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A Comparative Study of Approximate SCF MO Treatments of Hydrides*

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A comparative study of approximate and exact *ab initio* treatments of H_2O, NH_3 and CH_4 has been carried out. Three approximate schemes based on the NDDO approach are introduced. The results compare well with best results obtained by other authors.

Die angenäherte und exakte *ab initio* Behandlung von H_2O, NH_3 and CH_4 wird verglichen. Drei Verfahren, die auf die NDDO-Näherung zurückgehen, werden eingeführt. Die Resultate sind von vergleichbarer Qualität wie die besten Ergebnisse anderer Autoren.

1. Introduction

In the early stage of quantum chemistry a basic method of treatment of polyatomic molecules was that of the simple LCAO MO method with an effective one-electronic Hamiltonian. With the rapid development of computers interest has rapidly shifted towards more complex semiempirical schemes. At present most common approaches are the CNDO, INDO, MC ZDO, MINDO, NDDO and related methods [1–7]. Unfortunately, despite the considerable number of apparently successful applications, all these methods are lacking in rigour. The S-expansion technique of the $S^{-1/2}$ matrix which was used in an attempt to justify these methods has failed to do so [7–10].

While semi-empiricism has been having these difficulties there has been remarkable progress in the development of non-empirical (*ab initio*) methods. Numerical approximations of integrals have been worked out which reduce the necessary computer time and the required storage capacity significantly. Hence we anticipate that approximate non-empirical schemes are going to replace the oversimplified semiempirical ones. Finding a simple and satisfactory approach of this kind is certainly one of the principle goals of the present day quantum chemistry.

The purpose of this work is to analyze the applicability of three partially new approximate treatments based on the NDDO scheme and the Gaussian lobe function expansion. The analysis has been carried out for three molecules, H_2O, NH_3 and CH_4. For these cases a rather large body of comparative material is available.

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2. Notation

In what follows we have adopted an abbreviated notation for the various schemes:

1) The notation for the theoretical framework is the standard one, i.e. SCF, CI, MC SCF. If not stated differently the standard SCF scheme is always implied.

2) The types of the basis functions are denoted by S – for STO's, by H – for approximate or exact Hartree-Fock atomic orbitals, by C – for a formal contracted set of any type of functions, by G – for single Cartesian Gaussian functions, by L – for single Gaussian lobe functions and by F – for floating spherical Gaussian functions; a symmetrical orthogonalization of the whole basis is denoted by a wavy bar, e.g. $\tilde{\mathrm{S}}$, $\tilde{\mathrm{H}}$ or $\tilde{\mathrm{C}}$.

3) The degree of the zero differential overlap is symbolized in a standard way (CNDO, INDO, MC ZDO, NDDO, etc.) [1–7].

Additionally we use throughout the paper the following two symbols: NMTC – for a method Neglecting More than Two-Center integrals and FS – for a Full Scheme method, with no ZDO-type approximations at all.

4) The dimensions of the contracted and of the uncontracted sets strongly influence the computer time and the required storage capacity. Let us assume that independently of the parent atom the uncontracted set consists of altogether N_s *s*-type functions, N_p *p*-type and N_d *d*-type ones. Let us similarly assume that we have altogether n_s *s*-type contractions, n_p *p*-type ones and n_d *d*-type ones. We shall use the notation $(n_s, n_p, n_d\,\mathrm{X};\ N_s, N_p, N_d\,\mathrm{Y})$ where X stands for S, H, C or F and the symbol Y stands for G, L or F. If a still more detailed specification is required we shall use the notation of contractions in accordance with Johansen's work [11].

5) Except in the FS approach many molecular integrals are neglected at first and evaluated approximately afterwards. Depending on the approximation we shall put:

$/R$ – for the Ruedenberg approximation of the remaining many-center integrals [12],

$/M$ – for the Mulliken formula [13] and

$/N_s', N_p', N_d'\,\mathrm{Z}$ where $\mathrm{Z} = \mathrm{G}$, L or F – in the case of calculation of the remaining integrals with a smaller basis set of uncontracted functions. If the smaller uncontracted set is contained in the original one (truncation of the set) we shall put $\mathrm{Z} = \mathrm{Y}$. Otherwise we put $\mathrm{Z} = \mathrm{Y}'$.

3. Details of the Approach

The calculations to be reported are based on the following four schemes:

$$\mathrm{FS}(n_s, n_p\,\mathrm{C};\ N_s, N_p\,\mathrm{L}), \quad \text{equivalent to} \quad \mathrm{FS}(n_s, n_p\,\mathrm{H};\ N_s, N_p\,\mathrm{L}), \tag{1}$$

$$\mathrm{NDDO}(n_s, n_p\,\mathrm{C};\ N_s, N_p\,\mathrm{L})/N_s', N_p'\,\mathrm{L}, \tag{2}$$

$$\mathrm{NDDO}(n_s, n_p\,\mathrm{H};\ N_s, N_p\,\mathrm{L})/R, \tag{3}$$

$$\mathrm{NDDO}(n_s, n_p\,\mathrm{C};\ N_s, N_p\,\mathrm{L})/R. \tag{4}$$

We use Whitten's expansion of Hartree-Fock atomic orbitals of oxygen, nitrogen and carbon into Gaussian lobe functions [14]. In Johansen's notation it has the general form $\langle X|3,3,4;5\rangle$. To distinguish them from atomic orbitals the three Whitten type contracted sets of "*s*-type" are denoted in what follows by $1S$, $2S$ and $3S$. The larger expansion of the $1s$ orbital of a hydrogen atom, $\langle \mathrm{H}|3\rangle$, and the smaller one, $\langle \mathrm{H}|2\rangle$ were those given by Veillard *et al.* [15]. The smaller uncontracted set for oxygen, nitrogen and carbon atoms was obtained by truncation. Let $f_s = \Sigma\, c_{js} g_j$ be a typical form of a contracted set function where $|c_{1s}| \geqq |c_{2s}| \geqq \cdots \geqq |c_{Ks}|$. Then, in the truncated form, $f_s \approx N_s(c_{1s}g_1 + c_{2s}g_2)$ where N_s is a renormalization constant.

The geometry of H_2O was taken over from Neumann and Moskowitz [16]: $R_{\mathrm{OH}} = 1.80$ a.u. and $\sphericalangle = 105°$. It differs only slightly from the experimental one. In the remaining two cases the approximate equilibrium parameters were taken as: $R_{\mathrm{NH}} = 1.91$ a.u., $\sphericalangle = 106.7°$ and $R_{\mathrm{CH}} = 2.05$ a.u., $\sphericalangle = 109°28'$. In calculating the inversion barrier of NH_3 the bond lengths were kept constant.

The framework of Roothaan's SCF theory for closed shell systems, the details of the NDDO approach and the description of the Ruedenberg approximation for many-center integrals are described elsewhere [17, 1, 6, 12]. Probably the only explanation required is for the Ruedenberg approximation in terms of non-orthogonal contracted sets; it is to be noted that the original approximation is based on orthogonal atomic orbitals.

Let $\boldsymbol{f}_{\mathrm{A}}$ be a row vector of non-orthogonal (in general) contracted sets of atom A and let $\boldsymbol{f}_{\mathrm{B}}$ have a similar meaning for atom B. In the case of a sufficiently large basis we can write that $\boldsymbol{f}_{\mathrm{A}} \approx \boldsymbol{f}_{\mathrm{B}} \boldsymbol{C}_{\mathrm{AB}}$ and $\boldsymbol{f}_{\mathrm{B}} \approx \boldsymbol{f}_{\mathrm{A}} \boldsymbol{C}_{\mathrm{BA}}$. It follows that $\boldsymbol{S}_{\mathrm{BA}} \approx \boldsymbol{S}_{\mathrm{BB}} \boldsymbol{C}_{\mathrm{AB}}$ and $\boldsymbol{S}_{\mathrm{AB}} \approx \boldsymbol{S}_{\mathrm{AA}} \boldsymbol{C}_{\mathrm{BA}}$, where $\boldsymbol{S}_{\mathrm{BA}} = \int \boldsymbol{f}_{\mathrm{B}}^{+} \boldsymbol{f}_{\mathrm{A}}\, dV$, $\boldsymbol{S}_{\mathrm{BB}} = \int \boldsymbol{f}_{\mathrm{B}}^{+} \boldsymbol{f}_{\mathrm{B}}\, dV$, $\boldsymbol{S}_{\mathrm{AB}} = \boldsymbol{S}_{\mathrm{BA}}^{+}$ and $\boldsymbol{S}_{\mathrm{AA}} = \int \boldsymbol{f}_{\mathrm{A}}^{+} \boldsymbol{f}_{\mathrm{A}}\, dV$. Therefore

$$\boldsymbol{f}_{\mathrm{A}} \approx \boldsymbol{f}_{\mathrm{B}} \boldsymbol{S}_{\mathrm{BB}}^{-1} \boldsymbol{S}_{\mathrm{BA}}\,, \tag{5}$$

$$\boldsymbol{f}_{\mathrm{B}} \approx \boldsymbol{f}_{\mathrm{A}} \boldsymbol{S}_{\mathrm{AA}}^{-1} \boldsymbol{S}_{\mathrm{AB}}\,. \tag{6}$$

Considering the product $\boldsymbol{f}_{\mathrm{A}}^{+} \boldsymbol{f}_{\mathrm{B}}$ we can expand either $\boldsymbol{f}_{\mathrm{A}}$ or $\boldsymbol{f}_{\mathrm{B}}$, or take the average product of both these expansions. We come in this way to a generalization of the Ruedenberg formula,

$$\boldsymbol{f}_{\mathrm{A}}^{+} \boldsymbol{f}_{\mathrm{B}} \approx \tfrac{1}{2}(\boldsymbol{f}_{\mathrm{A}}^{+} \boldsymbol{f}_{\mathrm{A}} \boldsymbol{S}_{\mathrm{AA}}^{-1} \boldsymbol{S}_{\mathrm{AB}} + \boldsymbol{S}_{\mathrm{AB}} \boldsymbol{S}_{\mathrm{BB}}^{-1} \boldsymbol{f}_{\mathrm{B}}^{+} \boldsymbol{f}_{\mathrm{B}})\,. \tag{7}$$

In general the expansion is restricted to orbitals (contracted sets) of occupied shells. In such a case the accuracy of this approximation is not very high. If the nonorthogonality of contracted sets of atom A and similarly of atom B is not large then with an accuracy comparable to that of expansion (7) we can write that

$$\boldsymbol{f}_{\mathrm{A}}^{+} \boldsymbol{f}_{\mathrm{B}} \approx \tfrac{1}{2}(\boldsymbol{f}_{\mathrm{A}}^{+} \boldsymbol{f}_{\mathrm{A}} \boldsymbol{S}_{\mathrm{AB}} + \boldsymbol{S}_{\mathrm{AB}} \boldsymbol{f}_{\mathrm{B}}^{+} \boldsymbol{f}_{\mathrm{B}})\,. \tag{8}$$

This is the approximation which is the basis of the NDDO modified scheme denoted by $\mathrm{NDDO}(n_s, n_p\,\mathrm{C};\ N_s, N_p\,\mathrm{L})/R$.

Ruttink [18] has shown that the Ruedenberg approximation leads to results which are invariant under rotations of the local axes and which are independent of the choice of hybrid orbitals. The familiar Mulliken approximation does not exhibit such a property [18]. Therefore we have not investigated the Mulliken approximation in any greater detail.

The program for methods (1)–(4) was written in Algol 60 and is available on request. The calculations were performed on the ODRA 1204 computer at the University Computer Center. Also a FORTRAN IV version is now being prepared for use with a larger computer.

When passing from Cartesian Gaussian functions to Gaussian lobe functions the number of basic integrals increases very rapidly. For example the one center integral $(d_{xy}d_{xz}|d_{xy}d_{xz})$ is reducible to 256 integrals over branch functions. However, taking into account all equivalences one can reduce the number of basic integrals. In the particular case the reduction is by a factor of 20. In our program the equivalence of integrals is treated automatically.

4. Results

In Tables 1–3 we compare the results of the full scheme method (1) and the NDDO mixed basis approach (2) with representative results of other authors. Comparisons are made for the total energy, the orbital energies, the ionization potentials via the Koopmans theorem and, to a lesser extent, for the binding energy.

As seen in the tables, despite the significantly smaller number of variation parameters, the full scheme approach FS(...C; ...L) yields results of a comparable quality to those obtained by Roos and Siegbahn. The results obtained for the ammonia molecule are also comparable to those obtained by Kaldor and Shavitt who used Slater type orbitals.

Our results with the NDDO(...C; ...L)/...L approximation compare rather well with the FS results of other authors. In none of the considered cases is the calculated total energy below the Hartree-Fock limit. The calculated total energy is however sometimes slightly below the appropriate FS value (Table 1).

In a non-approximate SCF treatment the ionization potentials estimated via the Koopmans theorem are usually too high when compared to experiment.

Table 1. Comparison of SCF results for H_2O

Quantity	Neumann, Moskowitz [16]	Roos, Siegbahn [19]	Johansen [11]		Present work	
	FS(9, 15, 10C; 18, 21, 10G)	FS(8, 6C; 15, 9G)	FS(4, 3C; 23, 21G)	NDDO(4, 3C; 23, 21G)/8, 6G′	FS(5, 3C; 16, 15L)	NDDO(5, 3C; 16, 15L)/10, 6L
Total energy	−76.044	−75.875	−75.808	−75.663	−75.891	−75.955
Binding energy	0.235	—	—	—	0.100	0.164
Orbital energy						
$1a_1$	−20.550	−20.550	−20.42	−20.47	−20.514	−20.171
$2a_1$	− 1.347	− 1.347	− 1.28	− 1.17	− 1.359	− 1.394
$1b_2$	− 0.714	− 0.694	− 0.66	− 0.66	− 0.697	− 0.578
$3a_1$	− 0.577	− 0.544	− 0.55	− 0.55	− 0.569	− 0.491
$1b_1$	− 0.503	− 0.486	− 0.52	− 0.52	− 0.529	− 0.424

Experimental total energy = −76.485 [20]; Hartree-Fock limit = −76.093 [21], −76.06 [31]; Experimental binding energy = 0.370, 0.349 [21]; Ionization potentials: $I_1 = 0.463$, $I_2 = 0.533$, $I_3 = 0.595$ [22].

Table 2. Comparison of SCF results for NH_3

Quantity	Rauk, Allen, Clementi [23][a]	Roos, Siegbahn [19]	Kaldor, Shavitt [24]	Present work	
	FS(20, 24, 12C; 37, 42, 12G)	FS(10, 6C; 19, 9G)	FS(5, 3S; 5, 3S)	FS(6, 3C; 19, 15L)	NDDO(6, 3C; 19, 15L)/12, 6L
Total energy	−56.222	−56.093	−56.006	−56.041	−55.917
Binding energy	—	—	0.241	0.153	0.129
Inversion barrier	0.008	—	0.017	− 0.00046	− 0.052
Orbital energy					
$1a_1$	−15.535	−15.535	−15.540	−15.583	−15.168
$2a_1$	− 1.148	− 1.142	− 1.102	− 1.174	− 1.170
$1e$	− 0.635	− 0.615	− 0.583	− 0.645	− 0.464
$3a_1$	− 0.428	− 0.407	− 0.369	− 0.471	− 0.346

Experimental total energy = −56.605 [20]; Hartree-Fock limit = −56.222 [25], −56.227 [26]; Experimental binding energy = 0.474 [24]; Experimental inversion barrier = 0.0092 [27]; Ionization potentials: $I_1 = 0.379$ [28], 0.404 [29]; $I_2 = 0.562$ [30], 0.625 [29].

[a] Optimized geometry.

Table 3. Comparison of SCF results for CH_4

Quantity	Ritchie, King [31]	Klessinger [32]		Present work	
	FS(21, 27C; 25, 27G)	FS(6, 3S; 20, 9G)	FS(6, 3S; 18, 9G)	FS(7, 3C; 22, 15L)	NDDO(7, 3C; 22, 15L)/14, 6L
Total energy	−40.198	−40.001	−39.812	−40.033	−39.909
Binding energy	—	0.424	0.432	0.352	0.228
Orbital energy					
$1a_1$	−11.222	−11.389	−11.308	−11.385	−10.088
$2a_1$	− 0.930	− 0.972	− 0.971	− 1.010	− 1.041
$1t_2$	− 0.535	− 0.576	− 0.576	− 0.607	− 0.425

Experimental total energy = −40.526 [20]; Hartree-Fock limit = −40.23 [31]; Experimental binding energy = 0.625 [34], 0.668 [31]; Ionization potentials: $I_1 = 0.500$, $I_2 = 0.849$, $I_3 = 10.617$ [33].

The same conclusion is obviously true with our FS approach. The mixed basis scheme (2), on the other hand, yields results which almost in every case are too low. The average values resulting from these two methods compare surprisingly well with experiment:

	I_{average}	I_{exp}	$I_{\text{best SCF}}$
H_2O	0.476	0.463	0.503
	0.530	0.533	0.577
	0.637	0.595	0.714
NH_3	0.408	0.379; 0.404	0.428
	0.554	0.562; 0.625	0.635
CH_4	0.516	0.500	0.535
	1.025	0.849	0.930
	10.736	10.617	11.222

It is to be noticed that the results of best exact SCF calculations are in general worse.

The inversion barrier of the ammonia molecule is almost a classic problem in quantum chemistry. Many SCF calculations have been performed in order to evaluate its magnitude [23–25, 35, 36]. It has been shown at the SCF level, with non-varied bond lengths that to obtain a correct sign of the barrier a large extended basis set is required [23, 25]. Good agreement with experiment obtained with a small basis set should be considered accidental. Kaldor and Shavitt, for example, obtained a less satisfactory value of the total energy than we in our FS approach. Yet their prediction of the barrier was qualitatively correct while ours was not. We would like to point out, however, that we tried to estimate the barrier also with the smaller of the two considered sets i.e. the truncated one. The barrier of this FS(6, 3C; 12, 6L) calculation was in still better agreement with experiment: 0.0106. Let us recall that even the extended calculations of Body, McClure and Clementi yielded a negative barrier (−0.000436) the value of which, by the way, is almost exactly the same as that following from our FS(6, 3C; 19, 15L) treatment (−0.000457). The barrier to inversion is thus a very subtle effect and we believe it should not be treated by approximate SCF methods.

The idea of a mixed basis scheme is not entirely new. The closest approach is that developed by McWeeny, Hollis, Cook and Palmieri [37, 38] and the NDDO(...C; ...G)/...G′ scheme elaborated by Johansen [11]. We shall discuss the latter work only as the results obtained in the former one were relatively poor. Johansen used Cartesian Gaussian functions and two optimized independently uncontracted sets. Thus, in principle, her approach should be more accurate than ours. In practice it is not precisely so (Table 1) despite the use of a much larger uncontracted set.

Another somewhat related work is that published by Brown, Burden and Hart [39]. It is based on Gaussian lobe functions. Similarly to Johansen they optimized the smaller basis set. However, their ZDO assumption was less restrictive; their NMTC scheme should be in principle more accurate than any one based on the NDDO method. However, the number of integrals to be calculated exactly is in their case several times larger than in the NDDO case and increases for larger molecules very rapidly. A comparison of some of their results with ours is given in Table 6.

In Table 6 we compare the expansion coefficients of molecular orbitals for H_2O, for two related SCF schemes: FS(5, 3C; 16, 15L) and NDDO(5, 3C; 16, 15L)/10, 6L. It follows from the table that except for the lowest state the reproduction of the coefficients by the mixed basis scheme is not satisfactory. Exactly the same result was found for NH_3 and CH_4. The total electron density is not expected to differ greatly but the contours of orbitals may differ significantly.

The applicability of the two suggested NDDO(...)/*R* schemes is analysed in Table 5. The pure NDDO scheme, perhaps accidentally, gives a good estimate of the highest occupied level. The estimation of the total energy, however, is very poor. Such a large error in a non-empirical scheme does not help in under-

Table 4. Comparison of expansion coefficients of molecular orbitals of H_2O for two related SCF schemes: FS(5, 3C; 16, 15L) and NDDO(5, 3C; 16, 15L)/10, 6L. Coefficients of the second scheme are given in brackets

Orbital	O 1 S	O 2 S	O 3 S	O $2p_x$	O $2p_y$	O $2p_z$	H_1 1s
$1a_1$	0.0511	0.0066	0.9792	0.0021	—	—	−0.0011
	(0.0514)	(0.0017)	(0.9800)	(0.0007)	—	—	(0.0018)
$2a_1$	−0.0103	0.8663	−0.2279	0.1640	—	—	0.1188
	(−0.0084)	(0.6361)	(−0.1927)	(0.0799)	—	—	(0.2850)
$1b_2$	—	—	—	—	0.6569	—	0.4120
	—	—	—	—	(0.9393)	—	(0.0876)
$3a_1$	−0.0042	0.4651	−0.0879	0.8456	—	—	−0.1908
	(−0.0012)	(0.0625)	(−0.0294)	(1.0328)	—	—	(+0.1197)
$1b_1$	—	—	—	—	—	1.0 (1.0)	—

Table 5. Applicability of the Ruedenberg approximation and the mixed basis scheme in the SCF MO calculations for ammonia molecule

Quantity	NDDO(5, 3H; 19, 15L)	NDDO(5, 3H; 19, 15L)/R	NDDO(6, 3C; 19, 15L)/R	NDDO(6, 3C; 19, 15L)/12, 6L	FS(6, 3C; 19, 15L)[a] FS(5, 3H; 19, 15L)
Total energy	−79.649	−55.448	−55.880	−55.917	−56.041
Orbital energies					
$1a_1$	−16.478	−14.760	−15.116	−15.168	−15.583
$2a_1$	− 8.219	− 0.855	− 1.017	− 1.170	− 1.173
$1e$	− 2.580	− 0.271	− 0.366	− 0.464	− 0.645
$3a_1$	− 0.451	− 0.140	− 0.246	− 0.346	− 0.471

[a] Within quoted decimal numbers the results of these two calculations are the same.

Table 6. On applicability of simplified SCF treatments of hydrides

Method	Authors	− Total energy		
		H_2O	NH_3	CH_4
Hartree-Fock limit	see Tables 1–3	76.093	56.222	40.173
			56.227	40.198
Minimal STObasis with an approximate estimation of integrals	Body [42]	75.723	55.872	40.078
Double Gaussian modification of the FSGO model	Rouse, Frost [43]	72.792	53.814	38.485
Small Gaussian expansion of the minimal STO basis				
FS($n+2$, 3S; $3n+8$, 9G)	Klessinger [32]	75.571	55.907	40.001
FS($n+2$, 3S; $3n+6$, 9G)	Hehre *et al.* [44]	—	—	39.715
NDDO($n+2$, 3$\tilde{S}$; $n+2$, 3S)/R	Brown *et al.* [41]	75.387	55.590	—
NDDO(4, 3C; 23, 21G)/8, 6G′	Johansen [11]	75.663	—	—
NMTC($n+3$, 3C; $5n+10$, 15L)/$3n+5$, 9L′	Brown *et al.* [39]	75.959	56.088	40.101
NDDO(6, 3C; 19, 15L)/R	present work	—	55.880	—
NDDO(5, 3H; 19, 15L)/R	present work	—	55.448	—
NDDO($n+3$, 3C; $3n+10$, 15L)/$2n+6$, 6L	present work	75.955	55.917	39.909

standing the success of appropriate semiempirical schemes. Comparing the results of the three approximate schemes

$$\mathrm{NDDO}(\ldots\mathrm{C};\ldots\mathrm{L})/\ldots\mathrm{L}$$
$$\mathrm{NDDO}(\ldots\mathrm{H};\ldots\mathrm{L})/R$$
$$\mathrm{NDDO}(\ldots\mathrm{C};\ldots\mathrm{L})/R$$

with those which follow from the appropriate FS approach one finds that the mixed basis scheme is definitely the best. Noteworthy is that the Ruedenberg approximation when applied to slightly non-orthogonal contracted sets yielded better results than in the standard case.

Let us also note that the more or less typical case, NDDO(...H; ...L)/R, has so far not been investigated. The closest attempts at this are the NDDO(...$\tilde{\mathrm{S}}$; ...S)/R and NDDO(...S; ...S)/R schemes proposed by Brown *et al.* [40, 41].

5. A Comparative Study of Simplified SCF Treatments

In Table 6 we compare the total energy of H_2O, NH_3 and CH_4 as obtained in various approximate SCF treatments found in the literature. According to the table the result closest to the Hartree-Fock limit is obtained using the NMTC(...C; ...L)/...L′ method of Brown, Burden and Hart. Not far behind are the results of our NDDO(...C; ...L)/...L scheme. Optimizing the smaller set and increasing the dimension of the uncontracted set (at least to that used by Brown *et al.*) would certainly give still better results. Therefore, in our opinion, the more laborious NMTC scheme is not superior to the NDDO one.

Results obtained with other approximate treatments are usually worse. Only the small Gaussian expansion method on a minimal STO basis, as worked out by Klessinger [32] or Hehre, Stewart and Pople [44], is of comparable quality.

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