CNDO/2 and INDO all-valence-electron calculations on the dipole moment of iodine compounds

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Abstract. An application of the semi-empirical CNDO/2 and INDO methods to calculate the molecular dipole moment of iodine compounds has been made with all-valence electron scheme. Equilibrium geometries are obtained using experimental bond lengths and the various semi-empirical parameters required in SCF-MO scheme are obtained from atomic Hartree-Fock calculations and by comparison with *ab initio* calculations. Both *sp* and *spd* valence basis sets are used.

1. Introduction

The iodine compounds, in general, possess a large number of electrons and hence the full *ab initio* Hartee-Fock calculations are quite tedious and time consuming. Hence in the present calculations, semi-empirical methods have been adopted in the determination of dipole moments of molecules containing such heavy elements. Such methods have been in use for quite some time for the successful prediction of the shapes of a large number of molecules containing elements of the first and second rows of the periodic table (Golebiewski and Parczewski 1974).

The earlier CNDO/2 computer program (Program: QCPE 141) allowed valence electron calculations of molecules containing hydrogen and first and second-row atoms of the periodic table. Subsequently the method was extended and the program modified to include third-row atoms also (Hase *et al* 1973). On similar lines, the method has now been extended to include fourth-row elements, following Pople's parametrisation scheme. Several simple molecules containing iodine have been chosen to run test-calculation to justify the correctness of the extension scheme developed in the present work.

2. Method

The details of CNDO/2 and INDO methods for molecular orbital calculations have been given elsewhere (Pople and Beveridge 1970). The extension of CNDO/2 and INDO methods to fourth-row elements involves five steps.

2.1 *Choice of the basis AO's for iodine*

Valence basis sets, which comprised of just those orbitals of the valence shell of each atom in the molecule, are used in all our calculations. As for the preceding row elements, Slater-type orbitals (STO) are used for all atomic orbitals in the valence basis set. Since Slater rules are not true for cases with the principal quantum number, $n > 3$, the orbital exponent ζ is chosen as the arithmetic mean of ζ_s and ζ_p (Clementi and Raimondi 1963; Clementi *et al* 1967). The same orbital exponent is used for $5s$, $5p$ and $5d$ atomic orbitals of iodine. Its numerical value is 2·5015 (Galasso 1974).

2.2 *Evaluation of overlap integrals and coulomb integrals*

The earlier CNDO/2 version provides for the evaluation of overlap and repulsion integrals involving AO's of fourth-row atoms. Accordingly several new expansion coefficients have been carefully determined and added to the program listing for evaluating many such integrals involving AO's of iodine.

2.3 *Choice of orbital electronegativities*

The electronegativity of any valence orbital ϕ_μ is given by $\frac{1}{2}(A_\mu + I_\mu)$ where A_μ is the electron affinity and I_μ, the ionization potential for the atomic orbital ϕ_μ. The orbital electronegativities required for calculating local core matrix elements are determined by a method described elsewhere (Pople and Segal 1966; Hinze and Jaffe 1963). For iodine, they are 17·704 eV for the $5s$ orbital and 6·423 eV for the $5p$ orbital (Galasso 1974). Values for $5d$ orbitals are assumed to be zero (Santry 1968).

2.4 *Choice of bonding parameter β^0_{AB} and Slater-Condon parameters G^1 and F^2*

The bonding parameters β^0_{AB} are usually written in terms of atomic parameters β^0_A and β^0_B. These atomic parameters for the first-row elements are taken from Pople and Segal (1965) while those for the other row atoms $[X]$ have been determined from those of the corresponding first-row atoms $[Y]$ using the following recursion relation (Santry and Segal 1967),

$$\beta^0_X = \frac{\beta^0_Y(U^X_{ns} + U^X_{np})}{(U^Y_{2s} + U^Y_{2p})}, \tag{1}$$

where U is the appropriate local core matrix element. The β^0 value for iodine, used in the present calculation is $-17\cdot81$ eV. The basic approximations involved in INDO and CNDO/2 methods are the same except that the INDO procedure takes care of the exchange terms by retaining monoatomic differential overlap while CNDO/2 does not. These monoatomic differential terms are retained in the name of Slater-Condon parameters in the INDO method. In order that the theory is as close as possible to CNDO/2, the integral F^0 (or γ_{AA}), which is the average repulsion between any two electrons in a given atom A, is evaluated theoretically using Slater atomic orbitals, while the values for G^1 and F^2 are chosen semi-empirically. The theoretical values, adopted in the present calculation, for iodine are $G^1 = 7\cdot1057$ eV; $F^2 = 5\cdot2354$ eV (Deb and Coulson 1971). For the other lower group elements, such as fluorine, carbon, etc the values given by Pople and Beveridge (1970) have been used.

2.5 *Derivation of the formula for calculation of dipole moment of molecules containing iodine*

Basically there are three contributions to the molecular dipole moment (Pople and Beveridge 1970). μ_{charge} is the contribution due to the net atomic charges on the atoms of the molecule; μ_{sp} is the sp atomic polarization which arises because of the mixing of s and p atomic orbitals; μ_{pd} is again the atomic polarization resulting from the mixing of p and d atomic orbitals. The x-component of net atomic charge contribution, namely $\mu_{charge}(x)$ is given by

$$\mu_{charge}(x) = 2\cdot5416\left[\sum_A Q_A x_A\right] \text{Debyes,} \tag{2}$$

where $2\cdot5416$ is a multiplicative constant to be used when we go over to the Debye unit from the atomic unit of the dipole moment. Similar expressions can be written for other components. The contribution from atomic polarization due to the mixing of s and p orbitals is

$$\mu_{sp}(x) = -\sum_A P_{s(A),\,p_x(A)} \int \phi_{s(A)}\, x \phi_{px(A)} d\tau, \tag{3}$$

where $\int \phi_{s(A)} \times \phi_{px(A)} d\tau$ is the one centre matrix element of x-component of $\hat{r}$, the position operator in Slater basis, the values of which are given elsewhere (McGlynn *et al* 1972). The typical component of the sp contribution to the dipole moment now becomes,

$$\mu_{sp}(x) = -2\cdot5416\sum_A \left[3\zeta_A^{-1}\, P_{5s(A),\,5p_x(A)}\right] \text{Debyes} \tag{4}$$

and similar expressions can be obtained for y and z-components.

Similarly the components of the atomic polarization contribution to the dipole moment resulting from the mixing of p and d orbitals are

$$\mu_{pd}(x) = -2\cdot5416\sum_A \frac{9}{\sqrt{5}}\zeta_A^{-1}\left[P_{5p_x(A),\,5d_{x^2-y^2}(A)}\right.$$
$$\left. + P_{5p_y(A),\,5d_{xy}(A)} + P_{5p_z(A),\,5d_{xz}(A)} - \frac{1}{\sqrt{3}}P_{5p_x(A),\,5d_{z^2}(A)}\right]$$

$$\mu_{pd}(y) = -2\cdot5416\sum_A \frac{9}{\sqrt{5}}\zeta_A^{-1}\left[P_{5p_x(A),\,5d_{xy}(A)} + P_{5p_z(A),\,5d_{yz}(A)} -\right.$$
$$P_{5p_y(A),\,5d_{x^2-y^2}(A)} - \frac{1}{\sqrt{3}}P_{5p_y(A),\,5d_{z^2}(A)}\left.\right]$$

$$\mu_{pd}(z) = -2\cdot5416\sum_A \frac{9}{\sqrt{5}}\zeta_A^{-1}\left[P_{5p_x(A),\,5d_{xz}(A)} + P_{5p_y(A),\,5d_{yz}(A)}\right.$$
$$\left. + \frac{2}{\sqrt{3}}P_{5p_z(A),\,5d_{z^2}(A)}\right]. \tag{5}$$

3. Numerical results and discussion

Results of the present MO calculations carried out at INDO and CNDO levels of approximation using both *spd* and *sp* basis sets are reproduced in table 1. In all the

Table 1. Results of INDO and CNDO calculations with both *sp* and *spd* basis sets.

Compound	Calculated dipole moments (μ/Debye)				Experimental (μ/Debye)
	INDO		CNDO		
	spd	*sp*	*spd*	*sp*	
CF_3I	1·81	0·47	2·28	0·674	1·0 ± 0·1
CH_3I	0·26	1·25	0·05	0·96	1·64
C_2H_3I	0·18	1·47	0·36	1·07	1·27
C_2H_5I	0·33	1·81	0·23	1·36	1·63–1·95
ICl	−2·14	−2·00	−2·07	−1·97	0·5 (gas) 1·5 (CCl₄)
IF	−3·57	−2·39	−3·67	−2·28	—
LI	4·35	5·83	4·35	5·83	7·07 ± 0·2
HI	−0·86	0·83	−1·10	0·60	0·38 (gas) 0·58 (benzene)

compounds selected for study, experimental geometries have been used (Sutton 1965). For comparison, the experimental values of the dipole moment (McClellan 1963) are also given along with the calculated results. In all the cases, the calculated and the experimental values of the dipole moment show poor correlation if the results of the calculation with *spd* basis set are taken for comparison. On the other hand, when the results with *sp* basis set are considered, the matching improves and in many cases, the calculated values fall close to the experimental values. Inclusion of *d*-orbitals in the valence basis set, should normally improve the accuracy of the calculation of molecular properties and many authors (Norby Svendsen and Stroyer-Hansen 1978; Teixiera and Mursell 1970; Teixeira and Sarre 1975; Facelli and Contreras 1980) have realized the need for explicit consideration of such polarization functions into the basis set for better prediction of molecular properties. But in the present calculations on iodine compounds, *d*-orbital inclusion has spoiled the calculation totally as far as the estimation of dipole moment is concerned. The reason might be that in the case of iodine compounds, mixing of 5*p* and 5*d* orbitals has very little significance owing to the large energy gap between them. If one could provide for the inclusion of orbitals between 5*p* and 5*d* orbitals and for the mixing of orbitals with different principal quantum numbers, we can expect better results at these levels of approximations. On the other hand, if we look at the energy values, the calculations with *spd* basis set lead to better stability than the calculations with *sp* basis set. Hence one can draw an important conclusion that the role of *d*-orbitals is to stabilize the molecule as a whole rather than to be an essential factor in determining the molecular shape. Since the molecular shape is not properly determined with *spd* basis set calculations, the molecular dipole moment, which is critically dependent on the correct distribution of charges, cannot be reproduced with a reasonable degree of accuracy.

Of all the diatomic molecules studied, iodo flourine contains fluorine which is by far the most electronegative of atoms, followed by chlorine occupying the second place, while iodine and carbon come third, having equal electronegativities. Since electronegativity of an atom in a molecule is its power to attract an electron to itself, the centre of gravity of the negative charge in a diatomic molecule will in principle be shifted towards

the more electronegative atom. Thus in ICl molecule, since chlorine is more electronegative than iodine, the centre of gravity of the negative charge would be close to chlorine. Since dipole moment is conventionally defined as a vector directed from the centre of gravity of the negative electric charge to the centre of gravity of the positive electric charge, the resultant dipole moment vector in ICl molecule will be along its bond directed from chlorine to iodine and that is what is precisely observed in the present calculation. The same is the case with IF molecule wherein the resultant dipole moment vector is directed from fluorine to iodine. On the other hand, in LI and HI, iodine is more electronegative and the direction of the dipole moment vector is from iodine to lithium or hydrogen. As a matter of fact, calculations on HI with *spd* basis set gives a reverse trend. Coming to molecules such as CF_3I and CH_3I, possessing C_{3v} symmetry, one could expect the resultant dipole moment vector along the C_3 axis. But it is found that the resultant dipole moment vector is always inclined with the C_3 axis in both CF_3I and CH_3I although the concept of electronegativity counts very much in deciding the nature of the bond. The reason could be due to the presence of carbon and iodine with different electronegativities on the C_3 rotation axis. Although the molecules possess C_s symmetry, C_2H_3I is planar while C_2H_5I is non-planar. Hence the resultant dipole moment vector in C_2H_3I is in the plane of the molecule, making a definite angle with $C_2 = C_2$ bond while that in C_2H_5I is awkwardly oriented in space. But in all these calculations, the orientation of the resultant dipole moment vector closely depicts the behaviour of the atoms in terms of their electronegativities.

Acknowledgement

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