Extension of MINDO/3-FORCES Method

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Z. Naturforsch. **58a**, 162 – 166 (2003); received October 1, 2002

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 subrou-

tine [13]. The the analytical derivative of each overlap is calculated. The overlap integrals, S , and their derivatives, SD , are described as follows:

$$Z_1 = .5(Z_A + Z_B), \quad (1)$$

$$Z_2 = .5(Z_A \cdot Z_B), \quad (2)$$

$$R = R_1 / .529167, \quad (3)$$

$$P = Z_1 R, \quad (4)$$

$$Q = Z_2 R, \quad (5)$$

$$T = Z_2 / Z_1, \quad (6)$$

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:

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

$$S(1s, 3s) = .0132P_1 \left[A(4)B(0) - B(4)A(0) - 2\{A(3)B(1) - B(3)A(1)\} \right], \quad (8)$$

$$\begin{aligned} SD(1s, 3s) = \frac{5S}{R} - P_1 \left[Z_1 \left\{ A(5)B(0) - B(4)A(1) - 2(A(4)B(1) - B(3)A(2)) \right\} \right. \\ \left. + Z_2 \left\{ A(4)B(1) - B(5)A(0) - 2(A(3)B(2) - B(4)A(1)) \right\} \right], \end{aligned} \quad (9)$$

$$S(1s, 3p_\sigma) = .0228P_1 \left[A(3)(B(0)+B(2)) + B(3)(A(0)+A(2)) - B(1)(A(2)+A(4)) - A(1)(B(2)+B(4)) \right], \quad (10)$$

$$\begin{aligned} SD(1s, 3p_\sigma) = \frac{5S}{R} - P_1 \left[Z_1 \left\{ A(4)(B(0)+B(2)) + B(3)(A(1)+A(3)) - B(1)(A(3)+A(5)) \right. \right. \\ \left. \left. - A(2)(B(2)+B(4)) + Z_2 \left\{ A(3)(B(1)+B(3)) + B(4)(A(0)+A(2)) \right. \right. \right. \\ \left. \left. \left. - B(2)(A(2)+A(4)) - A(1)(B(3)+B(5)) \right\} \right\} \right]. \end{aligned} \quad (11)$$

Second Row – Third Row:

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

$$S(2s, 3s) = .0038P_1 \left[A(5)B(0) - A(4)B(1) - 2\{A(3)B(2) - A(2)B(3)\} + A(1)B(4) - A(0)B(5) \right], \quad (13)$$

$$\begin{aligned} SD(2s, 3s) = \frac{6S}{R} - P_1 \left[Z_1 \left\{ A(6)B(0) - A(5)B(1) - 2(A(4)B(2) - A(3)B(3)) + A(2)B(4) - A(1)B(5) \right\} \right. \\ \left. + Z_2 \left\{ A(5)B(1) - A(4)B(2) - 2(A(3)B(3) - A(2)B(4)) + A(1)B(5) - A(0)B(6) \right\} \right], \end{aligned} \quad (14)$$

$$S(2s, 3p_\sigma) = .0066P_1 \left[-A(5)B(1) + A(4)B(0) + 2(A(3)B(3) - A(2)B(2)) - A(1)B(5) + A(0)B(4) \right], \quad (15)$$

$$\begin{aligned} SD(1s, 3p_\sigma) = \frac{6S}{R} - P_1 \left[Z_1 \left\{ A(6)(B(1) + (A(5)B(0) + 2(A(4)B(3) - A(3)B(2)) - A(2)B(5) + A(1)B(4)) \right. \right. \\ \left. \left. + Z_2 \left\{ -A(5)B(2) + A(4)B(1) + 2(A(3)B(4) - (A(2)B(3)) - A(1)B(6) + A(0)B(5)) \right\} \right\} \right]. \end{aligned} \quad (16)$$

$$\begin{aligned} S(2p_\sigma, 3s) = .0066P_1 \left[-A(4)\{2B(2) - B(0)\} + B(4)\{2A(2) - A(0)\} \right. \\ \left. - A(1)\{B(5) - 2B(3)\} + B(1)\{A(5) - 2A(3)\} \right], \end{aligned} \quad (17)$$

$$\begin{aligned} S(2p_\sigma, 3s) = .0066P_1 \frac{6S}{R} - P_1 \left[Z_1 \left\{ -A(5)(2B(2) - B(0)) + B(4)(2A(3) - A(1)) - A(2)(B(5) - 2B(3)) \right. \right. \\ \left. \left. + B(1)(A(6) - 2A(4)) \right\} + Z_2 \left\{ -A(4)(2B(3) - B(1)) \right. \right. \\ \left. \left. + B(5)(2A(2) - A(0)) - A(1)(B(6) - 2B(4)) + B(2)(A(5) - 2A(3)) \right\} \right], \end{aligned} \quad (18)$$

$$S(2p_\sigma, 3p_\sigma) = -.0114P_1 \left[-B(3)(A(0) + A(4)) - A(3)(B(0)(B(4) + B(4)) \right. \\ \left. + B(2)(A(1) + A(5)) + A(2)(B(1) + B(5)) \right], \quad (19)$$

$$SD(2p_\sigma, 3p_\sigma) = \frac{6S}{R} - P_1 \left[Z_1 \left\{ -B(3)(A(1) + A(5)) - A(4)(B(0) + B(4)) + B(2)(A(2) + A(6)) \right. \right. \\ \left. \left. + A(3)(B(1) + B(5)) \right\} + Z_2 \left\{ -B(4)(A(0) + A(4)) - A(3)(B(1) + B(5)) \right. \right. \\ \left. \left. + B(3)(A(1) + A(5)) + A(2)(B(2) + B(6)) \right\} \right], \quad (20)$$

$$SD(2p_\pi, 3p_\pi) = .0057P_1 \left[A(5)\{B(0) - B(2)\} + B(5)\{A(0) - A(2)\} - A(4)\{B(1) - B(3)\} \right. \\ \left. - B(4)\{A(1) - A(3)\} - A(3)(B(0) - B(3)A(0) + A(2)B(1) + B(2)A(1)) \right], \quad (21)$$

$$SD(2p_\pi, 3p_\pi) = \frac{6S}{R} - P_1 \left[Z_1 \left\{ A(6)(B(0) - B(2)) + B(5)(A(1) - A(3)) - A(5)(B(1) - B(3)) \right. \right. \\ \left. \left. - B(4)(A(2) - A(4)) - A(4)B(0) - B(3)A(1) + A(3)B(1) + B(2)A(2) \right\} \right. \\ \left. + Z_2 \left\{ A(5)(B(1) - B(3)) + B(6)(A(0) - A(2)) - A(4)(B(2) - B(4)) \right. \right. \\ \left. \left. - B(5)(A(1) - A(3)) - A(3)B(1) - B(4)A(0) + A(2)B(2) + B(3)A(1) \right\} \right]. \quad (22)$$

Third Row – Third Row:

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

$$S(3s, 3s) = .0007P_1 \left[A(6)B(0) - 3\{A(4)B(2) - A(2)B(4)\} - A(0)B(6) \right], \quad (24)$$

$$SD(3s, 3s) = \frac{7S}{R} - P_1 \left[Z_1 \left\{ -A(7)B(0) - 3\{A(5)B(2) - A(3)B(4)\} - A(1)B(6) \right\} \right. \\ \left. + Z_2 \left\{ -A(6)B(1) - 3\{A(4)B(3) - A(2)B(5)\} - A(0)B(7) \right\} \right], \quad (25)$$

$$S(3s, 3p_\sigma) = .0012P_1 \left[A(5)(B(0) - B(2)) - 2A(3)(B(2) - B(4) + A(1))(B(4) - B(6)) \right. \\ \left. + B(5)(A(0) - A(2)) - 2B(3)(A(2) - A(4)) - B(1)(-A(4) + A(6)) \right], \quad (26)$$

$$SD(3s, 3p_\sigma) = \frac{7S}{R} - P_1 \left[Z_1 \left\{ A(6)(B(0) - B(2)) - 2A(4)(B(2) - B(4)) + A(2)(B(4) - B(6)) \right. \right. \\ \left. \left. + B(5)(A(1) - A(3)) - 2B(3)(A(3) - A(5)) + B(1)(-A(5) + A(7)) \right\} \right. \\ \left. + Z_2 \left\{ A(5)(B(1) - B(3)) - 2A(3)(B(3) - B(5)) + A(1)(B(5) - B(7)) \right. \right. \\ \left. \left. + B(6)(A(0) - A(2)) - 2B(4)(A(2) - A(4)) - B(2)(-A(4) + A(6)) \right\} \right], \quad (27)$$

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
1-CH ₃ SH	-22.1 -22.5 -33.0	— — 2.857	9.44 9.93 9.52	2-CCL ₄	-102.8 -101.5 -102.8	0.003 0 0	11.47 11.32 11.32
3-CL ₂	0 0 -.5	0 0 0	11.63 10.82 10.81	4-S ₂	— 204.8 202.3	— — —	— 8.36 8.40
5-CS ₂	117.0 113.7 112.9	0 0 0	10.08 9.68 9.7	6-H ₂ S	-20.5 -7.9 -12.1	— — 3.23	10.48 9.9 10.8
7-HCl	-92.4 -89.9 -89.9	1.08 1.71 1.66	12.8 12.11 12.10	8-CH ₃ Cl	-80.7 -63.9 -63.9	1.87 1.62 1.55	11.26 11.11 11.10
9-C ₆ H ₆ Cl	-52.8 -84.0 -84.4	1.69 1.96 1.90	9.70 9.08 9.08	10-C ₆ H ₆ SH	12.4 95.3 92.4	— — 2.78	— 8.48 8.48

$$S(3p_\sigma, 3p_\sigma) = .0021P_1 \left[A(2)(B(6) - 2B(2)) - A(4)(B(0) + 2B(4)) - B(4)A(0) + A(6)B(2) \right], \quad (28)$$

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

$$S(3p_\pi, 3p_\pi) = .0021P_1 \left[A(6)(B(0) - B(2)) + B(6)(A(0) - A(2)) + A(4)(B(4) - B(2) - B(0)) \right. \\ \left. + B(4)(A(4) - A(2) - A(0)) + 2A(2)B(2) \right], \quad (30)$$

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

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 min-

imization procedure. In the MINDO/3-method [15], the Davidon-Fletcher-Powell minimization procedure [16] is used, whereas the MINDO/3-FORCES method uses the Murtagh-Sargent minimization technique [5].

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