Equilibrium Geometry of 

\[[\text{AH}_2, \text{AH}_2\text{F}, \text{AHF}_2, \text{AF}_2]\] 

by NDDO Method

A. N. Dixit* & S. R. Tripathi

Chemistry Department, University of Allahabad, Allahabad 211 002

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The all valence NDDO-MO method after correction for S-function is used to calculate the bond angles and bond lengths for the equilibrium configurations of some radicals and molecules. The results obtained are in good agreement with the experimental values. Unlike in 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 and also in molecules in which d-orbitals play vital role in bonding.

The NDDO approximation has been subjected to considerable theoretical analysis, but very few numerical calculations have been attempted. Roby formulated a theoretical NDDO-MO scheme which did not seriously jeopardize the simplicity of Pople's scheme. We have presently calculated equilibrium geometry of a number of molecules using Roby's formulation with a view to ascertaining its capabilities and limitations and to probe the effects of several refinements which have been suggested. To provide a consistent interpretation for the results, a minimum basis set of Slater type orbitals, expanded in terms of three Gaussians each by a variational fit was employed in the calculations. Clementi-Raimondi exponents were used for the orbital exponents of atoms of the first row of Periodic Table. The exponent for hydrogen was taken as 1.2. The integrals occurring in such computations can be evaluated to a high degree of accuracy with considerable ease using GTO basis.

The secular equation to be solved over the \(\{\lambda\}\) basis then becomes

\[F\lambda = C\lambda E\]  

\[F\lambda = H\lambda + G\lambda\]  

where \(H\lambda\) and \(G\lambda\) are the one- and two-electron parts of Fock matrix \(F\lambda\). The MO coefficients \(C\lambda\) and \(F\lambda\) may be expressed in terms of their non-orthogonal counterparts as

\[F\lambda = S^{-1/2} F S^{-1/2}\]  

\[C\lambda = S^{1/2} C\]  

where \(S\) is overlap matrix over the non-orthogonal basis the OAO basis does not pose any difficult problem because it is easily evaluated over the non-orthogonal basis. However, Roby has effected a simplification, by proving the following interesting theorem.

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

\[G_{\lambda} = G_{\text{NDDO}}\]  

i.e. \((\mu_{\lambda\mu}^{\text{NDDO}}) = (\mu_{\lambda\mu}^{\text{Ruedenberg}})\)  

The truncated Ruedenberg expansion for a minimum basis set of atomic orbital is obviously far from correct. However in Roby's scheme is that the source of error may easily be pin-pointed, and hence the method may be subjected to systematic refinements. Two possible modes of improvement have been considered in this work.

In the first mode the columb repulsion integrals have been scaled by an amount determined empirically and which also covered the prescriptions of Cook et al. In the second mode, scale factors for columb repulsion integrals evaluated using the S-expansion technique, correct through second order in overlap, have been employed. For one-center columb repulsion integrals the corrections are given by

\[\lambda_{\nu\nu}^{\text{AA}} = \nu_{\nu\nu}^{\text{AA}} + \sum_{B \neq A} \Sigma_{\nu B \nu} (S^{\lambda})_{\nu B \nu} (\nu_{\nu B}^{\text{AA}} - \nu_{\nu\nu}^{\text{AB}}) + (S^{\lambda})_{\nu B \nu} (\nu_{\nu B}^{\text{AA}} - \nu_{\nu\nu}^{\text{AB}})\]  

\[\lambda_{\nu\nu}^{\text{AB}} = \nu_{\nu\nu}^{\text{AB}} + \sum_{C \neq \nu} \Sigma_{\nu C} (S^{\lambda})_{\nu C \nu} (\nu_{\nu C}^{\text{AB}} - \nu_{\nu\nu}^{\text{AA}}) + \Sigma_{C \neq \nu} (S^{\lambda})_{\nu C \nu} (\nu_{\nu C}^{\text{AB}} - \nu_{\nu\nu}^{\text{BB}})\]  

The core-valence separation was carried out closely
along the lines suggested by Lykos and Parr. The total wave function is written in the form

$$\psi = A (\psi_{\text{core}} \psi_{\text{val}})$$

where $\psi_{\text{core}}$ and $\psi_{\text{val}}$ are antisymmetrized functions for the core and valence electrons respectively. $A$ is an antisymmetrization operator which interchanges electrons between the core and valence shells. The core orbitals are taken to be the original unpolarized atomic orbitals of neutral atom.

The expectation value of electronic energy may be written as

$$E = E_{\text{core}} + E_{\text{val}}$$

where

$$E_{\text{core}} = \int \psi_{\text{core}}^* K_{\text{core}} \psi_{\text{core}} \, dt$$

and

$$E_{\text{val}} = \int \psi_{\text{val}}^* K_{\text{val}} \psi_{\text{val}} \, dt$$

Here $K_{\text{core}}$ is the kinetic energy plus the nuclear attraction term, the remaining terms representing the coulomb and exchange potentials from the core electrons.

The 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 on any atom has been made orthogonal to the 1s core orbital 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 too small to have any contribution. The conventional and more convenient way of treating the core as a point charge collapse at the nucleus has also been studied.

**Calculation of Equilibrium Geometry of Molecules**

The theoretical calculation of the equilibrium geometry has been made of molecules containing the atoms H, C, N and F with NDDO theory with only one or two polyvalenta toms (C or N). If we denote polyvalent atoms by symbol A and other atoms (H or F) by X and Y, the class of molecules considered is $AX_3$, $AX_2Y$, $AXY_2$ and $AY_3$ molecules. The following constraints are placed on the nuclear configuration: $AX_3$ and $AY_3$: $C_{3v}$ symmetry; and $AX_2Y$, $AXY_2$: at least $C_2$ symmetry.

We preferred here the Schoenflies notation of expressing point symmetry. The calculations were performed by starting with an initial guess of the nuclear configuration and individual parameters (bond length and bond angles) in turn until a minimum in the total NDDO energy was found. In all these cases, bond angles were varied initially in steps of 100 and bond length in steps of 0.1 Å. After one complete cycle through all parameters, the step sizes were decreased by a factor of 10 for a second cycle. Certain repulsion integrals of the form $(SAPXA_j SBPXB_j)$ which during internal rotation make crucial contribution to the energy changes, due to dipole-dipole interaction, are retained in this method.

In Table 1, the equilibrium geometries of $AH_3$, $AHF_2$, $AHF_3$ and $AF_3$ molecules are given. The calculated geometries are in overall agreement with the available experimental data. However, the theory correctly predicts that the HNH angle in NH$_3$ is larger than the corresponding angle in NF$_3$ although the difference is less than observed experimentally. Further successive fluorine substitution on ammonia e.g. NH$_2$F and NHF$_2$ causes the molecule to become increasingly non-planar.

The methyl radical is calculated to be slightly non-planar by this method, but trifluoromethyl CF$_3$ is predicted to be so, in agreement ESR evidence. Along the series, increasing fluorination leads to increasing deviation from planarity.

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**Table 1 -- Calculated and Experimental Geometries for $AH_3$, $AHF_2$ and $AF_3$ Molecules**

| Molecule | RAH | Exptl. | RAH | Exptl. | $\theta_{\text{RAH}}$ | Exptl. | RAH | Exptl. | RAH | Exptl. | $\theta_{\text{RFAH}}$ | Exptl. | RAH | Exptl. | RAH | Exptl. | $\theta_{\text{RF}}$ | Exptl. | RAH | Exptl. | RAH | Exptl. | $\phi$ |
|----------|-----|--------|-----|--------|-----------------|--------|-----|--------|-----|--------|-----------------|--------|-----|--------|-----|--------|-----------------|--------|-----|--------|-----|--------|-----------------|--------|
| NH$_3$   | 1.06| 1.019  | —   | —      | 107.0          | 109.1  | —   | —      | 104.0| 104.0  | 104.0           | —      | —   | —      | —   | —      | 106.0           | —      |
| NH$_3$F  | 1.073| 1.304 | 1.302| 1.4    | 103.0          | 102.2  | —   | —      | 102.9| 99.8   | 65.8            | 74.1   |
| NH$_2$F  | 1.07 | 1.062 | 1.371| 1.4    | 103.0          | 102.2  | —   | —      | 102.9| 99.8   | 65.8            | 74.1   |
| CH$_3$   | 1.092| 1.31  | 1.33  | 1.36   | 110.0          | 116.0  | 111.5| 111.1  | 13.0 | 112.0  | 30.3            | —      |
| NH$_2$F  | 1.109| 1.31  | 1.33  | 1.36   | 110.0          | 116.0  | 111.5| 111.1  | 13.0 | 112.0  | 30.3            | —      |
| CHF$_3$  | 1.109| 1.31  | 1.33  | 1.36   | 110.0          | 116.0  | 111.5| 111.1  | 13.0 | 112.0  | 30.3            | —      |

where $(180-\phi)$ is angle between bond $AY$ and the bisector $XAX$ for $AXY$. 

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167
Theoretical & Experimental Study of Hydroxycoumarins


Department of Chemistry, University of Delhi, Delhi 110007

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Acid dissociation constants \( (pK_a)^\text{a} \) and half-wave potentials \( (E_{1/2}) \) of 3-hydroxy-, 4-hydroxy-, 6-hydroxy-, 7-hydroxy- and 8-hydroxy-coumarins have been determined experimentally. The \( pK_a \) and \( E_{1/2} \) values have been correlated with the theoretically calculated values. The theoretical values of charge density on the hydroxyl oxygen \( (q_0) \) and the energy of the lowest unoccupied molecular orbital \( (E_{\text{LUMO}}) \) have been calculated using HMO treatment. The calculated values are in good agreement with the experimental values.

The chemistry of coumarins, chromones and flavones has drawn the attention of many workers and a great wealth of experimental data are available in the literature. All these systems, being conjugated are ideally suited for theoretical investigations. It was considered worthwhile to carry out a systematic theoretical study for a series of coumarins. In the present work \( pK_a \) values of 3-hydroxy-, 4-hydroxy-, 6-hydroxy-, 7-hydroxy- and 8-hydroxy-coumarins have been determined pH-metrically. The values of charge density on the hydroxyl oxygen \( (q_0) \) were calculated for these coumarins using HMO treatment. The values of \( q_0 \) were employed for the calculation of theoretical \( pK_a \)'s. Similarly, \( E_{1/2} \) values have been determined polarographically and the values of energy of the lowest unoccupied molecular orbitals \( (E_{\text{LUMO}}) \) have been calculated using HMO treatment. These values of \( E_{\text{LUMO}} \) have been used to calculate the half-wave potentials. The experimentally determined values of \( pK_a \) and \( E_{1/2} \) have been compared with the theoretical values.

All the HMO calculations reported in this paper have been carried out using an IBM 360/44 computer. The hydroxycoumarins employed were prepared by the literature methods. The compounds were repeatedly crystallised before use.

The following stock solutions were prepared: 0.005M solution of each coumarin, 2.0M solution of sodium perchlorate, 0.02M solution of perchloric acid and 0.05M solution of tetramethylammonium-hydroxide (TMAH).

The titrations were performed on a Beckman Expandomatic, SS-2, pH-meter fitted with a glass electrode (0-14 pH range) and calomel electrode. Constant temperature (35 ± 1°C) was maintained with the help of a thermostat fitted with a contact thermometer.

For each set, two titrations were carried out : (i) Acid blank containing water, HClO₄ and NaClO₄ and (ii) ligand blank containing water, HClO₄, NaClO₄ and the coumarin. The volumes of various solutions were added in such amounts that the final concentrations in a solution of 20 ml were 0.0025M w.r.t. coumarin, 0.001M w.r.t. HClO₄ and 0.1M w.r.t. NaClO₄. Titrations were performed for all the five hydroxycoumarins in 50\% (v/v) ethanol against standard 0.05M TMAH solution at 35±1°C and \( \mu = 0.1 \) (NaClO₄).

The polarographic studies were carried out on an automatic OH-105 polarograph (Radelkis Hungary) at 30° ± 1°C with 1x10⁻⁸ M solutions of the coumarins. The half-wave potentials were determined in 50\% ethanol (v/v) at an ionic strength of 0.3 \( \text{M} \). Tetramethylammoniumbromide was used as the supporting electrolyte.

From the titrations performed, \( \bar{n}_H \) values were determined using the method of Bjerrum. The \( pK_a \) values were obtained from the intercepts of the plots of \( \log [n_H/(1-n_H)] \) against \( \text{pH} \) (Table 1). Good agreement is seen between calculated and experimental \( pK_a \) values. The half wave potentials \( (E_{1/2}) \) and \( E_{\text{LUMO}} \) values are recorded in Table 2.

The acidity of the hydroxycoumarin depends upon the ease with which the proton of the OH group is released, which in turn, depends upon the charge density on the hydroxy oxygen atom. The charge density is observed to be minimum (1.9124) for 4-hydroxycoumarin and so the proton should be most easily removed in this case and hence the acidity.

### Table 1 — Calculated and Experimental \( pK_a \) Values

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<th>Coumarin</th>
<th>( q_0 )</th>
<th>( pK_a )</th>
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<th>Expl.</th>
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