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NDDO MO Calculations

I. Analysis of the Method

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The Roby version of the NDDO MO method has been analysed by performing extensive calculations on several molecular systems employing a minimum basis set of STO-3G functions. The effect of using uniform scale factors and those derived from the S-expansion technique, for electron repulsion integrals has also been studied. At the all-electron level, the method, with all its refinements, does not appear promising. The all-valence NDDO MO method after correction by S-expansion, however, yields results which are in good agreement with *ab initio* results. The performance of this scheme is comparable to that of the simplified *ab initio* method of Brown and Roby.

Key word: NDDO

1. Introduction

Of the several approximations studied to simplify the Roothaan procedure without compromising on its predictive power, the Zero Differential Overlap (ZDO) approximation [1–3] has remained the focal point of interest for quite some time. Considerations of invariance under unitary transformations necessitate the application of the ZDO approximation in differing degrees of rigour to the different segments of the electron repulsion integral supermatrix. Thus a whole series of MO schemes, requiring varying magnitudes of computational effort, have been generated [4, 5]. Of these, some of the simpler schemes, like the CNDO, have enjoyed widespread popularity and have been applied, quite successfully, considering the drastic nature of the approximations, to a variety of problems of chemical interest. These methods, however, perform poorly at the nonempirical level and require a rather heavy parameterization in order to give meaningful results. It is in fact a moot point whether the success or failure of these methods in certain problems are not the direct consequence of the parameterization scheme which is being employed. The problem of efficient parameterization becomes particularly acute if extension of these methods to transition metal complexes is attempted. The NDDO MO scheme, coming as it does higher up on the scale of sophistication of the various ZDO methods, might perhaps be amenable to a fully nonempirical treatment which is capable of yielding results resembling those of the full *ab initio* calculations.

The NDDO approximation has been subjected to considerable theoretical analysis, but very few numerical calculations have been attempted. The initial parameterized versions were not much superior to the CNDO and INDO methods [6]. In a brilliant piece of analysis, Roby formulated a theoretically pleasing NDDO MO scheme which did not seriously jeopardize the simplicity of the Pople's scheme [7]. It was applied to the case of CO molecule [8] with satisfactory results, but with some scope for improvement, particularly in evolving a method for systematically scaling the electron repulsion integrals to nullify the error produced by the NDDO approximation. We decided to perform exhaustive calculations with this method to ascertain its capabilities and limitations and to probe the effects of the several refinements which have been suggested. Various quantities like total energy, orbital energies, Mulliken population, dipole moment, expectation value of other one-electron operators like $1/r$ etc. have all been used to judge the merits of the method.

In the present work the degree of success one might hope to achieve from the several NDDO schemes has been described with illustrative examples. In the forthcoming series of papers the results obtained for numerous closed and open shell systems using the scheme which we consider to be the best will be presented.

Section 2 describes the features common to all the calculations. The theoretical basis for the Roby scheme is briefly recapitulated in section 3. After discussing all the results the conclusions have been summarised.

2. Common Features of the Calculations

To provide a consistent interpretation for all the results, a minimum basis set of Slater type orbitals, expanded in terms of three Gaussians each by a variational fit [9], was employed in all the calculations. Clementi-Raimondi exponents [10] were used for the orbital exponents of atoms in the first row of the Periodic Table. The exponent for hydrogen was taken as 1.2.

The reasons for using a Gaussian type orbital basis are multifarious. The first and the obvious one is that it considerably simplifies the integral evaluation in the MO calculations. In addition, we intend using the resultant wave functions for the evaluation of several second order properties. The integrals occurring in such computations can be evaluated to a high degree of accuracy with considerable ease using a GTO basis [11]. Also, comparison of results with *ab initio* will be on an equal footing since a large number of these calculations now employ the STO-3G basis. We firmly believe that none of the general conclusions we have arrived at need be altered if a minimum basis set of STO's is used instead of the one we have used.

The molecules chosen for study are the first row hydrides, non-hydride molecules like O_3, FNO etc., and organic molecules like ethane, glyoxal and butadiene. Experimental geometry was used when available and standard geometry [5] otherwise.

All calculations were performed using an IBM 370/155 computer at IIT/Madras. Some of the subroutines in the integral package of the IBMOL 5 program were used in the development of the computer programs for performing the MO calculations and subsequently calculating some one-electron properties.

3. The Roby Scheme

The atomic orbital basis set $\{\chi\}$ is transformed to the Löwdin symmetry orthogonalized (OAO) set $\{\lambda\}$ using the transformation [12],

$$\lambda = \chi S^{-1/2} \tag{1}$$

The secular equation to be solved over the $\{\lambda\}$ basis then becomes,

$$F^{\lambda} C^{\lambda} = C^{\lambda} E \tag{2}$$

$$F^{\lambda} = H^{\lambda} + G^{\lambda} \tag{3}$$

where H^{λ} and G^{λ} are the one- and two-electron parts of the Fock matrix F^{λ}. The MO coefficients C^{λ} and the Fock matrix F^{λ} may be expressed in terms of their nonorthogonal counterparts as

$$F^{\lambda} = S^{-1/2} F S^{-1/2} \tag{4}$$

$$C^{\lambda} = S^{1/2} C \tag{5}$$

where S is the overlap matrix over the nonorthogonal basis.

The evaluation of the one-electron part of the Fock matrix over the OAO basis does not pose any problem of particular severity because it is easily evaluated over the nonorthogonal basis and transformed.

$$H^{\lambda} = S^{-1/2} H S^{-1/2} \tag{6}$$

Calculation of the two-electron part of the matrix remains a difficult task even if the NDDO approximation over the OAO basis is made since the surviving integrals would still require the evaluation of many-centered integrals over the nonorthogonal basis. However, Roby [7] has effected a drastic simplification, which makes the scheme conveniently workable, by proving the following interesting theorem.

The electron repulsion integral supermatrix over the OAO basis may be equated to that over the nonorthogonal basis in which the NDDO approximation has been made, provided the Ruedenberg expansion [13] is sufficiently valid. In mathematical form,

$$G^{\lambda} = G_{\mathrm{NDDO}} \tag{7}$$

$$\text{i.e. } (\mu_A^{\lambda} \nu_B^{\lambda} | \sigma_C^{\lambda} \rho_D^{\lambda}) = (\mu_A \nu_A | \sigma_C \rho_C) \delta_{AB} \delta_{CD} \tag{7a}$$

The Ruedenberg expansion is exact only when the atomic orbital subset on each constituent atom is orthonormal and complete. The truncated Ruedenberg expansion for a minimum basis set of atomic orbitals is obviously far from correct and it will be an objective of the present work to gauge the severity of the error produced. This original Roby scheme, without any refinements, will be referred to as scheme I hereafter in this paper.

A pleasing feature of the Roby scheme is that the source of error may easily be pinpointed, that due to Eq.(7) being the only one, and hence the method may be subjected to systematic refinements. Two possible modes of improvement have been considered in this work.

In the first method the Coulomb repulsion integrals have been scaled by an amount determined quite empirically and which also covered the prescriptions of Cook *et al.* [14]. These uniform scaling studies have been described as scheme II in this paper.

In scheme III scale factors for Coulomb repulsion integrals evaluated using the S-expansion technique, correct through second order in overlap, have been employed [4]. For one-center Coulomb repulsion integrals the corrections are given by:

$$^{\lambda}\gamma_{\mu\nu}^{AA}=\gamma_{\mu\mu}^{AA}+\sum_{B\neq A}\sum_{\delta}^{B}\tfrac{1}{4}[(S^2)_{\mu\delta}^{AB}(\gamma_{\mu\nu}^{AA}-\gamma_{\nu\delta}^{AB})+(S^2)_{\nu\delta}^{AB}(\gamma_{\mu\nu}^{AA}-\gamma_{\mu\delta}^{AB})] \tag{8}$$

The two-center Coulomb repulsion integrals after correction become:

$$\begin{aligned}^{\lambda}\gamma_{\mu\delta}^{AB}=\gamma_{\mu\delta}^{AB}&+\sum_{\nu}^{A}\tfrac{1}{4}(S^2)_{\delta\nu}^{BA}(\gamma_{\mu\delta}^{AB}-\gamma_{\mu\nu}^{AA})+\sum_{\varepsilon}^{B}\tfrac{1}{4}(S^2)_{\mu\varepsilon}^{AB}(\gamma_{\mu\delta}^{AB}-\gamma_{\delta\varepsilon}^{BB})\\&+\sum_{C\neq A,B}\sum_{\omega}^{C}\tfrac{1}{4}[(S^2)_{\delta\omega}^{BC}(\gamma_{\mu\delta}^{AB}-\gamma_{\mu\omega}^{AC})+(S^2)_{\mu\omega}^{AC}(\gamma_{\mu\delta}^{AB}-\gamma_{\delta\omega}^{BC})]\end{aligned} \tag{9}$$

This scheme has been studied both at the all-electron level and the valence-only level. In one set of valence-only calculations the core-valence separation was carried out closely along the lines suggested by Lykos and Parr [15]. The total wave function is written in the form

$$\Psi=\mathscr{A}(\psi^{\text{core}}\,\psi^{\text{val}}) \tag{10}$$

where ψ^{core} and ψ^{val} are antisymmetrized functions for the core and valence electrons respectively. $\mathscr{A}$ is an antisymmetrisation operator which interchanges electrons between the core and the valence shell. The core orbitals are taken to be the original unpolarised atomic orbitals of the neutral atom.

The expectation value of the electronic energy may be written as,

$$E_T=E_{\text{core}}^0+E_{\text{val}} \tag{11}$$

where

$$E_{\text{core}}^0=\int\psi^{\text{core}}\,\mathscr{H}_{\text{core}}^0\,\psi^{\text{core}}\,d\tau \tag{12}$$

$$E_{\text{val}}=\int\psi^{\text{val}}\,\mathscr{H}_{\text{val}}\,\psi^{\text{val}}\,d\tau \tag{13}$$

Here

$$\mathscr{H}_{\text{core}}^0\,(1,2\ldots n_c)=\sum_{\kappa=1}^{n_c}\mathscr{H}_N(\kappa)+\frac{1}{2}\sum_{\kappa,\lambda}^{n_c'}\frac{1}{r_{\kappa\lambda}} \tag{14}$$

and

$$\mathscr{H}_{\text{val}}\,(n_c+1\ldots,\,n_c+n_v)=\sum_{\mu=n_c+1}^{n_c+n_v}\mathscr{H}_{\text{core}}(\mu)+\frac{1}{2}\sum_{\mu,\nu=n_c+1}^{n_c+n_v'}\frac{1}{r_{\mu\nu}} \tag{15}$$

$$\mathscr{H}_{\text{core}}(\mu)=\mathscr{H}_N(\mu)+\sum_{j=1}^{n_c}\,[2\hat{J}_j(\mu)-\hat{K}_j(\mu)] \tag{16}$$

in which $\mathscr{K}_N$ is the kinetic energy plus the nuclear attraction term, the remaining term representing the Coulomb and the exchange potentials from the core electrons.

This procedure of core-valence separation is justified only if all valence orbitals are kept orthogonal to all core orbitals. In the present set of calculations the $2s$ orbital has been made orthogonal to the $1s$ core on the same atom by the Schmidt procedure. The valence orbitals on any atom have not been orthogonalized to the core on another atom but the overlap is expected to be so small that for all intents and purposes they may be assumed to be so.

The conventional and more convenient way of treating the core as a point charge collapsed at the nucleus has also been studied.

4. Results and Discussion

In the first calculation by Roby [8] on the CO molecule using scheme I, the total energy was quite close to the *ab initio* value and the orbital energies were reasonable although the core levels were far too deep. Atomic populations were not the same as in the *ab initio* calculations, the net charges on carbon and oxygen bearing the wrong signs. In spite of its far from impressive performance it was thought worthwhile to carry out more calculations with this method because there was the hope that at least relative energies might be predicted correctly. The poor values for the core binding energies may perhaps be attributed to the use of Burns' exponents [16] which provide a fair representation of the valence region only. Clementi-Raimondi exponents, obtained by minimizing the energy and hence describing the core quite well, may be expected to give better core energies.

In Table 1, the results obtained for the water molecule are given. The total energy is seen to be within 1% of the corresponding *ab initio* value but the orbital

Table 1. Results for H_2O molecule

Orbital	*ab initio*[f]	SAI[g]	(1)[a]	(2)[b]	(3)[c]	(4)[d]	(5)[e]
$1a_1$	−20.434	−20.316	−19.306	−19.924	—	—	—
$2a_1$	− 1.306	− 1.276	− 1.765	− 1.238	− 1.331	− 1.197	− 2.294
$1b_2$	− 0.642	− 0.438	− 0.426	− 0.403	− 0.545	− 0.556	− 0.492
$3a_1$	− 0.478	− 0.338	− 0.176	− 0.175	− 0.298	− 0.279	− 0.349
$1b_1$	− 0.428	− 0.306	− 0.094	− 0.135	− 0.292	− 0.301	− 0.242
E_{Total}	−75.226	−75.387	−75.375	−74.845	−75.082	−15.864	−18.356
Population on Hydrogen	0.80	—	—	0.51	0.73	0.84	0.70
μ(Debye)	1.64	2.72	—	—	2.39	2.27	1.17
$\langle 1/r_M \rangle$	5.833	5.766	—	—	5.761	5.771	5.837
$\langle z \rangle$	1.463	1.149	—	—	1.262	1.311	1.745

[a] All-electron NDDO; no scaling–Scheme I.
[b] All-electron NDDO + OAO Scaling.
[c] All-valence NDDO + OAO Scaling.
[d] All-valence NDDO with point charge core + OAO Scaling. $2s$ orthogonal to $1s$.
[e] All-valence NDDO with point charge core + OAO Scaling. $2s$ not orthogonal to $1s$.
[f] Ref. [23].
[g] Ref. [19].

energies are hopelessly bad. Results for the other hydrides exhibit an identical trend. The expectation that relative energies might be predicted correctly so that the method would be of some value in conformational analysis, has not been fulfilled judging from a few representative results for ethane, glyoxal, butadiene and formamide.

Results for the nonhydride molecule O_3 are given in Table 2. The performance here is much better, the total energy and orbital energies being quite satisfactory. But the gross atomic population is predicted incorrectly. Charge distributions, in general, are poorly calculated by scheme I. So the use of the wave functions obtained by this method for the calculation of other molecular properties does not appear promising.

It appears, therefore, that the error produced due to Eq.(7) in the case of minimum basis set calculations is too severe to permit a meaningful representation of molecular electronic structure. The hydrides yield the worst results since the truncated Ruedenberg expansion in terms of the single function on hydrogen is far from adequate in describing the orbitals on the heavy atoms. From the evidence gathered against it so far, it may be concluded that the original Roby scheme, without any refinements, has little to offer to merit further application and therefore may be abandoned.

Table 2. Results for O_3

Orbital	*ab initio*[e]	SAI[f]	(1)[a]	(2)[b]	(3)[c]	(4)[d]
$1a_1$	−20.960	−20.779	−20.303	−20.565		
$1b_1$	−20.677	−20.630	−20.178	−20.480		
$2a_1$	−20.677	−20.629	−20.180	−20.474		
$3a_1$	−1.688	−1.454	−1.739	−1.361	−1.574	−1.464
$2b_1$	−1.336	−1.299	−1.516	−1.262	−1.301	−1.126
$4a_1$	−1.006	−1.260	−1.491	−1.245	−1.143	−0.749
$5a_1$	−0.712	−0.608	−0.600	−0.600	−0.698	−0.676
$1b_2$	−0.680	−0.461	−0.452	−0.486	−0.600	−0.632
$3b_1$	−0.673	−0.702	−0.664	−0.636	−0.715	−0.611
$4b_1$	−0.441	−0.469	−0.418	−0.473	−0.467	−0.448
$6a_1$	−0.418	−0.462	−0.414	−0.462	−0.432	−0.395
$1a_2$	−0.350	−0.381	−0.337	−0.344	−0.328	−0.287
E_{Total}	−223.48	−223.93	−222.23	−222.33	−222.43	−44.04
Charge on Central Oxygen	+0.14	—	−0.13	−0.09	+0.02	+0.05
μ(Debye)	−0.47	0.43	—	0.22	0.11	−0.24
$\langle z \rangle$	20.432	20.074	—	20.027	20.202	20.341
$\left\langle \frac{1}{r_0} \right\rangle$	[g]28.629	28.871	—	28.684	28.612	28.364
	[h]27.501	27.538	—	27.288	27.379	27.279

[a] All-electron NDDO; no scaling-scheme I.

[b] All-electron NDDO + OAO scaling.

[c] All-valence NDDO + OAO scaling.

[d] All-valence NDDO with point charge core + OAO scaling.

[e] Ref. [24].

[f] Ref. [20].

[g] Central oxygen.

[h] End oxygen.

There are two avenues open for redeeming the Roby method. The error produced by the approximation in the electron repulsion part may somehow be corrected by making compensating errors in the one-electron part of the Fock Hamiltonian. The successful accomplishment of this type of cancellation of errors is indeed one of the reasons for the success of cruder MO methods, like the CNDO, which strike a delicate balance between the errors in the positive and the negative contributions of the energy functional. However, it has its pitfalls: the errors in the derivative of the functional with respect to certain parameters of interest need not parallel those of the functional itself and hence the gradient properties of the energy eigenfunction might be very poorly reproduced. It has been pointed out recently [17] that the failure of the Pople's CNDO method in predicting diagonal stretching force constants is a direct consequence of the fact that while compensating for some errors due to the nonorthogonality of the AO basis set, contributions vital to the gradient of the energy with respect to nuclear displacement are lost. Our aim is to develop a method possessing the utility which is commensurate with the effort expended on it and having none of the limitations of the CNDO type calculations. Clearly then, making compensating errors is not the preferable way of improving the performance of scheme I.

The only alternative is to carefully compare the two sides of Eq.(7) and attempt to introduce corrections to make them equal.

After comparing integrals over the OAO basis and the non-orthogonal basis in a number of cases Cook *et al.* [14] have found that significant differences exist only in the case of Coulomb repulsion integrals. Based on this conclusion Roby suggested [8] that Eq.(7) could be rewritten as

$$G^{\lambda} = \mathrm{SCALE} \times \mathrm{G}_{\mathrm{NDDO}} \tag{17}$$

where SCALE is a matrix of scale factors for Coulomb repulsion integrals. It was suggested that all one-center repulsion integrals be increased and two-center integrals be decreased by an amount anywhere between 9–14%.

Roby found, for the CO molecule, that the uniform scaling had a pronounced effect on the charge distribution and the total energy. Our experience parallels this earlier study. For example by an appropriate scaling it was possible to reverse the net atomic charge on the atoms of O_3, but this was at the expense of the total energy which became poor. A detailed study of the effect of uniform scaling was done on the series of homonuclear diatomics C_2, N_2, O_2 (triplet, of course) and F_2. Use of different scaling factors for one- and two-center Coulomb integrals was also tried. The orbital energies and the total energy changed monotonically with the scaling in all the cases. Cases in which the ordering of levels was reversed remained uncorrected by this kind of scaling. In the case of glyoxal, the π levels which had been buried below some σ levels in the unscaled version, could not be pushed up by scaling without at the same time seriously impairing the value of the total energy.

The failure of scheme II may be attributed to the lack of flexibility of the static scaling which was employed. The Löwdin orthogonalized orbitals depend directly on the overlap matrix and therefore are quite different in different molecules. The integrals over the Löwdin basis must also, then, vary considerably and the scale matrix must be capable of closely following these variations. A gross scaling factor for all one-center Coulomb integrals on an atom is obviously incapable of doing so. Perhaps in the case of a series of molecules exhibiting similar bonding, like the hydrocarbons, it might be possible to find a set of scaling factors that would give reliable results. In the general case, however, it is absolutely essential to have a dynamic scaling procedure.

Such a procedure has indeed been worked out by Roby *et al.* [4] using the S-expansion technique. The $S^{-1/2}$ matrix, appearing in the transformation of the integrals over the OAO basis to those over the nonorthogonal basis, is expanded in a binomial series. Terms involving the cubic powers of the overlap are neglected and the resultant expression is then simplified using Ruedenberg's approximation to yield the correction factors given in Eqs.(8) and (9). These do not require the calculation of any new repulsion integrals other than those already calculated for the NDDO MO calculation, although a little extra effort in organising the Fock matrix is necessitated. A simplified version, suitably rotationally averaged to be used in conjunction with the INDO method using OAO basis set, has been tested by Craig *et al.* [18] without significant improvement in their results. They had expressed the hope that the results may be far better if the full expressions of Eqs.(8) and (9) are used with the Roby NDDO method. Ours is the first attempt to verify this possibility.

The results for H_2O are again given in Table 1 and those for HF molecule in Table 3. It can be seen that the core level and some of the inner valence levels have registered a significant improvement in the case of water, although the ionization potential still remains unsatisfactory. The atomic charges show a greater degree of plausibility but the polarity of the bonds is not entirely satisfactory.

The results for O_3 and CO, presented in Table 2 and Table 4 respectively, are again distinctly superior to those of the hydrides. The orbital energies and the total energy compare favourably with the *ab initio* values. The net charges on the atoms still have the wrong signs although the values are somewhat better than in scheme I.

Scheme III, then, at the all-electron level, while being indisputably superior to scheme I, remains far from being perfect. It may be expected to fare much

Table 3. Results for HF

Orbital	*ab initio*[d]	(1)[a]	(2)[b]	(3)[c]
1σ	−26.139	−25.682	—	—
2σ	− 1.476	− 1.438	− 1.512	− 1.284
3σ	− 0.566	− 0.299	− 0.457	− 0.354
1π	− 0.465	− 0.284	− 0.382	− 0.339
E_{Total}	−98.913	−98.666	−98.816	−23.009
Population on Hydrogen	—	0.41	0.69	0.74

[a] All-electron NDDO + OAO scaling.

[b] All-valence NDDO + OAO scaling.

[c] All-valence NDDO with point charge core + OAO scaling.

[d] Ref. [23].

Table 4. Results for CO

Orbital	*ab initio*[d]	SAI	(1)[a]	(2)[b]	(3)[c]
1σ	−20.812	−20.685	−20.952	—	—
2σ	−11.444	−11.457	−11.673	—	—
3σ	−1.534	−1.570	−1.888	−1.628	−1.509
4σ	−0.760	−0.980	−1.002	−0.820	−0.584
1π	−0.612	−0.556	−0.653	−0.582	−0.594
5σ	−0.507	−0.617	−0.648	−0.620	−0.481
E_{Total}	−112.33	−112.75	−112.11	−112.16	−20.15
Charge on Carbon	—	—	+ 0.90	+ 0.29	+ 0.12

[a] All-electron NDDO + OAO scaling.
[b] All-valence NDDO + OAO scaling.
[c] All-valence NDDO with point charge core + OAO scaling.
[d] Ref. [20].

better at the all-valence level of calculation. This is because of the fact that the inadequacy of the Ruedenberg expansion in providing a fair representation of an orbital on one center in terms of the orbitals on another atomic center is particularly severe for a core orbital which has negligible overlap with all the orbitals on the other center.

That this is indeed true may be clearly seen from Tables 1–4 in which results of "valence-only" calculations, performed according to the method of Lykos and Parr [15] described earlier, have been presented. The orbital energies show satisfactory agreement with *ab initio* values while the total energy continues to remain good. The most gratifying improvement is in the atomic population which appears perfectly plausible now. Results are, of course, vastly superior in the case of nonhydride molecules.

We have also included in the tables results obtained by Roby *et al.* [19, 20] using their simplified *ab initio* (SAI) scheme. In this ZDO method the one-electron integrals are evaluated over the Löwdin orthogonalized basis, as is done in the present case. The NDDO approximation is invoked to simplify the electron repulsion part. But, unlike in the present method, the surviving integrals are evaluated over the Löwdin basis, though only approximately. The integrals over the OAO basis, are expanded in terms of those over the nonorthogonal basis. Out of these, the usual NDDO type integrals over the non-orthogonal basis are evaluated exactly and the others simplified by the Ruedenberg approximation. This method is superior to the present scheme in that the hybrid repulsion integrals are also treated at the same level of accuracy as the Coulomb repulsion integrals. The SAI gave good results in the case of nonhydride molecules but in the case of hydrides it was found "suitable for application where limited numerical accuracy would be sufficient".

The similarity between the results of the all-valence NDDO method with OAO scaling using S-expansion and those of the SAI method is striking. For the hydrides it should therefore prove possible to understand the gross features of electronic structure and to infer the main trends in the properties of a series of chemically related compounds, with a comparatively lesser effort. In the case of nonhydrides

Table 5. Results for FNO

Orbital	SAI[c]	*ab initio*[d]	(1)[a]	(2)[b]
1*a*	− 26.388	− 26.312	—	—
2*a*	− 20.663	− 20.797	—	—
3*a*	− 15.720	− 15.863	—	—
4*a*	− 1.541	− 1.634	− 1.607	− 1.548
5*a*	− 1.471	− 1.475	− 1.457	− 1.158
6*a*	− 1.208	− 0.902	− 1.071	− 0.695
7*a*	− 0.648	− 0.709	− 0.702	− 0.665
8*a*	− 0.575	− 0.652	− 0.655	− 0.570
1*b*	− 0.565	− 0.648	− 0.582	− 0.586
9*a*	− 0.560	− 0.496	− 0.469	− 0.447
2*b*	− 0.486	− 0.491	− 0.461	− 0.439
10*a*	− 0.412	− 0.374	− 0.366	− 0.322
E_{Total}	−228.24	−227.71	−226.71	−46.24
Mulliken Population				
N	—	6.904	6.888	6.925
O	—	8.046	8.043	8.016
F	—	9.050	9.069	9.058

[a] All-valence NDDO + OAO scaling.
[b] All-valence NDDO with point charge core + OAO scaling.
[c] Ref. [20].
[d] Ref. [24].

the method appears to be even superior to the SAI scheme: the ordering of levels is more exact and the dipole moment is closer to the *ab initio* value for ozone. Table 5 which contains the results for FNO emphatically establishes the truly impressive performance of this NDDO scheme.

We have calculated the diagonal stretching force constant, and the equilibrium bond length in H_2O and HF, by first minimizing the total energy of the system with respect to the internal displacement coordinates and then evaluating the curvature of the potential energy function at the calculated minimum. From the results in Tables 6 and 7 it may be seen that the bond lengths are overestimated in both cases, but the values are closer to the experimental distances than those calculated by the CNDO method. The force constants provide the striking proof of the superiority of the present NDDO scheme over CNDO and INDO methods.

An interesting behaviour is seen in the all-valence calculations in which the core is treated as a point charge. In some calculations the 2*s* orbital on each first row

Table 6.

	CNDO[a]	NDDO[b]	*ab initio*[c]	Exp.[c]
O–H Stretching Force Constant (mdyne/Å)	17.0	10.0	9.9	8.5
Equilibrium O–H Distance (Å)	1.03	1.00	0.94	0.96

[a] Ref. [5]. [b] This work. [c] Ref. [25].

Table 7.

	CNDO[a]	INDO[a]	NDDO[b]	Exp.
H–F Stretching Force Constant (mdyne/Å)	19.12	18.64	7.1	9.6
Equilibrium H–F Distance (Å)	1.000	1.006	0.983	0.917

[a] Ref. [5]. [b] This work.

atom was maintained Schmidt-orthogonal to the corresponding 1*s* orbital on the atom although the 1*s* orbital was not used in the calculation. The results obtained from such calculations (Table 1) resemble those of the more rigorous "all-valence" calculations described earlier. The only change is that the polarity of the bond is reduced as evidenced from the Mulliken population analysis. If the 2*s* orbital is given more freedom by restoring it the original nonorthogonality, there is a marked change in the total energy which has now come close to the CNDO total energy (-19 a.u.) with some of the orbital energies diving deep down correspondingly. Although there is no obvious reason why the 2*s* orbital has to be orthogonalized to the core when the core is treated as a point charge it appears from the present study that it is in fact necessary for obtaining good orbital energies. It of course remains to be seen whether this orthogonalization is essential for the calculation of other molecular properties.

It may be concluded from the results in Table 5 that, at least in the case of molecules containing only first row atoms, the point charge core approximation does not lead to any serious error.

There still remains room for quantitative improvement of the results obtained by the all-valence NDDO method, particularly with reference to the inadequacy of the minimum basis set of STO-3G functions used in these calculations. Any extension of the basis set destroys the simplicity of this scheme. The Hartree-Fock scaling procedure, employed by Roby in his calculations on CO [8], appears quite promising in this context. Certain key integrals are evaluated over Hartree-Fock atomic orbitals and compared with the values over the functions employed in the NDDO calculations. An appropriate set of one-center Hartree-Fock scaling factors is thus found out which may be used in the NDDO calculations to reduce the errors due to the poor quality of the basis functions. Preliminary calculations on the first row hydrides using the scale factors calculated for STO functions [8], showed pronounced effects, not always for the better, of such scaling on the orbital energies and charge distribution. A more detailed study is required for evolving an optimum set of Hartree-Fock scale factors.

In Table 8 the Coulomb repulsion integrals evaluated over the nonorthogonal basis and the corresponding correction factors calculated using Eqs.(8) and (9) are given. It may be seen that the direction of error has been correctly anticipated in the uniform scaling procedure. At the same time the inadequacy of the uniform scaling method is also evident. However, as mentioned earlier, the possibility of

Table 8. Coulomb integrals[a] for H_2O in matrix form[b]

	$2s$	$2p_x$	$2p_y$	$2p_z$	H_{1s}	H_{2s}
$2s$	0.791					
$2p_x$	0.799	0.873				
$2p_y$	0.799	0.778	0.873			
$2p_z$	0.799	0.778	0.778	0.873		
H_{1s}	0.499	0.518	0.480	0.502	0.751	
H_{2s}	0.499	0.518	0.480	0.502	0.341	0.751
Corrections to Coulomb Integrals in Matrix Form						
$2s$	0.069					
$2p_x$	0.048	0.034				
$2p_y$	0.038	0.014	0.0			
$2p_z$	0.044	0.020	0.008	0.021		
H_{1s}	−0.034	−0.030	−0.030	−0.031	0.062	
H_{2s}	−0.034	−0.030	−0.030	−0.031	−0.045	0.061

[a] In a.u. [b] The γ_{ij}th element corresponds to the integral (ii/jj); $\gamma_{ij}=\gamma_{ji}$.

arriving at a set of uniform scale factors to improve scheme I at the all-valence level, for a series of related molecules, cannot be ruled out.

5. Summary

From the present study a highly promising procedure for performing an approximate MO calculation capable of treating a variety of problems of chemical interest has emerged. In this all-valence scheme, the one-electron integrals are evaluated exactly over the Löwdin symmetry orthogonalised basis. The electron repulsion integrals are evaluated over the nonorthogonal basis and simplified further by making the NDDO approximation. Corrections are made for one-center and two-center Coulomb repulsion integrals using the S-expansion technique correct through second-order in overlap. The total energy, orbital energies and charge distributions, as evidenced from population analyses and expectation values of some one-electron operators are all in satisfactory agreement with *ab initio* results. In the case of hydrides the results are of limited accuracy, though remaining useful, while for the nonhydrides there is little difference between the approximate scheme and full SCF calculations. It is pleasing to note that no disposable parameter whatsoever is needed in this scheme.

This method requires more effort than some of the popular semiempirical methods like the CNDO, but it should be applicable to a wider range of compounds with a higher expectancy of success. Unlike in the CNDO or INDO methods no rotational averaging of repulsion integrals, at the expense of information about the directional properties of orbitals, is done and hence this method should be able to handle the problem of electronic structure in molecules possessing one or more lone pairs, like the carbanions [21] and also in molecules in which d orbitals play a vital role in bonding.

Certain repulsion integrals of the form $(s_A p_{xA}|s_B p_{xB})$, which during internal rotation make crucial contributions to the energy changes, due to dipole-dipole interaction [22] are retained in this method. The present NDDO scheme should therefore prove useful in studying problems in conformational analysis.

By not succumbing to the temptation of making compensating errors in the one-electron part of the Fock matrix to obviate those produced in the two electron part by the NDDO approximation, the gradient characteristics of the resultant energy functional have been preserved. We may expect the solution of the approximate scheme to behave much like that of the Hartree-Fock solution under perturbations and hence to yield reliable values for second order properties like force constants, chemical shifts, susceptibility etc.

The general trends, at least, in some of the interesting properties like the electric field gradient, isotropic and dipolar hyperfine coupling constants in free radicals etc. should be predicted correctly by this fully nonempirical method since almost all of the integrals which make the chief contributions to these quantities are retained in the calculations.

Calculations are well under way to verify all these expectations and the results will be reported in forthcoming papers.

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References

1. Pariser,R., Parr,R.G.: J. Chem. Phys. **21**, 466, 767 (1958)
2. Pople,J.A.: Trans. Faraday Soc. **49**, 1375 (1953)
3. Fischer-Hjalmars,I.: Advan. Quantum Chem. **2**, 25 (1965)
4. Brown,R.D., Roby,K.R.: Theoret. Chim. Acta (Berl.) **16**, 175 (1970)
5. Pople,J.A., Beveridge,D.L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
6. (a) Sustman,R., Williams,J.E., Dewar,M.J.S., Allen,L.C., von Schleyer,R.: J. Am. Chem. Soc. **91**, 5350 (1969);
   (b) Davidson,R.B., Jorgensen,W.L., Allen,L.C.: J. Am. Chem. Soc. **92**, 749 (1970);
   (c) Brown,R.D., Roby,K.R.: Theoret. Chim. Acta (Berl.) **16**, 278 (1970)
7. Roby,K.R.: Chem. Phys. Letters **11**, 6 (1971)
8. Roby,K.R., Sinanoglu,O.: Intern. J. Quantum Chem. IIIS 223, (1969)
9. Huzinaga,S.: J. Chem. Phys. **42**, 1293 (1965)
10. Clementi,E., Raimondi,D.L.: J. Chem. Phys. **38**, 2686 (1963)
11. Kern,C.W., Karplus,M.: J. Chem. Phys. **43**, 415 (1965)
12. Löwdin,P.O.: J. Chem. Phys. **18**, 365 (1950)
13. Ruedenberg,K.: J. Chem. Phys. **19**, 1433 (1951)
14. Cook,D.B., Hollis,P.C., McWeeney,R.: Mol. Phys. **13**, 553 (1967)
15. Lykos,P.G., Parr,R.G.: J. Chem. Phys. **24**, 1166 (1956)
16. Burns,G.: J. Chem. Phys. **41**, 1521 (1964)
17. Jug, K.: J. Am. Chem. Soc. **95**, 7575 (1973)
18. Casey,A.T., Craig,R.A., Scarlett,M.J.: J. Chem. Soc. Farad. Trans. II **69**, 132 (1973)
19. Brown,R.D., Roby,K.R.: Theoret. Chim. Acta (Berl.) **21**, 205 (1971)
20. Brown,R.D., Roby,K.R.: ibid. **18**, 98 (1970)
21. Streitweisser,A., Jesaitis,R.G.: Theoret. Chim. Acta. (Berl.) **17**, 165 (1970)
22. Jug,K.: Int. J. Quant. Chem. IIIS 241 (1969)
23. Klessinger,M.: Theoret. Chim. Acta (Berl.) **15**, 353 (1969)

24. Petrongolo,C., Scrocco,E., Tomasi,J.: J. Chem. Phys. **48**, 407 (1968)
25. Schaefer III, H.F.: The electronic structure of atoms and molecules. Reading, Mass.; Addison-Wesley 1972

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