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NDDO MO Calculations

III. Detailed Results for Molecules Containing First-Row Atoms

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Three "valence-only" schemes based on the Roby version of NDDO MO theory, which differ only in the core-valence treatment and the choice of the basis set, have been applied to the study of molecules containing first-row atoms. Orbital energies, charge distribution, dipole moments, field gradients, and a few other one-electron molecular properties are calculated to satisfactory accuracy. The schemes appear unreliable in the prediction of barriers to internal rotation in molecules, presumably due to errors in the core contribution to the total energy. An alternative treatment is suggested.

Key words: NDDO approximate MO theory

1. Introduction

In a previous paper, hereafter referred to as I [1] it was suggested that a modified version of Roby's NDDO MO method, at the all-valence electron level, has the potential to yield results nearly as accurate as those obtainable from *ab initio* calculations. The method possesses two important merits: (1) it rests on a firm theoretical basis, and (2) no explicit disposable parameter is included in the method. Two schemes, which differed only in the core-valence treatment, were described in I. The possible advantages of using a Hartree–Fock scaling procedure was mentioned. In the present paper, along with the previous two schemes, a third version which includes Hartree–Fock scaling has been studied in detail.

A large number of molecules containing the first-row atoms have been taken as test molecules. Orbital energies, population analyses, several one-electron molecular properties, and barriers to internal rotation have been considered. Comparisons are made with *ab initio* results and also with results obtained from some currently popular semiempirical MO methods.

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2. Method of Calculation

As described in I, the Roothaan equations are solved over the Löwdin symmetric orthogonalized (OAO) basis. The one-electron part of the Fock matrix is evaluated exactly over the OAO basis. The electron repulsion integrals are equated to their nonorthogonal counterparts in which the NDDO approximation is invoked. One- and two-centre Coulomb integrals however are evaluated over the OAO basis using the S-expansion techniques correct to second order in overlap.

A minimum basis set of STO's, each expanded in terms of 3 Gaussians by a variational fit [2], is employed in this method. In one scheme, referred to as NDDO 1, the core-valence separation is effected along the lines of Lykos and Parr in their π-electron calculations [3]. The potential provided by the core to the valence electron is explicitly evaluated using a set of unpolarized AO's. In another scheme, NDDO 2, the core is treated as a point charge collapsed at the nuclear site. In both schemes the valence orbitals on each atom are Schmidt-orthogonalized to the core orbitals sharing the same nuclear centre. This is essential to prevent the valence orbital energies from becoming too negative. Clementi–Raimondi exponents [4] are used for the first-row atoms and a value of 1.2 for the hydrogen $1s$ orbital in both the schemes.

Considering the limitations of the basis set described above, a third version which incorporates the Hartree–Fock scaling procedure suggested by Roby *et al.* [5] has been developed. In this scheme the valence AO's are described by STO's with Burns' exponents [6] and are orthogonalized to the core represented by Clementi–Raimondi exponents. The reason for this particular choice of the mixed basis is the following: Burns' exponents are more suited to describe the valence region, having been obtained by matching the values of various moments with Hartree–Fock orbitals, and Clementi–Raimondi exponents depict the core region better since they have been obtained by energy minimization in which the core contribution plays a considerable role. The limitations of this basis set are sought to be removed by Hartree–Fock scaling. On comparing several key integrals encountered in SCF calculations evaluated over Hartree–Fock AO's with those over STO-3G functions with Burns' exponents, it is found that significant differences occur only for one-centre integrals. A set of scaling factors have thus been found from oxygen $2s$ orbitals. These have been used as scaling factors for the appropriate integrals in the NDDO 3 scheme for all first-row atoms. The scaling factors are 0.045 for nuclear attraction integrals, 0.110 for the kinetic energy term, and 0.040 for Coulomb integrals. These values are somewhat less than the corresponding ones employed by Roby *et al.* [5] as they used the oxygen $1s$ function with Burns' exponents to arrive at their scaling factors.

The parameters which appear in NDDO 3 have thus been found in a predefined way and not by matching with the results of *ab initio* calculations or experiment. However, it must be admitted that they introduce a certain degree of arbitrariness in an otherwise parameter free MO theory. The characteristic features of the three schemes are summarized in Table 1.

Expectation values of all one-electon operators have been evaluated exactly over

Table 1. The characteristic features of the NDDO schemes

Method	Exponents	Core-treatment	Hartree–Fock scaling
NDDO 1	Clementi–Raimondi	Lykos and Parr	No
NDDO 2	Clementi–Raimondi	Point charge	No
NDDO 3	Clementi–Raimondi for core Burns for valence	Point charge	Yes

deorthogonalized wave functions. Thus the NDDO wave functions have been treated in the *ab initio* sense while evaluating molecular properties like dipole moment etc. (unlike in most semiempirical methods). Electric field gradients at the nitrogen nucleus in a few molecules have, however, been estimated using Gordy's MO version of the Townes–Dailey theory [7].

All calculations were performed on the IBM 370/155 computer at IIT, Madras using FORTRAN IV programmes developed in this laboratory. The molecular geometries used in all these calculations correspond to experimental and/or the ones employed in the *ab initio* calculations selected for comparison of the results.

3. Results and Discussion

Orbital energies and charge distribution based on the Mullikan population analysis scheme [8] have been obtained for a large number of molecules. Representative results are presented in Tables 2 and 3. *Ab initio* results have been included for comparison. It may be concluded that for first-row atoms the point charge core approximation does not lead to additional errors. With these schemes the inner levels are predicted to have energies which are close to the *ab initio* values. But the

Table 2. Results for H_2CO[a]

Orbital	*ab initio*[b]	NDDO 1	NDDO 2	NDDO 3
1 a_1	−1.430	−1.388	−1.291	−1.433
2 a_1	−0.861	−0.941	−0.833	−0.927
1 b_2	−0.689	−0.614	−0.628	−0.691
3 a_1	−0.632	−0.534	−0.441	−0.507
1 b_1 (π)	−0.524	−0.408	−0.431	−0.504
2 b_2 (n)	−0.427	−0.311	−0.313	−0.410
2 b_1 unocc (π)	0.147	0.299	0.299	0.171
E_{Total}	−113.672	−112.934	−21.155	−20.879
Gross population:				
C	5.800	4.386	4.175	4.090
O	8.420	6.301	6.085	6.211
H	0.890	0.657	0.870	0.849

[a] Geometry as in Ref. [25]. [b] Ref. [25].

Table 3. Results for Glyoxal[a] (*trans*)

Orbital	*ab initio*[b]	NDDO 1	NDDO 2	NDDO 3
1	−1.482	−1.389	−1.321	−1.503
2	−1.464	−1.381	−1.280	−1.454
3	−0.988	−0.950	−0.865	−1.003
4	−0.835	−0.882	−0.785	−0.860
5	−0.716	−0.681	−0.640	−0.773
6	−0.712	−0.660	−0.540	−0.645
7	−0.662	−0.578	−0.519	−0.611
8	−0.610	−0.399	−0.392	−0.547
9	−0.546	−0.411	−0.410	−0.514
10	−0.539	−0.394	−0.470	−0.490
11	−0.446	−0.318	−0.336	−0.476
Charge				
C	+0.217	−0.341	−0.180	−0.246
O	−0.477	+0.205	−0.037	−0.073
H	+0.260	−0.547	+0.219	+0.320

[a] Geometry taken from Ref. [26]. [b] Ref. [27].

agreement becomes progressively inferior along the energy scale so that the first ionization potential (after invoking Koopmans' theorem [9]) is invariably underestimated for all molecules, the reason being attributable to the Clementi–Raimondi exponents employed in these calculations which provide a better representation of orbitals in regions close to the nucleus.

Hartree–Fock scaling improves the results significantly. With the NDDO 3 scheme the first few ionization potentials are consistently in good agreement with *ab initio* predictions. However, in a few cases the innermost levels show larger deviation indicating the limitations of this rather arbitrary scaling procedure.

In Table 4 the orbital energies calculated by the NDDO 3 scheme are compared with the results of a few popular semiempirical MO methods [10–12]. Although a couple of orbital energies in the set of molecules considered show some deviation from experimental ionization potentials, the general quality of results of NDDO 3 is quite impressive.

The gross atomic charges calculated by the three schemes are not quite the same, but they show similar trends for a series of molecules. The methods invariably place a large positive charge on hydrogen atoms and hence atoms bonded to hydrogen generally tend to accumulate a negative charge by these methods. However, the relative variation of the charge in H_2CO, H_2NCHO and glyoxal is correctly calculated. The predicted trends in the polarity of C—H bonds in the series of the hydrocarbons CH_4, C_2H_4 and C_2H_2 and in the series CH_3F, CH_3OH, CH_3NH_2, C_2H_6 are correct. Of the three schemes, the charge distribution obtained from NDDO 2 appears more plausible in most cases.

The dipole moments calculated from some molecules with these three methods gave quite satisfactory values considering that even *ab initio* dipole moments are

Table 4. Comparison of NDDO 3 orbital energies (in eV) with semiempirical MO results

Molecule	Orbital	CNDO-M2	CNDO-PS	EHT	NDDO 3	Exp.	*ab initio*
CO	σ	−13.20	−17.26	−14.39	−12.83	14.00	−15.08
	π	−13.76	−21.09	−17.80	−16.05	16.54	−17.40
	σ	−20.83	−24.67	−20.09	−20.21	19.65	−21.87
	σ	−33.40	−45.33	−39.44	−42.89	—	−41.39
CO_2	π_g	−13.78	−15.70	−17.20	−11.01	13.79	−14.81
	π_u	−16.26	−24.81	−18.14	−18.36	17.59	−19.45
	σ_u	−13.58	−20.43	−17.51	−16.23	18.07	−20.23
	σ_g	−20.69	−24.42	−19.56	−17.84	19.36	−21.77
	σ_u	−33.73	−43.99	−32.59	−41.34	—	−40.19
	σ_g	−34.67	−45.40	−35.50	−44.57	—	−41.63
C_2H_2	π_u	−10.49	−17.46	−13.39	−11.66	11.40	−11.17
	σ_g	−12.33	−20.62	−15.30	−18.76	16.44	−18.58
	σ_u	−18.20	−26.55	−19.47	−23.66	18.42	−20.95
	σ_g	−24.20	−36.84	−26.64	−36.44	—	−28.02
C_2H_4	b_{3u}	−10.30	−16.60	−13.07	−10.83	10.48	−10.38
	b_{3g}	−11.10	−15.82	−14.49	−16.13	12.50	−14.08
	a_g	−11.63	−19.15	−14.48	−17.26	14.39	−15.86
	b_{2u}	−14.73	−25.11	−16.24	−18.00	15.63	−17.97
	b_{1u}	−19.14	−27.49	−20.38	−23.72	(19.13)	−21.95
	a_g	−25.43	−39.06	−26.47	−31.72	—	−28.80

CNDO-M2: Sichel–Whitehead parameters – Ref. [11]; CNDO-PS: Pople–Segal parameters – Ref. [10]; EHT: Hoffmann's version – Ref. [12]; all results other than those of NDDO 3 are from Ref. [11].

critically dependent on the choice of the basis set [13]. The performance of NDDO 2 was found to be superior to that of the other two schemes. The general level of accuracy with this scheme is quite similar to those of Pople's CNDO and INDO methods.

We have compared a number of molecular properties such as second moment, quadrupole moment, potentials at various atoms, diamagnetic shielding, electric field vectors and charge densities for a large number of molecules with those of *ab initio* results [14] obtained with a large Gaussian basis. The values obtained for the components of the second moments indicate that NDDO 2 provides the most faithful representation of the spatial extension in the outer regions of electronic charge distribution. The NDDO 1 results also compare favourably with *ab initio* values but those of the NDDO 3 scheme show substantial deviation. A consideration of the individual orbital contributions to these expectation values in the case of H_2CO reveals an interesting pattern. The values of NDDO 1 are quite close to the *ab initio* ones for the inner valence levels but the agreement worsens as contributions of orbitals higher-up in energy are considered. The values for the outer levels as calculated by NDDO 1 and NDDO 2 are similar. The total values obtained from the NDDO 2 schemes are in impressive concordance with *ab initio* results only through cancellation of errors in the individual orbital contributions. Indeed this effective cancellation of errors occurs consistently as may be verified from Table 5 in which is presented the trace of the diamagnetic contribution to the

Table 5. Table of χ^d_{av} (10^{-6} cm^3/mole)

Molecule	NDDO 2	*ab initio*[a]
CO	-42.34	-40.15
CH_4	-28.72	-27.36
NH_3	-19.66	-19.66
H_2O	-14.13	-15.30
H_2CO	-47.43	-48.30[b]

[a] Ref. [28] except for H_2CO. [b] Ref. [14].

magnetic susceptibility tensor, χ^d_{av}, defined as in Eq. (1), calculated for several molecules using the NDDO 2 method.

$$\chi^d_{\text{av}} = \frac{Ne^2}{6mc^2}\langle\psi^0|r^2_{iA}|\psi^0\rangle \tag{1}$$

The quadrupole moment tensor components of H_2CO obtained from NDDO 2 are much more accurate than those from the other two schemes. An orbital by orbital analysis shows a pattern identical to the one noted before. The electrostatic potential at the various nuclear sites of H_2CO are calculated quite accurately by all the schemes. This is not surprising since the corresponding operation $1/r$ enters directly in the variational calculation of the wave function. It is gratifying to note that the electric fields at the nuclei are also calculated in satisfactory agreement with *ab initio* values.

The NDDO 2 scheme has been employed to calculate ^{14}N quadrupole coupling constants in a few molecules using the MO version of Townes and Dailey [7]. In Table 6 the calculated *qcc*'s are compared with experimental values and the ones obtained from Pople's CNDO/2 theory [29]. Considering the crude nature of the model employed, ambiguities concerning the need for deorthogonalizing the MO coefficients and the neglect of the Sternheimer effect [16], the performance of NDDO 2 is impressive.

The NDDO schemes have been applied to the study of conformational analysis in several molecules. The relative energies of various conformers and the barrier to their interconversion in ethane, methyl amine, methanol, glyoxal, and formamide have been calculated and compared with their *ab initio* counterparts [30]. The results are discouraging. Although both NDDO 1 and NDDO 2 correctly predict that the staggered form is more stable than the eclipsed one for ethane [31] and methanol [32], the wrong result is obtained for methyl amine [32]. The NDDO 3 scheme

Table 6. ^{14}N quadrupole coupling constants (MHz)

Molecule	Cal.	Exp.	CNDO/2[a]
NH_3	-4.68	-4.08	-4.26
N_2	-3.21	-4.65	-2.32
*N*NO	-1.63	-0.79	0.43
N*N*O	0.55	-0.24	-0.52
CH_3CN	-4.21	-4.21	-1.90
CH_3NC	0.11	0.50	—

[a] Ref. [29].

yields incorrect results for all these molecules. Again, for glyoxal [26] all the methods predict the conformer with the two CHO groups at right angles to each other to be more stable than the *trans* planar form. Incidentally, CNDO/2 yields a similar result [17]. In the case of formamide the lowest energy conformer is identical to that obtained from *ab initio* calculations [18] with both NDDO 1 and NDDO 2 methods. However, the barrier to internal rotation around the N—C bond is underestimated considerably. The relative energies of methyl cyanide and isocyanide and those of the *cis* and *trans* forms of 1,3-butadiene are also incorrectly calculated by the NDDO 2 scheme.

Our earlier hope, stated in I, that errors are not cancelled through compensating errors but effectively corrected in the present NDDO method and hence it would lead to reliable predictions of small energy differences, is therefore subject to revision. A possible reason for the failure of the present schemes may be due to the error introduced by the core valence separation effected in these which was not envisaged in original Roby version of the NDDO MO method.

It is interesting to note that in two approximate MO methods which are successful in predicting equilibrium geometry, viz. MINDO/3 [19] and CNDO/BW [20], the core repulsion energy is not calculated exactly, unlike in the present case, but parameterized with a rather flexible function. The good results obtained by Hofmann *et al.* [21] in their conformational analysis studies using a parameterized version of the NDDO MO method reinforces our claim that the failure in the present case is not due to the errors produced by the NDDO approximation itself.

4. Summary and Conclusions

Several molecules containing first-row atoms have been studied using three "valence-only" versions of the NDDO MO method. The orbital energies compare favourably with *ab initio* results and experimental ionization potentials, particularly after Hartree–Fock scaling. The trends in atomic charges in various molecules are correctly reproduced. The quality of the wave functions is consistently good as revealed by the expectation values of one-electron operators. The gross values of these properties obtained with NDDO 2 are particularly in good agreement with *ab initio* values. Hartree–Fock scaling, however, has an adverse effect on these results.

All the schemes prove unreliable in the prediction of barriers to internal rotation in molecules. A promising course of action would be to use the Phillips–Kleinman [22] type of pseudopotential to effect perfect orthogonality between core and valence orbitals. A suitable model potential may also be incorporated as was done recently in valence-only *ab initio* calculations [23]. Such an approach, while holding out the promise of more reliable results, would also simplify the calculations further, particularly for transition metal complexes. Work along these lines is in progress.

The schemes discussed in this paper, notably NDDO 2, may be applied to certain specific problems, crucially dependent on the quality of wave functions, for which

CNDO type theories fail to yield sufficiently accurate results and *ab initio* calculations would be too expensive. An example is provided in a subsequent paper [24] in which the excellent results obtained with NDDO 2 in the correlation of core binding energy shifts, using the potential model including dipole and quadrupole corrections, are discussed.

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