Extension of MINDO/3-FORCES Method

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The semi-empirical MINDO/3-FORCES method is extended to include the third row elements Si, P, S and Cl. The extended method is tested by calculation of heats of formation, dipole moments, and the first ionization potentials of molecules containing S and Cl. The results agree well with the experimental and theoretical values known in the literature.

Key words: MINDO/3-FORCES; Third Row Elements.

1. Introduction

The semi-empirical MINDO/3-FORCES method was applied by M. Shanshal et al. [1 – 3]. In this method the molecular energy, obtained with the MINDO/3 method suggested by Dewar et al. [4] was completely minimized with the Murtagh-Sargent minimization technique [5]. The derivative of the energy was calculated analytically with Pulay's Force method [6]. The MINDO/3-FORCES method was used to reproduce the following ground state properties: Molecular geometries [1,7 – 10], heats of formation [1,7 – 10], dipole moments [7 – 9], ionization potentials [7 – 9], vibrational frequencies, and infrared absorption intensities [11 – 13]. On the other hand, the MINDO/3-FORCES method was restricted to the first and second row elements H, B, C, N, O, F [1]. In the present paper the MINDO/3-FORCES method is extended to the third row elements Si, P, S, Cl, and the validity of this method is examined for molecules containing S and Cl.

2. The Extension Procedure

The extension of the MINDO/3-FORCES method to include third row elements is summarized as follows:

2.1. The calculation of the two center overlap integrals involved the application of the overlap integral formulas given by Mullikan et al. [14] for 1s, 2s, 3s, 2p, 3p atomic orbitals in the extended overlap subroutine [13]. The the analytical derivative of each overlap is calculated. The overlap integrals, S, and their derivatives, SD, are described as follows:

$$Z_1 = .5(Z_A + Z_B), \tag{1}$$

$$Z_2 = .5(Z_A \cdot Z_B), \tag{2}$$

$$R = R_1/.529167, \tag{3}$$

$$P = Z_1 R, \tag{4}$$

$$Q = Z_2 R, \tag{5}$$

$$T = Z_2/Z_1, \tag{6}$$

where Z_A and Z_B are the Slater orbital exponents of atom A and B, respectively. R_1 is the interatomic distance between A and B. The $A(k)$ and $B(k)$, see below, are functions of the Slater orbital exponents used in evaluating the overlap integrals.

First Row – Third Row:

$$P_1 = P^5(1 - T^2)^{7/2} \tag{7}$$

$$\mathrm{S}(1\mathrm{s},3\mathrm{s}) = .0132P_1\Big[A(4)B(0) - B(4)A(0) - 2\big\{A(3)B(1) - B(3)A(1)\big\}\Big], \tag{8}$$

$$\mathrm{SD}(1\mathrm{s},3\mathrm{s}) = \frac{5S}{R} - P_1\Big[Z_1\Big\{A(5)B(0) - B(4)A(1) - 2\big(A(4)B(1) - B(3)A(2)\big)\Big\} + Z_2\Big\{A(4)B(1) - B(5)A(0) - 2\big(A(3)B(2) - B(4)A(1)\big)\Big\}\Big], \tag{9}$$

$$\mathrm{S}(1\mathrm{s},3\mathrm{p}_\sigma) = .0228P_1\Big[A(3)\big(B(0)+B(2)\big)+B(3)\big(A(0)+A(2)\big)-B(1)\big(A(2)+A(4)\big)-A(1)\big(B(2)+B(4)\big)\Big], \tag{10}$$

$$\mathrm{SD}(1\mathrm{s},3\mathrm{p}_\sigma) = \frac{5S}{R} - P_1\Big[Z_1\Big\{A(4)\big(B(0)+B(2)\big)+B(3)\big(A(1)+A(3)\big)-B(1)\big(A(3)+A(5)\big) - A(2)\big(B(2)+B(4)\big)\Big\} + Z_2\Big\{A(3)\big(B(1)+B(3)\big)+B(4)\big(A(0)+A(2)\big) - B(2)\big(A(2)+A(4)\big)-A(1)\big(B(3)+B(5)\big)\Big\}\Big]. \tag{11}$$

Second Row – Third Row:

$$P_1 = P^6(1-T)(1-T^2)^{5/2} \tag{12}$$

$$\mathrm{S}(2\mathrm{s},3\mathrm{s}) = .0038P_1\Big[A(5)B(0) - A(4)B(1) - 2\big\{A(3)B(2) - A(2)B(3)\big\} + A(1)B(4) - A(0)B(5)\Big], \tag{13}$$

$$\mathrm{SD}(2\mathrm{s},3\mathrm{s}) = \frac{6S}{R} - P_1\Big[Z_1\Big\{A(6)B(0) - A(5)B(1) - 2\big(A(4)B(2) - A(3)B(3)\big) + A(2)B(4) - A(1)B(5)\Big\} + Z_2\Big\{A(5)B(1)-A(4)B(2)-2\big(A(3)B(3)-A(2)B(4)\big)+A(1)B(5)-A(0)B(6)\Big\}\Big], \tag{14}$$

$$\mathrm{S}(2\mathrm{s},3\mathrm{p}_\sigma) = .0066P_1\Big[-A(5)B(1)+A(4)B(0)+2\big(A(3)B(3)-A(2)B(2)\big)-A(1)B(5)+A(0)B(4)\Big], \tag{15}$$

$$\mathrm{SD}(1\mathrm{s},3\mathrm{p}_\sigma) = \frac{6S}{R} - P_1\Big[Z_1\Big\{A(6)(B(1)+(A(5)B(0)+2\big(A(4)B(3)-A(3)B(2)\big)-A(2)B(5)+A(1)B(4)\Big\} + Z_2\Big(-A(5)B(2)+A(4)B(1)+2\big(A(3)B(4)-(A(2)B(3)\big)-A(1)B(6)+A(0)B(5)\Big\}\Big]. \tag{16}$$

$$\mathrm{S}(2\mathrm{p}_\sigma,3\mathrm{s}) = .0066P_1\Big[-A(4)\big\{2B(2)-B(0)\big\}+B(4)\big\{2A(2)-A(0)\big\} - A(1)\big\{B(5)-2B(3)\big\}+B(1)\big\{A(5)-2A(3)\big\}\Big], \tag{17}$$

$$\mathrm{S}(2\mathrm{p}_\sigma,3\mathrm{s}) = .0066P_1\frac{6S}{R} - P_1\Big[Z_1\Big\{-A(5)\big(2B(2)-B(0)\big)+B(4)\big(2A(3)-A(1)\big)-A(2)\big(B(5)-2B(3)\big) + B(1)\big(A(6)-2A(4)\big)\Big\}+Z_2\Big\{-A(4)\big(2B(3)-B(1)\big) + B(5)\big(2A(2)-A(0)\big)-A(1)\big(B(6)-2B(4)\big)+B(2)\big(A(5)-2A(3)\big)\Big\}\Big], \tag{18}$$

$$\mathrm{S}(2\mathrm{p}_\sigma,3\mathrm{p}_\sigma) = -.0114P_1\Big[-B(3)\big(A(0)+A(4)\big)-A(3)\big(B(0)(B(4)+B(4)\big) + B(2)\big(A(1)+A(5)\big)+A(2)\big(B(1)+B(5)\big)\Big], \tag{19}$$

$$\mathrm{SD}(2\mathrm{p}_\sigma,3\mathrm{p}_\sigma) = \frac{6S}{R}-P_1\Big[Z_1\Big\{-B(3)\big(A(1)+A(5)\big)-A(4)\big(B(0)+B(4)\big)+B(2)\big(A(2)+A(6)\big) + A(3)\big(B(1)+B(5)\big)\Big\}+Z_2\Big\{-B(4)\big(A(0)+A(4)\big)-A(3)\big(B(1)+B(5)\big) + B(3)\big(A(1)+A(5)\big)+A(2)\big(B(2)+B(6)\big)\Big\}\Big], \tag{20}$$

$$\mathrm{SD}(2\mathrm{p}_\pi,3\mathrm{p}_\pi) = .0057P_1\Big[A(5)\big\{B(0)-B(2)\big\}+B(5)\big\{A(0)-A(2)\big\}-A(4)\big\{B(1)-B(3)\big\} - B(4)\big\{A(1)-A(3)\big\}-A(3)\big(B(0)-B(3)A(0)+A(2)B(1)+B(2)A(1)\big)\Big], \tag{21}$$

$$\mathrm{SD}(2\mathrm{p}_\pi,3\mathrm{p}_\pi) = \frac{6S}{R}-P_1\Big[Z_1\Big\{A(6)\big(B(0)-B(2)\big)+B(5)\big(A(1)-A(3)\big)-A(5)\big(B(1)-B(3)\big) - B(4)\big(A(2)-A(4)\big)-A(4)B(0)-B(3)A(1)+A(3)B(1)+B(2)A(2)\Big\} + Z_2\Big\{A(5)\big(B(1)-B(3)\big)+B(6)\big(A(0)-A(2)\big)-A(4)\big(B(2)-B(4)\big) - B(5)\big(A(1)-A(3)\big)-A(3)B(1)-B(4)A(0)+A(2)B(2)+B(3)A(1)\Big\}\Big]. \tag{22}$$

Third Row – Third Row:

$$P_1 = P^7(1-T^2)^{7/2}, \tag{23}$$

$$\mathrm{S}(3\mathrm{s},3\mathrm{s}) = .0007P_1\Big[A(6)B(0)-3\big\{A(4)B(2)-A(2)B(4)\big\}-A(0)B(6)\Big], \tag{24}$$

$$\mathrm{SD}(3\mathrm{s},3\mathrm{s}) = \frac{7S}{R}-P_1\Big[Z_1\Big\{-A(7)B(0)-3\big(A(5)B(2)-A(3)B(4)\big)-A(1)B(6)\Big\} + Z_2\Big\{-A(6)B(1)-3\big(A(4)B(3)-A(2)B(5)\big)-A(0)B(7)\Big\}\Big], \tag{25}$$

$$\mathrm{S}(3\mathrm{s},3\mathrm{p}_\sigma) = .0012P_1\Big[A(5)\big(B(0)-B(2)\big)-2A(3)\big(B(2)-B(4)+A(1)\big)\big(B(4)-B(6)\big) + B(5)\big(A(0)-A(2)\big)-2B(3)\big(A(2)-A(4)\big)-B(1)\big(-A(4)+A(6)\big)\Big], \tag{26}$$

$$\mathrm{SD}(3\mathrm{s},3\mathrm{p}_\sigma) = \frac{7S}{R}-P_1\Big[Z_1\Big\{A(6)\big(B(0)-B(2)\big)-2A(4)\big(B(2)-B(4)\big)+A(2)\big(B(4)-B(6)\big) + B(5)\big(A(1)-A(3)\big)-2B(3)\big(A(3)-A(5)\big)+B(1)\big(-A(5)+A(7)\big)\Big\} + Z_2\Big\{A(5)\big(B(1)-B(3)\big)-2A(3)\big(B(3)-B(5)\big)+A(1)\big(B(5)-B(7)\big) + B(6)\big(A(0)-A(2)\big)-2B(4)\big(A(2)-A(4)\big)-B(2)\big(-A(4)+A(6)\big)\Big\}\Big], \tag{27}$$

Table 1. Comparison of our MINDO/3-FORCES's results (third rows) with Dewar's MINDO/3 [15] ones (second rows) and the observed [15] ones (first rows).

Compound	ΔH_f kJ/mole	Dipole moment (D)	Ionization potential	Compound	ΔH_f kJ/mole	Dipole moment (D)	Ionization potential
	−22.1	—	9.44		−102.8	0.003	11.47
1-CH_3SH	−22.5	—	9.93	2-CCL_4	−101.5	0	11.32
	−33.0	2.857	9.52		−102.8	0	11.32
	0	0	11.63		—	—	
3-CL_2	0	0	10.82	4-S_2	204.8	—	8.36
	−.5	0	10.81		202.3	—	8.40
	117.0	0	10.08		−20.5	—	10.48
5-CS_2	113.7	0	9.68	6-H_2S	−7.9	—	9.9
	112.9	0	9.7		−12.1	3.23	10.8
	−92.4	1.08	12.8		−80.7	1.87	11.26
7-HCl	−89.9	1.71	12.11	8-CH_3Cl	−63.9	1.62	11.11
	−89.9	1.66	12.10		−63.9	1.55	11.10
	−52.8	1.69	9.70		12.4	—	—
9-C_6H_6Cl	−84.0	1.96	9.08	10-C_6H_6SH	95.3	—	8.48
	−84.4	1.90	9.08		92.4	2.78	8.48

$$S(3p_\sigma,3p_\sigma) = .0021P_1\Big[A(2)\big(B(6)-2B(2)\big)-A(4)\big(B(0)+2B(4)\big)-B(4)A(0)+A(6)B(2)\Big], \tag{28}$$

$$SD(3p_\sigma,3p_\sigma) = \frac{7S}{R}-P_1\Big[Z_1\Big\{A(3)\big(B(6)+2B(2)\big)-A(5)\big(B(0)+2B(4)\big)-B(4)A(1)+A(7)B(2)\Big\} + Z_2\Big\{A(2)\big(B(7)+2B(3)\big)-A(4)\big(B(1)+2B(5)\big)-B(5)A(0)+A(6)B(3)\Big\}\Big], \tag{29}$$

$$S(3p_\Pi,3p_\Pi) = .0021P_1\Big[A(6)\big(B(0)-B(2)\big)+B(6)\big(A(0)-A(2)\big)+A(4)\big(B(4)-B(2)-B(0)\big) + B(4)\big(A(4)-A(2)-A(0)\big)+2A(2)B(2)\Big], \tag{30}$$

$$SD(3p_\Pi,3p_\Pi) = \frac{7S}{R}-P_1\Big[Z_1\Big\{A(7)\big(B(0)-B(2)\big)+B(6)\big(A(1)-A(3)\big)+A(5)\big(B(4)-B(2)-B(0)\big) + B(4)\big(A(5)-A(3)-A(1)\big)+2A(3)B(3)\Big\} + Z_2\Big\{A(6)\big(B(1)-B(3)\big)+B(7)\big(A(0)-A(2)\big)+A(4)\big(B(5)-B(3)-B(1)\big) + B(5)\big(A(4)-A(2)-A(0)\big)+2A(2)B(3)\Big\}\Big]. \tag{31}$$

2.2. The MINDO/3-FORCES's FORTRAN program, used in this study, consists of more than twenty subroutines [10] and among them the OVERLAP, ZOTZ, and FORCE subroutines should be extended [13].

2.3. Introduction the numerical data corresponding the parameters required for the atoms of third row elements (Si, P, S, Cl) [4].

3. Results and Discussion

For testing the validity of the extended MINDO/3-FORCES method, in Table 1 the calculated heats of formations, dipole moments and ionization energies of ten molecules containing S and Cl atoms are compared with those observed [15] and with Dewar's MINDO/3

results [15]. The agreement is very good, and in some cases our calculated values are nearer to the observed ones. The difference between our results and the corresponding Dewar-ones [15] is due to the different minimization procedure. In the MINDO/3-method [15], the Davidon-Fletcher-Powell mimimization procedure [16] is used, whereas the MINDO/3-FORCES method uses the Murtagh-Sargent minimization technique [5].

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