2.40 (2.44)	2.95	3.01
Li_2	4.40 (2.79)	5.33	5.05
Be_2	4.23 (4.22)	8.00	
BH	2.30 (2.38)	2.35	
CH^+	1.73 (1.88)	2.17	
NH	1.68 (1.62)	1.92	1.96
NO^-	1.20	1.83	
FH^a	1.35 (1.22)	1.80	1.733
BeO	1.85 (1.60)	4.05	2.52
LiF	2.02 (2.03)	2.99	2.85
Co	1.75 (1.69)	2.25	2.13
N_2	1.94 (1.99)	2.09	2.05
BF	1.72 1.68)	2.45	2.39
F_2	2.00 (1.99)	2.70	2.68
Triatomics; all predicted to be linear by NDDO, unless bond angle (θ) given			
BeH_2	2.60	2.60	2.53
NH_2-	1.55	1.85; $\theta = 100°$	
$OH_2{}^b$	1.30	1.76; $\theta = 104°$	1.80; 104°
FH_2^+	1.35	1.79; $\theta = 109°{}^d$	
LiOH	rLiO 1.9 rOH 1.35	2.95 1.76	3.02; 1.80°
Tetra- and Polyatomics			
BH_3	2.30	2.35	2.36
NH_3	1.65 $\theta = 60°$	1.87; $\theta = 68°$	1.92 $\theta = 71°$
CH_4	1.85	2.10	2.07
NH_4^+	1.55	1.90	
CH_5^+	D_{2h} predicted ax. 1.93) eq. 1.70)	C_{4v} predicted ax. 2.16) eq. 2.20)	
$B_2H_5^+{}^c$	D_{2h} Form I preferred	Forms II and III preferred	

[a,b] Ref. [4IV] Chandresakar et al. find that *scaled* NDDO *overestimates* internuclear distances. They are calculated to be 1.94 and 1.86 au, for water.

[c] B. J. Duke and D. G. Stephens. Theoret. Chim. Acta (Berl.) **26**, 28 (1972).

[d] G. H. F. Dierksen, W. von Niessen, W. P. Kraemer, Theoret. Chim. Acta (Berl.) **31**, 205 (1973).
All distances in a.u.

estimation proportionately increases as the number of bonds in the system increases. Secondly, N.D.D.O. uniformly gives high values of the molecular dipole moment. Thirdly, it gives highly truncated bond distances. In both these last two instances the fully *ab initio* results are far superior with respect to experimental values. These trends have been substantially confirmed by McConkey [15] and Gleghorn [16] who find that these trends continue, and even worsen, with extended basis computations. This has also been our experience with our limited number of "double-zeta" N.D.D.O. computations.

5. Discussion

In this Section we will try to account for the failings of N.D.D.O. in a rather simple-minded manner. The expression for the total energy of a polyatomic molecule is (using conventional notation):

$$E_{\mathrm{mol}} = \tfrac{1}{2}\,\mathrm{tr}\,(\boldsymbol{P}(\boldsymbol{F}+\boldsymbol{H})) + \sum_{A<B}\sum Z_A Z_B / R_{AB} \tag{5.1}$$

where $\boldsymbol{P}$ denotes the Mulliken Density matrix. The second term in Eq. (5.1) is the nuclear-nuclear repulsion energy. The two-electron parts of $\boldsymbol{F}$ can, in principle, be treated as multipole-multipole expansions, as does Dewar [2] in his parametric N.D.D.O. method.

Truncating the latter to the rotationally invariant monopole-monopole interactions (5.1) can be re-expressed:

$$\begin{aligned} E_{\mathrm{mol}} = {} & \tfrac{1}{2}\sum_a^A \sum_b^B 2P_{ab}\beta_{ab} - \tfrac{1}{2}P_{ab}^2\gamma_{AB} + \sum_{A<B} Z_A Z_B / R_{AB} \\ & + \sum^a P_{aa}U_{aa} - \sum_A P_A \sum_{A<B} V_{AB} + \tfrac{1}{2}\sum_{A<B} P_A P_B + \tfrac{1}{4}\sum_a \sum_b P_{ab}\gamma_{ab} \end{aligned} \tag{5.2}$$

where χ_{AB} is the monopolar repulsion integral between centres A and B, U_{ab} is a "core integral", V_{AB} is a "penetration integral" and β_{AB} is a "resonance integral". It is important to note that Eq. (5.2) is equally valid for either the $\{\xi\}$ or $\{\chi\}$ basis. Defining the number of "bonds" between a diatomic fragment A, B as n_{AB}

$$n_{AB} = \tfrac{1}{2}\sum_{a,b} P_{ab}^{\star} P_{ba} \tag{5.3}$$

the bicentric part of the energy may be written:

$$\begin{aligned} \sum E_{AB} = {} & \sum_{a,b}^{A,B} P_{ab}\beta_{ab} + \sum P_A P_B \gamma_{AB} - \sum Z_B P_A V_{AB} \\ & + \sum Z_A Z_B / R_{AB} - \tfrac{1}{2}\{\sum n_{AB}\gamma_{AB}\} \end{aligned} \tag{5.4}$$

where the term in curly brackets, or braces, separated from the others represents *bicentric exchange.*

If the integrals are calculated in a Slater, or Slater-simulating[1] (e.g. cGTO) basis then we permissively make the approximation that in the region of equilibrium internuclear separation (see Zerner [17] for extensive discussion of this):

$$1/R_{AB} \simeq V_{AB} \simeq \gamma_{AB}. \tag{5.5}$$

This leads to:

$$\sum E_{AB} = \sum P_{ab}\beta_{ab} - \{\sum \tfrac{1}{2} n_{AB}/R_{AB}\} - \sum (Z_A P_A - P_A P_B + Z_A Z_B)/R_{AB}.$$

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[1] By a Slater, or Slater-simulating, orbital we mean an atom centred orbital which simulates the behaviour of an exponential orbital and *overlaps* with orbitals on other atomic centres.

For diatomic molecules this simplifies to:

$$E_{AB} = \sum P_{ab}\beta_{ab} - \{\tfrac{1}{2}n_{AB}/R_{AB}\} - Q_A Q_B/R_{AB} \tag{5.7}$$

where Q_A and Q_B denote "net" charges on atoms A and B:

$$Q_A = P_A - Z_A : \qquad Q_B = P_B - Z_B.$$

For homonuclear systems we may finally note:

$$E_{AA'} = \sum_{a,b} P_{ab'}\beta_{ab'} - \{\tfrac{1}{2}n_{AB}/R_{AB}\}. \tag{5.8}$$

The above analysis is most revealing. The terms in 5.8 are all attractive; and in principle Eq. (5.8) need not display any minimum. This accounts for the reason that Slater based ZDO methods in general, and N.D.D.O. results in particular, give anomalously short bond distances and high (negative) molecular energies for homonuclear systems. It is seen that the origin of this behaviour lies in the bicentric exchange term. This effect increases as the number of bonds in the system increases, *via* the n_{AB} dependence, and this effect is seen in this work. For heteronuclear systems there is a pronounced tendency to maximise the net

Table 3. Sample wavefunction for HF

		N.D.D.O.	*abitio*
Molecular energy		−100.0219	−99.6563
Dipole moment		1.7498	0.7473
Eigenvalues (occupied)		−25.7928	−26.1143
		−1.5297	−1.4876
		−0.6031	−0.6524
		-0.4068^{π}	-0.5440^{π}
Mulliken population over A.O.'s	H(1s)	0.0240	0.5635
	$F(1s)$	1.9995	2.0004
	$F(2s)$	1.8602	1.9016
	$F(p\sigma)$	2.1167	1.5345

Molecular size and electronic energy neglect for HF polymers; model geometries assumed

Molecule	$(E_{\mathrm{NDDO}} - E_{ab\text{-}initio})$
(HF)	0.5292
$(HF)_2$	1.4821
$(HF)_3$	2.3339
$(HF)_4$	3.4943
$(HF)_5$	4.0133
$(HF)_6$	4.6287
$(HF)_7$	5.6713
$(HF)_8$	6.5000

molecular charges, Q_A and Q_B at the expense of the n_{AB} term. This might be rationalised as they enter the energy expression 5.7 with the relative weight 2 : 1. Consequently dipole moments become dramatically overestimated. Again this gross "electrostatic" feature may account for the predicted (by N.D.D.O.) linear geometry of water and the unusual structure of the $B_2H_5^+$ cation (see Table 2). Table 3a gives details of *ab initio* and N.D.D.O. wavefunctions for HF; note how charges Q_A, Q_B are high, minimizing n_{AB}.

These trends are further illustrated by some details of the wavefunctions for the $(HF)_n$ oligomers shown in Table 3b ($n = 1, 8$). It is notable that the deviations of N.D.D.O. energies from corresponding *ab initio* energies are almost linearly dependent on the number, n_{HF}, of hydrogen fluoride intermolecular bonds (hydrogen bonds are neglected for the present purposes).

6. Results (ii)

Tables 4(a–d) summarize relative *ab initio* and N.D.D.O. one-electron properties. As might be expected on the basis of the above results the computed N.D.D.O. properties deviate widely, and wildly, with respect to comparable *ab initio* values. The relative deviations are considerably larger than errors in molecular energies. This is a simple reflection that molecular energy is a poor guide to the "quality" of a wavefunction. Thus, say, an error of $N\%$ in the molecular energy may have an associated $N^2\%$ error in the expectation value of quartic operators, etc. Tables 4(a–d) list N.D.D.O. errors in values of r^2, etc.; similar errors are found in diamagnetic shielding and Hellman–Feynman forces.

7. Concluding remarks

There are several important points that can be made. Firstly, the employment of a "Slater-type" minimal basis is shown to lead to gross errors in structural and bonding properties using the Roby N.D.D.O. method, compared both with respect to directly comparable *ab initio* calculations and experimental results. Thus the N.D.D.O./Simplified *Ab Initio* schemes proposed by Roby et al. [4]

Table 4a. Som virial ratios and $\langle r^2 \rangle$ from NDDO and Comparable *ab-initio* calculations (*Ab-initio* result followed by NDDO value in brackets)

Molecule	Virial		$\langle r^2 \rangle^a$ (Centre of mass)		% Error
Methane	1.9565	(2.1188)	20.7616	(29.8528)	+43.8
Ammonia	1.9982	(2.1810)	25.9818	(30.6450)	+18.0
Water	1.9734	(2.1086)	12.7877	(14.0178)	+9.6
Hydrogen fluoride	1.9930	(2.0465)	12.9167	(18.9904)	+47.0
Lithium hydroxide	1.9587	(2.0921)	36.0843	(52.0948)	+44.4
Ethylene	1.9633	(2.1284)	52.8077	(86.9620)	+64.7

[a] Units are $(a.u.)^2$.

Table 4b. Charge density at the nucleus Fermi *S*-contacts in a.u.[a,b]

Centre	*Ab-initio*	% error in NDDO value
1		
C	103.8523	−0.44
H	0.1936	−77.60
2		
N	170.0392	−0.42
H	0.1892	−81.02
3		
O	258.0389	+0.24
H	0.2020	−93.3
4		
F	373.4452	−0.05
H	0.1894	−31.03
5		
Li	11.0601	+2.60
O	257.6335	−2.12
H	2.0202	+71.4
6		
C	103.9195	−0.54
H	0.1933	−8.10

[a] 1 a.u. ≈ 1.0812×10^{12} cm^{-3}

[b] Key to molecules and atoms, used in subsequent Tables

1	CH_4
2	NH_3
3	OH_3
4	FH
5	LiOH
6	H_4C_2

Table 4c. Electronic potential in a.u. electronic values followed by overall total in parentheses

Centre	*Ab-initio*		% Error total value N.D.D.O.
1			
C	−4.6914	(−0.9212)	+15.4
H	−16.4758	(−14.5505)	−47.4
2			
N	−5.1247	(−0.8218)	+0.6
H	−20.1504	(−19.0693)	−0.9
3			
O	−5.3658	(−0.5936)	+0.6
H	−24.6553	(−23.5496)	−4.6
4			
F	−6.2172	(−1.0239)	+3.6
H	−28.1798	(−27.6028)	−4.0
5			
Li	−6.4501	(−1.3224)	+1.4
O	−24.4170	(−22.5595)	+1.1
H	−8.7465	(−5.7751)	−32.0
6			
C	−18.3567	(−14.5107)	−9.0
H	−9.6120	(1.2446)	+17.4

1 a.u. ≈ 2.7211 V.

Table 4d. Electric Field Gradient Asymmetry Parameter ρ

Molecule	*Ab-initio*	N.D.D.O.	% Error
2			
N	0.843	0.859	+1.2
H	0.104	0.159	+52.8
3			
O	0.749	0.971	+29.7
H	0.091	0.175	+92.3
6			
C	0.370	0.897	+142.4
H	0.012	0.413	+3341.6

must be rejected as a practical tool for the computation of "reliable" wavefunctions. Certainly it must be rejected as a device for calculating wavefunctions, one-electron properties, etc., for large molecules. For example for a small molecule, CH_4, the N.D.D.O. errors in the computed electronic potentials at the C and H nuclei are 15.4 and 47.4% respectively. In the non-empirical S.A.M.O. approach of Duke and others [18] it has been demonstrated that errors in computed S.A.M.O. one-electron properties for octane, C_8H_{18}, are very small, even when the same basis functions are employed on the C and H atoms. For example, the largest error in the computed electronic potential for an atom in this system is 0.061%.

Secondly, from the above analysis it follows that the only realistic chance for the success of N.D.D.O. might come when two-centre two-electron interactions are scaled. This has been an essentially empirical observation of several workers [3iv, 4v, 19]. Based on the work of Cook et al. [19], Roby and Sinangolu [3iv] suggested the matrix relationship:

$$\boldsymbol{G}^{x} = \boldsymbol{SCALE}.\, \boldsymbol{G}^{\xi} \tag{7.1}$$

where ***SCALE*** is a matrix of scale factors for Coulomb repulsion integrals. It was suggested that two-centre integrals be decreased by an amount between 9–14% to obtain "better" results. This work endorses the vital need for scaling repulsion integrals; but it does not show how to compute them *a priori.*

In parametric methods there is, of course, almost unlimited scope for optimising integrals to produce as "good" a set of results as available computer power and personal persistence allow. Thus, one must point to the very accurate N.D.D.O./Z.D.O. parametric techniques of Dewar and others [2, 20]. In this work we have conclusively rejected the Simplified *Ab Initio*/N.D.D.O. minimal basis set method. It follows that we raise severe doubts about the conjecture of King et al. that this technique "may have some significance with finite basis sets". An extensive investigation of the method with very advanced basis sets (McClean–Yoshimine quality [21]) will be published soon by co-workers [16]. This also leads to a pessimistic view of the Roby N.D.D.O. scheme.

It may well be that any Slater basis is inevitably doomed to failure for an *ab initio* N.D.D.O. scheme. Parametric schemes, of course, never deal with, or define, a basis. Cook et al. have suggested that a better N.D.D.O. basis may involve the use of localised, core separated valence orbitals [20i]. We conjecture that the only way to obtain satisfactory results for an *ab initio* scheme may actually be to employ an atom-centred Z.D.O. basis but this has only been attempted once, for H_2 [22]. The integrals necessary for such a scheme, which involve very complex surface terms are extremely difficult.

The increasing errors with increasing size where the number of three centre integrals increases is compatible with the conclusions of Chandler and Grader [9]. Our results also appear to support the view that any treatment of the N.D.D.O. using the series expansion truncated to second-order may be invalid.

Acknowledgements. We wish to thank Drs. J. T. Gleghorn and F. W. McConkey of the University of Lancaster for communication of their results. We are also indebted to Dr. M. C. Zerner of the University of Guelph for many useful discussions. The computational part of this work was performed on the University of Manchester Regional Computer Centre's CDC7600 while one of us (M.P.S.C.) was holding a Salter's Fellowship. One of us (B.J.D.) wishes to thank Professor R. D. Brown and Dr. F. P. Larkins for their hospitality at Monash University, Australia, where the final revised version was prepared.

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Received May 12/September 1, 1980

Announcement

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