Theoret. chim. Acta (Berl.) 31, 215—220 (1973)

CNDO/2 (Complete Neglect of Differential Overlap)-Method for Third-Row Molecules

H. L. Hase and A. Schweig

Fachbereich Physikalische Chemie der Universität, D-3550 Marburg (Lahn), Germany

Received February 23, 1973

An extension of the CNDO/2 method to compounds containing third-row elements (Germanium, Arsenic, Selenium and Bromine) is presented. Bond lengths, bond angles, dipole moments, and ionization potentials are considered.

Key words: CNDO/2-method for third-row atoms – All-valence electron calculations – Dipole moment formula for third-row molecules

1. Introduction

The currently available CNDO/2 computer program [1] based on the CNDO/2 (Complete Neglect of Differential Overlap)-method [2–8] permits valence electron calculations of molecules containing hydrogen, and first- and second-row atoms. We have now extended the method and corresponding program to third-row elements. A previous extension [9–14] did not follow the original CNDO/2 parametrization scheme.

2. Method

The elements of the CNDO/2 energy matrix are [5]:

$$F_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) + [(P_{AA} - Z_A) - \tfrac{1}{2}(P_{\mu\mu} - 1)]\,\gamma_{AA} + \sum_{B \neq A} (P_{BB} - Z_B)\,\gamma_{AB}\,, \tag{1}$$

$$F_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}\gamma_{AB}\,, \tag{2}$$

where μ and ν refer to two valence atomic orbitals (AOs) ϕ_μ and ϕ_ν. All valence AOs (*s*-, *p*- and *d*-AOs) are considered. I_μ and A_μ are the ionization potential and electron affinity of ϕ_μ. $P_{\mu\mu}$ and $P_{\mu\nu}$ are elements of the charge density matrix (number of electrons which populate ϕ_μ and the overlap region $\phi_\mu\phi_\nu$, respectively) and $S_{\mu\nu}$ elements of the overlap matrix. $P_{AA}(P_{BB})$ refers to the total number of valence electrons on atom $A(B)$ [found by summing all $P_{\mu\mu}$ on atom $A(B)$] and $Z_A(Z_B)$ to the total number of valence electrons contributed by atom $A(B)$. $\gamma_{AB}(\gamma_{AA})$ denotes the repulsion integrals between two electrons both in *s* AOs, one on atom A and the other on atom B (both in the same *s* AO on atom A). β^0_{AB} is a bonding parameter.

The extension of the CNDO/2 method to third-row molecules involves five steps.

2.1. Choice of Valence AOs *for Third-Row Elements*

As for the preceding row elements, we chose as basis AOs Slater-type orbitals (STOs) [15]. Their radial part is [5, 16]

$$R_{nl} = (2\xi)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}} r^{n-1} e^{-\xi r}, \tag{3}$$

where n is the principal quantum number and $\xi = (Z - s)/n^*$ the orbital exponent (Z is the atomic number, s a screening constant determined by Slater's rules [15] and n^* an effective principal quantum number). The same orbital exponent is given to 4s, 4p and 4d AOs (*spd* basis set). Its numerical values are: Ge = 1.527, As = 1.702, Se = 1.878, and Br = 2.054.

2.2. Evaluation of Overlap Integrals $S_{\mu\nu} = \langle\phi_\mu|\phi_\nu\rangle$, *where* ϕ_μ *or* ϕ_ν *Refers to* 4s, 4p *or* 4d AOs *and Repulsion Integrals* $\gamma_{AB} = \langle s_A^2(1)|e^2/r_{12}|s_B^2(2)\rangle$, *where* s_A *or* s_B *Denotes a* 4s AO

In the original CNDO/2 program [1] provision was made for evaluation of overlap and repulsion integrals involving AOs of third-row elements. Thus after the determination of several new expansion coefficients [17] the calculation of the integrals can be achieved without difficulty.

2.3. Choice of Orbital Electronegativities $\frac{1}{2}(I_\mu + A_\mu)$ *for* 4s, 4p, *and* 4d AOs

The orbital electronegativities [18] of 4s and 4p AOs are obtained by a previously described method [4, 19]. They are (in eV) for 4s AOs: Ge = 11.435, As = 13.335, Se = 16.315 and Br = 19.630 and for 4p AOs: Ge = 4.080, As = 5.345, Se = 7.100 and Br = 8.400. Values for 4d orbitals are assumed to be zero [7].

2.4. Empirical Determination of Bonding Parameters β_{AB}^0

The bonding parameters β_{AB}^0 are written in terms of the atomic parameters β_A^0 and β_B^0:

$$\beta_{AB}^0 = \tfrac{1}{2}K(\beta_A^0 + \beta_B^0) \tag{4}$$

Here β_A^0 or β_B^0 refer to third-row atoms. K is given the value 0.75 [5]. The best atomic parameters obtained from an optimization of bond lengths, bond angles, dipole moments, and ionization potentials are (in eV): Ge = −10, As = −13, Se = −16, and Br = −22.

2.5. Derivation of the Formula for Calculation of Dipole Moments of Molecules Containing Third-Row Elements

Three terms contribute to the molecular dipole moment [3, 5–7]: μ_Q due to the net atomic charges, μ_{sp} due to the *sp* atomic polarization (mixing of s and p AOs), and μ_{pd} due to *pd* mixing. The Cartesian components of the three contributions

[$\mu_Q(x)$ and $\mu_Q(y)$ are of the same form as $\mu_Q(z)$; the same is true for $\mu_{sp}(x)$ and $\mu_{sp}(y)$ when compared with $\mu_{sp}(z)$] are (in D):

$$\mu_Q(z) = 2.5416 \sum_A Q_A z_A \tag{5}$$

$$\begin{aligned}\mu_{sp}(z) = -2.5416 \sum_A \Bigg(& \frac{5}{\sqrt{3}} \xi_A^{-1} P_{2s(A),2p_z(A)} + \frac{7}{\sqrt{3}} \xi_A^{-1} P_{3s(A),3p_z(A)} \\ & + \frac{9}{\sqrt{3}} \xi_A^{-1} P_{4s(A),4p_z(A)} \Bigg),\end{aligned} \tag{6}$$

$$\begin{aligned}\mu_{pd}(x) = -2.5416 \sum_A \frac{7}{\sqrt{5}} \xi_A^{-1} \Bigg(& P_{3p_x(A),3d_{x^2-y^2}(A)} + P_{3p_y(A),3d_{xy}(A)} \\ & + P_{3p_z(A),3d_{xz}(A)} - \frac{1}{\sqrt{3}} P_{3p_x(A),3d_{z^2}(A)} \Bigg) + \frac{9}{\sqrt{5}} \xi_A^{-1} \Bigg(P_{4p_x(A),4d_{x^2-y^2}(A)} \\ & + P_{4p_y(A),4d_{xy}(A)} + P_{4p_z(A),4d_{xz}(A)} - \frac{1}{\sqrt{3}} P_{4p_x(A),4d_{z^2}(A)} \Bigg),\end{aligned} \tag{7}$$

$$\begin{aligned}\mu_{pd}(y) = -2.5416 \sum_A \frac{7}{\sqrt{5}} \xi_A^{-1} \Bigg(& P_{3p_x(A),3d_{xy}(A)} + P_{3p_z(A),3d_{yz}(A)} \\ & - P_{3p_y(A),3d_{x^2-y^2}(A)} - \frac{1}{\sqrt{3}} P_{3p_y(A),3d_{z^2}(A)} \Bigg) + \frac{9}{\sqrt{5}} \xi_A^{-1} \Bigg(P_{4p_x(A),4d_{xy}(A)} \\ & + P_{4p_z(A),4d_{yz}(A)} - P_{4p_y(A),4d_{x^2-y^2}(A)} - \frac{1}{\sqrt{3}} P_{4p_y(A),4d_{z^2}(A)} \Bigg),\end{aligned} \tag{8}$$

$$\begin{aligned}\mu_{pd}(z) = -2.5416 \sum_A \frac{7}{\sqrt{5}} \xi_A^{-1} \Bigg(& P_{3p_x(A),3d_{xz}(A)} + P_{3p_y(A),3d_{yz}(A)} \\ & + \frac{2}{\sqrt{3}} P_{3p_z(A),3d_{z^2}(A)} \Bigg) + \frac{9}{\sqrt{5}} \xi_A^{-1} \Bigg(P_{4p_x(A),4d_{xz}(A)} \\ & + P_{4p_y(A),4d_{yz}(A)} + \frac{2}{\sqrt{3}} P_{4p_z(A),4d_{z^2}(A)} \Bigg),\end{aligned} \tag{9}$$

where $Q_A = Z_A - P_{AA}$ is the net atomic charge on atom A and z_A its z-coordinate.

3. Numerical Results and Discussion

3.1. Bond Lengths and Bond Angles

Table 1 lists the calculated and experimental bond lengths and angles of the hydrides and interhalogen compounds. Whereas bond lengths tend to differ a little bond angles are reproduced well. Calculations performed on larger molecules (invertomers of arsols [26] and conformers of germylethyl cations and anions [27]) are published elsewhere.

Table 1. Calculated and experimental bond lengths and angles

Compound	Bond lengths (Å)		Bond angles (degrees)	
	cal.	exp.	cal.	exp.
GeH_4	1.726	1.527 [20]	109.5	109.5 [20]
AsH_3	1.633	1.519 [21]	91.0	91.83 [21]
SeH_2	1.551	1.460 [22]	92.1	91.0 [22]
BrH	1.464	1.414 [23]	—	—
BrF	1.618	1.7556 [24]	—	—
BrCl	1.810	2.138 [25]	—	—

Table 2. Calculated and measured values of the dipole moment. μ_Q, μ_{sp}, and μ_{pd} are the calculated contributions due to the net atomic charges and, *sp*- and *pd* atomic polarization, respectively

Compound [41]	Dipole moment (D) cal.	cal. contributions			exp.
		μ_Q	μ_{sp}	μ_{pd}	
$FGeH_3$	−0.18	−1.12	0.95	−0.01	—
$ClGeH_3$	1.03	−0.43	−0.46	1.92	2.124 [28]
AsH_3	1.13	1.59	−3.40	2.93	0.22 [29]
AsF_3	1.38	3.23	−3.15	1.30	2.57 [30]
$AsCl_3$	−0.15	1.95	−1.83	−0.27	1.6 [31]
$As(CH_3)_3$	−2.10	0.34	−4.62	2.19	0.86 [32]
SeH_2	0.02	0.02	−2.57	2.56	0.24 [22] 0.62 [33]
$Se(CH_3)_2$	1.05	0.51	−1.94	2.47	1.32 [34]
BrH	−0.43	−0.45	−1.72	1.73	0.788 [35]
BrF	1.45	1.48	−0.83	0.80	1.29 [24]
BrCl	0.34	0.26	−0.32	0.40	0.57 [25]
$BrCH_3$	−1.83	−1.25	−1.71	1.13	1.797 [36]
BrCN	1.62	0.38	−0.57	1.80	2.94 [37]
BrNO [42]	−0.60	−1.50	−0.66	1.30	1.80 [38]
BrC_2H_3 [42]	−2.09	0.72	−2.32	0.45	1.417 [39]
BrC_2H_5 [42]	−2.30	−1.47	−1.72	0.88	2.03 [40]

3.2. *Dipole Moments*

Table 2 presents the calculated dipole moments, the contributions μ_Q, μ_{sp}, and μ_{pd} and, where available, the measured moments. In all cases experimental geometries are used. The inclusion of *d* AOs is essential because of the large *pd* polarization contributions. Compared with the corresponding terms in molecules containing second-row atoms [6] both μ_{sp} and μ_{pd} are larger and more important for third-row molecules.

3.3. *Ionization Potentials*

As Table 3 shows, the calculated ionization potentials based on Koopmans' theorem [54] are systematically too high by 2–3 eV. This result is expected and consistent with previous findings for molecules containing first- and second-row atoms [55].

Table 3. Calculated and observed ionization potentials

Compound	Ionization potential (eV)	
	cal.	exp.
GeH_4	15.319	12.3 [43]
$FGeH_3$	15.472	15.0 [44]
$ClGeH_3$	15.482	11.34 [44]
GeF_4	19.210	16.03 [45]
AsH_3	12.674	10.6 [46]
AsF_3	14.446	—
$AsCl_3$	13.366	11.7 [46]
$As(CH_3)_3$	11.385	8.3 [46]
SeH_2	12.239	9.88 [47]
$Se(CH_3)_2$	11.328	8.2 [48]
BrH	13.904	11.62 [49]
BrF	14.098	11.9 [50]
BrCl	13.980	11.1 [50]
$BrCH_3$	12.789	10.54 [51]
BrCN	13.431	11.95 [52]
BrNO	12.397	—
BrC_2H_3	11.793	9.82 [53]
BrC_2H_5	12.519	10.29 [49]

Nevertheless the calculated and the observed values both show the same trends. A good correlation between calculated and experimental ionization potentials in the series pyridine, phosphorin and arsenin [56] has been published elsewhere.

Acknowledgements. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. We thank Dr. I. L. Wilson for reading the manuscript.

References

1. Dobosch, P. A.: Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Program: QCPE 141
2. Pople, J. A., Santry, D. P., Segal, G. A.: J. Chem. Phys. **43**, S 129 (1965)
3. Pople, J. A., Segal, G. A.: J. Chem. Phys. **43**, S 136 (1965)
4. Pople, J. A., Segal, G. A.: J. Chem. Phys. **44**, S 3289 (1966)
5. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
6. Santry, D. P., Segal, G. A.: J. Chem. Phys. **47**, 158 (1967)
7. Santry, D. P.: J. Am. Chem. Soc. **90**, 3309 (1968)
8. Sabin, J. R., Santry, D. P., Weiss, K.: J. Am. Chem. Soc. **94**, 6651 (1972)
9. Sichel, J. M., Whitehead, M. A.: Theoret. chim. Acta (Berl.) **7**, 32 (1967)
10. Sichel, J. M., Whitehead, M. A.: Theoret. chim. Acta (Berl.) **11**, 220 (1968)
11. Sichel, J. M., Whitehead, M. A.: Theoret. chim. Acta (Berl.) **11**, 239 (1968)
12. Sichel, J. M., Whitehead, M. A.: Theoret. chim. Acta (Berl.) **11**, 254 (1968)
13. Sichel, J. M., Whitehead, M. A.: Theoret. chim. Acta (Berl.) **11**, 263 (1968)

14. Galasso, V., Trinajstic, N.: Tetrahedron **28**, 4419 (1972)
15. Slater, J. C.: Phys. Rev. **36**, 57 (1930)
16. Original STOs have n^* instead of n in the power of r (cf. 15). Since $n^* = 3.7$ for third-row atoms the overlap integrals $S_{\mu\nu}$ and repulsion integrals γ_{AB} (cf. Section 2.2 in the text) cannot be evaluated analytically. Therefore we use in accordance with [5] n $(=4)$ instead of n^*
17. Cf. Eq. (B.20) in Ref. [5]
18. Mulliken, R. S.: J. Chem. Phys. **2**, 782 (1934)
19. Hinze, J., Jaffé, H. H.: J. Phys. Chem. **67**, 1501 (1963)
20. Lindemann, L. P., Wilson, M. K.: J. Chem. Phys. **22**, 1723 (1954)
21. Blevins, G. S., Jache, A. W., Gordy, W.: Phys. Rev. **97**, 684 (1955)
22. Jache, A. W., Moser, P. W., Gordy, W.: J. Chem. Phys. **25**, 209 (1956)
23. Naude, S. M., Verleger, H.: Proc. Phys. Soc. **63**A, 470 (1950)
24. Smith, D. F., Tidwell, M., Wiliams, D. V. P.: Phys. Rev. **77**, 420 (1950)
25. Smith, D. F., Tidwell, M., Williams, D. V. P.: Phys. Rev. **79**, 1007 (1950)
26. Hase, H. L., Schweig, A., Hahn, H., Radloff, J.: Tetrahedron **29**, 469 (1973)
27. Hase, H. L., Schweig, A.: Tetrahedron **29**, 1759 (1973)
28. Mays, J. M., Dailey, B. P.: J. Chem. Phys. **20**, 1695 (1952)
29. Loomis, C. C., Strandberg, M. W. P.: Phys. Rev. **81**, 798 (1951)
30. Buckingham, A. D., Raab, R. E.: J. Chem. Soc. **1961**, 5511
31. Grassi, U.: Nuovo cimento **14**, 461 (1937)
32. Lide, D. R.: Spectrochim. Acta **15**, 473 (1959)
33. Veselago, V. G.: Optics and Spectroscopy **6**, 286 (1959)
34. Chierici, L., Lumbroso, H., Passerini, R.: Compt. rend. **237**, 611 (1953)
35. Compton, K. T., Zahn, C. T.: Phys. Rev. **23**, 781 (1924)
36. Shulman, R. G., Dailey, B. P., Townes, C. H.: Phys. Rev. **78**, 145 (1950)
37. Townes, C. H., Schawlow, A. L.: Microwave Spectroscopy. New York: McGraw-Hill 1955
38. Eagle, D. F., Weatherly, T. L., Williams, Q.: J. Chem. Phys. **30**, 603 (1959)
39. Hugill, J. A. C., Coop, I. E., Sutton, L. E.: Trans. Faraday Soc. **34**, 1518 (1938)
40. Groves, L. G., Sugden, S.: J. Chem. Soc. **1937**, 158
41. The sign of the dipole moments is defined as follows: The molecules are assumed to lie (cf. [42]) with their symmetry axis parallel to one Cartesian axis with the first atom in the formulae shown pointing in the positive direction of this axis
42. In these molecules the Br–N and Br–C bonds are assumed to lie parallel to one Cartesian axis with the Br atom pointing in the positive direction. Because of the lack of symmetry the three contributions μ_Q, μ_{sp} and μ_{pd} have different directions in these cases
43. Neuert, H., Clasen, H.: Z. Naturforsch. **7**A, 410 (1952)
44. Cradock, S., Ebsworth, E. A. V.: Chem. Commun. (1971) 57
45. Basset, P. J., Lloyd, D. R.: J. Chem. Soc. A, **1971**, 641
46. Cullen, W. R., Frost, D. C.: Canad. J. Chem. **40**, 390 (1962)
47. Price, W. C., Teegan, J. P., Walsh, A. D.: Proc. Roy. Soc. (London) A**201**, 600 (1950)
48. Magini, A., Trombetti, A., Zauli, C.: J. Chem. Soc. B **1967**, 153
49. Watanabe, K.: J. Chem. Phys. **26**, 542 (1957)
50. Irsa, A. P., Friedman, L.: J. Inorg. Nucl. Chem. **6**, 77 (1958)
51. Bralsford, R., Harris, P. V., Price, W. C.: Proc. Roy. Soc. A**258**, 459 (1960)
52. Herron, J. T., Dibeler, V. H.: J. Am. Chem. Soc. **82**, 1555 (1960)
53. Momigny, J.: Bull. Soc. Chim. Belges, **70**, 241 (1961)
54. Koopmans, T.: Physica **1**, 104 (1934)
55. Davis, D. W.: Chem. Phys. Letters **2**, 173 (1968)
56. Hase, H. L., Schweig, A., Hahn, H., Radloff, J.: Tetrahedron **29**, 475 (1973)

Prof. Dr. A. Schweig
Fachbereich Physikalische Chemie
Philipps-Universität Marburg
D-3550 Marburg (Lahn)
Biegenstr. 12
Federal Republic of Germany