Theor Chim Acta (1987) 72: 373-378

Theoretica
Chimica Acta

Treatment of anions in SINDO1*

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(Received March 24/Accepted June 8, 1987)

The SINDO1 method is modified to include the calculation of molecular anions. Two versions of modifications are presented which are based on charge dependent orbital exponents. Calculated heats of formation and electron affinities are much improved compared to the standard version with fixed orbital exponents.

Key words: Molecular anions — Charge dependent exponents

1. Introduction

The semiempirical molecular orbital method SINDO1 was originally conceived [1] for and applied [2] to molecules with first-row elements from Li to F under inclusion of H. Its emphasis was on the reliable prediction of geometries and binding energies. We could show that for these properties SINDO1 is even better [1] than the widely used methods MINDO/3 [3] and MNDO [4]. In the past few years SINDO1 was extended on the CI level to thermal reactions [5], excited state equilibria [6] and photochemical reactions [7]. Now the development and parametrization for molecules with second-row elements is available [8]. All these studies show that SINDO1 was highly successful in dealing with a variety of topics. However, a few drawbacks remained. Among them was the inability of SINDO1 to deal properly with anions. It was not the geometry, but the total energy which was poor. This failure to produce acceptable binding energies for molecular anions was due to inflexibility of the minimal basis set and in particular the fixed exponents. These exponents had been proved to be adequate for neutral systems, but could not reflect the diffuse character of orbitals in anions. In the next section we suggest two methods to vary the orbital exponents in dependence on the net charge of an atom in a molecular anion. We apply the better version to selected compounds in the first row on which experimental data are available.

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

2. Method and application

The importance of orbital exponents becomes clear if we consider the exchange reaction

$$H^- + CH_4 \rightarrow CH_5^- \rightarrow CH_4 + H^-. \qquad (1)$$

In the neutral atom the hydrogen 1*s*-orbital exponent is 1.00. In neutral molecules like CH_4 [9, 10] the optimal orbital exponent of hydrogen 1*s* in minimal basis set calculations is about 1.20 and the orbital is contracted. For the H^- anion the optimal exponent is 0.7 and the orbital is diffuse [10]. For the transition structure of CH_5^- in D_{3h} symmetry the two axial hydrogens which carry the negative charge were assigned orbital exponents of 0.79 whereas the three equatorial hydrogens were given the normal values of 1.15. If we would assign a fixed orbital exponent of 1.20 for all hydrogens during the course of the exchange reaction (1), we would find that CH_5^- represents a minimum instead of the appropriate saddle point.

We therefore suggest that orbital exponents must vary from the value for the neutral atom if the atom carries a negative charge in the molecular anion. To establish a proper reference, we determined the exponents for the atomic anions H^- and Li^- to F^- in such a way that the experimental energy of the atomic anion is reproduced. In Table 1 we list the optimal exponents for these anions calculated for the SINDO1 method together with the standard exponents. We use a single exponent for 2*s* and 2*p* orbitals. For the standard exponents the total energies of the atomic anions were much too high and this problem is transferred to molecular anions. Our concept therefore was to use an exponent ζ^0 and ζ^- in Table 1 according to the following form if the atom X carries a negative net charge q_X in a molecular anion

$$\zeta'_X = \zeta^0_X - q_X(\zeta^-_X - \zeta^0_X). \qquad (2)$$

This represents a linear interpolation scheme. Our first method, which is labelled A in the following discussion, was therefore designed in such a way that we carried out a SINDO1 calculation for a molecular anion and determined its optimum structure with the standard exponents. From the net charges on the atoms we could determine the new exponents ζ'_X for negatively charged atoms according to Eq. (2). At this stage we maintained a single exponent for each type of atoms. To avoid problems in the energy calculations we made the following

Table 1. SINDO1 orbital exponents for neutral atoms (ζ^0) and anions (ζ^-) for first-row elements

Atom	ζ^0	Anion	ζ^-
H	1.17	H^-	0.788
Li	0.64	Li^-	0.483
Be	0.96	Be^-	0.862
B	1.25	B^-	1.185
C	1.55	C^-	1.505
N	1.90	N^-	1.856
O	2.15	O^-	2.116
F	2.40	F^-	2.372

two restrictions: 1) if the total negative net charge of a portion of the atoms exceeded the total molecular charge, we renormalized the net charge. 2) For atoms of the same type we averaged over the charges of all negative atoms, renormalized the charge and determined the exponents for all atoms of this type according to Eq. (2).

$$q'_X = q_X \frac{q_{\text{molecule}}}{\sum\limits_Y q_Y} \text{ with } q_X, q_Y < 0 \tag{3}$$

N_3^- may serve as an example. With SINDO1 we obtained $q_{N_o} = -0.66$ for the outer N atoms and $q_{N_i} = 0.33$ for the inner N atom. We renormalized the negative net charge to $q_N = -0.5$ and calculated an exponent of $\zeta_N = 1.878$. With this new exponent which was used for all nitrogen atoms a new SINDO1 calculation was performed at the SCF level and the corresponding total energy at the fixed geometry determined.

In the second procedure which is called B we gave up the restriction of a single exponent for all atoms of one type. The inner and outer nitrogen atoms in N_3^- were allowed different exponents. In principle each atom has its own charge dependent exponent. But in order to avoid a time consuming self-consistent iteration of the new exponents, we limited in this case the new integral calculation to Coulomb integrals and determined only these with the new exponents. This simplified the procedure considerably since it allowed an automated recalculation of the total energy with the obtained density matrix at the end of the SCF iteration procedure with the standard exponents. It is indeed the electronic repulsion which is reduced by the use of more diffuse orbital exponents in anions. It seems therefore proper in a semiempirical method with a minimal basis set in order to maintain the efficiency of the calculation in this way.

Again N_3^- can serve as an example. After renormalization of the charge for the outer N atoms according to Eq. (3), the new exponents for these atoms are $\zeta = 1.878$. The exponent of the inner N atom was chosen $\zeta = 1.90$ as for the neutral atom. With this set of exponents the Coulomb integrals were recalculated and the total energy was readjusted.

We have also tested the option of iterative adjustment of orbital exponents, density matrix and geometry. Since the resulting changes did not lead to significantly improved results, we abandoned this procedure to save computer time.

Table 2. Binding energies E_B (Hartree) of molecules and their anions for fixed and variable exponents (methods A and B)

Molecule	Binding energy neutral		Anion			
	exp	SINDO1	exp[a]	SINDO1 fixed	method A	method B
OH	−0.170	−0.1767	−0.2373	−0.0109	−0.2126	−0.2421
CH_3	−0.489	−0.4898	−0.4802	−0.3449	−0.3982	−0.4795
NO_3	−0.444	−0.444	−0.5873	−0.4306	−0.6505	−0.6059
N_3	−0.3628	−0.3850	−0.4841	−0.2480	−0.5329	−0.4491

[a] $E_B^- = E_B^0 - E_a^0$; E_a^0 electron affinity

Table 3. Heats of formation ΔHf^0 (kcal/mol) and electron affinities E_a (eV) for anions

Molecule	ΔHf_0^0			E_a			
	exp	SINDO1 method B	MNDO[e]	AM1[g]	exp[e]	SINDO1 method B	MNDO[e]
CH_2^-	87.7[f]	91.9	104.7		0.21	−0.02	−1.19
CH_3^-	38.3[f]	38.8	56.8	57.7	(−0.24)	−0.25	−1.34
C_2^-	118.5[f]	102.3	173.7		3.5	4.60	2.56
$C_2H_4^-$	46.8[f]	32.6	38.8		−1.55	−0.95	−1.02
$C_2H_5^-$		15.6	27.3	34.5	<0.34	0.003	−0.63
$C_3H_5^-$		5.9	26.0	27.6	0.55	0.93	0.40
$C_5H_5^-$	21.3[i]	18.6	18.8	25.2	<1.84	2.25	1.70
NH_2^-	25.4[i]	23.4	47.3	52.5	0.75	0.90	−0.44
CN^-	18.2[i]	13.9	54.9	44.0	3.82	4.20	3.21
Pyridine$^-$		26.6	23.7		−0.62	1.03	0.22
N_3^-	45.0[a]	62.0	52.5		3.1–3.5[c]	1.76	2.16
$C_2(CN)_4^-$		48.6	76.1		2.88[d]	4.19	3.06
OH^-	−32.3[a]	−35.5	−5.8	−14.1	1.83	1.78	0.27
OCH_3^-	−36.0[h]	−44.7	−39.8	−38.8[h]	1.59	1.52	1.72
O_2^-	−9.5[f]	−11.0	−19.0		0.44	0.08	0.16
CO_2^-	−80.9[f]	−101.1	−79.5		−0.60	0.99	0.18
p-Benzoquinone$^-$		−50.4	−76.5		1.89	2.75	1.88
NO_2^-	−83.7[b] ± 12	−52.5	−63.5		2.36	2.49	2.55
NO_3^-	−74.7[i]	−84.1	−67.0		3.9[d]	4.41	5.17
CF_3^-	−157.2[i]	−211.4	−178.9		2.82	3.32	1.81
OCF_3^-		−286.7	−241.6		1.35[d]	4.76	3.87
BF_2^-	−136[b] ± 30 −158.0[f]	−179.7	−177.4		2.65[d]	2.48	1.76
BF_3^-		−306.6	−271.1			1.27	0.43
BeH^-	59.6[f]	77.0	74.5		0.74	0.33	−0.62

[a] [11]
[b] [12]
[c] [13]
[d] [14]
[e] [15]
[f] $\Delta Hf_0^0(\text{exp}) = \Delta Hf^0(\text{calc}) + E_B(\text{exp}) - E_B(\text{calc})$
[g] [20]
[h] [21]
[i] [22]

The present version is applicable also in chemical reactions, since it contains a continuous adjustment of potential surfaces.

We wish now to present results for binding energies for a few compounds in Table 2. From a comparison with experimental data we see that method B is more reliable than method A. Both are much better than the usual procedure of fixed exponents where the total energy is usually much too high for anions. In the following we use only method B. In Table 3 we have collected SINDO1 calculations for heats of formation and electron affinities for more than 20 compounds with method B and compare these with experimental data [11–14] and MNDO data [15]. The average error of heats of formation in 16 compounds is 13.8 kcal/mol SINDO1 and 19.1 kcal/mol for MNDO. The corresponding average errors for electron affinities of 23 compounds is 0.70 eV for SINDO1 and

Table 4. Calculated geometries (Å, degrees) for anions (neutral molecules)

Molecule	Geometry
CH_2^-	CH 1.104 (1.059), HCH 109.2 (135.1)
CH_3^-	CH 1.061 (1.067), HCH 120.0 (120.0)
C_2^-	CC 1.212 (1.226)
$C_2H_4^-$	CC 1.404 (1.324)
$C_2H_5^-$	CC 1.464 (1.466)
$C_3H_5^-$	CC 1.388 (1.400), CCC 134.7 (128.9)
$C_5H_5^-$	CH 1.072 (1.075), CC 1.442 (1.473, 1.399, 1.549)
NH_2^-	NH 1.029 (1.015), HNH 105.7 (106.1)
CN^-	NC 1.145 (1.160)
Pyridine$^-$	NC^1 1.379 (1.343), C^1C^2 1.399 (1.424), C^2C^3 1.456 (1.419)
N_3^-	NN 1.169 (1.188)
$C_2(CN)_4^-$	C=C 1.469 (1.392), C-C 1.468 (1.483), CN 1.159 (1.159)
OH^-	OH 0.977 (0.970)
OCH_3^-	CO 1.265 (1.356), CH 1.123 (1.100), HCO 114.9 (105.8, 111.9)
O_2^-	OO 1.261 (1.181)
CO_2^-	CO 1.233 (1.191), OCO 143.4 (180.0)
p-Benzoquinone$^-$	OC^1 1.267 (1.226), C^1C^2 1.508 (1.552), C^2C^3 1.377 (1.347)
NO_2^-	NO 1.242 (1.198), ONO 122.3 (137.9)
NO_3^-	NO 1.275 (1.252, 1.315), ONO 120.0 (124.2)
CF_3^-	CF 1.392 (1.326), FCF 104.1 (114.1)
OCF_3^-	CO 1.271 (1.362), CF 1.388 (1.356, 1.358), FCO 115.7 (108.3, 111.9)
BF_2^-	BF 1.401 (1.328), FBF 106.2 (124.9)
BF_3^-	BF 1.387 (1.334)
BeH^-	BeH 1.391 (1.295)

0.83 eV for MNDO. The source for the large discrepancy between calculated and experimental values in OCF_3 is not clear. Both methods appear sufficiently reliable considering the difficulty of the problem.

After completion of this work AM1 calculations on heats of formation of a large number of cations and anions appeared [20], from which we have included those anions for comparison in Table 3 which we had originally selected from the MNDO paper. The AM1 method and its accuracy for neutral systems was described previously [21]. This paper contained also a small number of anions. Since the purpose of the present work is not to present a comprehensive set of molecules, rather to describe a new method, no further attempt to calculate additional molecules was made.

The SINDO1 optimized geometries for these anions are presented in Table 4 together with the geometries of neutral molecules. Since experimental data are not generally available, no conclusive comparison can be made. However, it is appropriate to mention that the changes in geometry from neutral to anion species show the same trend in SINDO1 as in MNDO [15] for most systems. Exceptions are CN^- and C_2^- for which SINDO1 predicts bond shortening and MNDO bond lengthening compared to the neutral form.

For these small systems both *ab initio* calculations with large basis sets and configuration interaction and experimental data are available. Taylor et al. [16] find practically no change from CN (calc 1.170 Å, exp 1.172 Å) to CN^- (calc 1.173 Å). Liu [17] obtains bond lengthening from C_2 (calc 1.239 Å, exp 1.242 Å) to C_2^- (calc 1.265 Å, exp 1.268 Å) in agreement with experiment. Our trend is correct in NH_2^- and CH_2^-. For the first system Bell [18] determined bond lengthening from NH_2 (calc 1.029 Å, 103.3°, exp 1.024 Å, 103.1°) to NH_2^-(calc 1.032 Å, 102.4°, exp 1.03 Å, 104°). Bond lengthening is predicted [19] from CH_2 (calc 1.0764 Å, 132.3°) to CH_2^- (calc 1.121 Å, 104.4°).

Finally we find with this method an activation energy of 59.9 kcal/mol compared to 69.8 kcal/mol *ab initio* [10] for exchange reaction (1). These results prove that SINDO1 is capable in dealing with energies and geometries of anions.

References

1. Nanda DN, Jug K (1980) Theor Chim Acta 57:95
2. Jug K, Nanda DN (1980) Theor Chim Acta 57:107, 131
3. Bingham RC, Dewar MJS, Lo DH (1975) J Am Chem Soc 97:1285, 1294, 1302, 1307; Dewar MJS, Lo DH, Ramsden CH (1975) J Am Chem Soc 97:1311
4. Dewar MJS, Thiel W (1977) J Am Chem Soc 99:4899, 4907
5. Jug K, Dwivedi CPD (1981) Theor Chim Acta 59:357; Jug K, Dwivedi CPD (1981) Theor Chim Acta 60:73; Jug K, Müller PL (1981) Theor Chim Acta 59:365; Jug K, Iffert R (1982) Theor Chim Acta 62:183; Jug K, Mishra PC (1983) Int J Quantum Chem 23:887
6. Mishra PC, Jug K (1982) Theor Chim Acta 61:559; Jug K, Hahn G (1983) J Comput Chem 4:410; Malar EJP, Jug K (1984) J Phys Chem 88:3508; Malar EJP, Jug K (1985) J Phys Chem 89:5235
7. Müller-Remmers PL, Mishra PC, Jug K (1984) J Am Chem Soc 106:2538; Müller-Remmers PL, Jug K (1985) J Am Chem Soc 107:7275; Buss S, Jug K, (1987) J Am Chem Soc 109:1044
8. Jug K, Iffert R, Schulz J (1987) Int J Quantum Chem (in press)
9. Hehre WJ, Stewart RF, Pople JA (1969) J Chem Phys 51:2657
10. Mulder JJC, Wright JS (1970) Chem Phys Lett 5:445
11. Wagman DD, Evans WH, Parker VB, Halow I, Bailey SM, Schumm RH (1968) NBS Technical Note 270-3. Nat Bur Stand, Washington
12. Stull DR, Prophet HP (1971) JANAF Thermochemical Tables, 2nd edn., NSRDS-NBS 37. Nat Bur Stand, Washington
13. Huheey JE (1972) Inorganic Chemistry. Harper & Row, New York
14. Weast RC, Astle MJ (1980) CRC Handbook of chemistry and physics, 60th edn. CRC Press, Boca Raton
15. Dewar MJS, Rzepa HS (1978) J Am Chem Soc 100:784
16. Taylor PR, Bacskay GB, Hush NS, Hurley AC (1980) J Chem Phys 70:4481
17. Dupuis M, Liu B (1980) J Chem Phys 73:337
18. Bell S (1978) J Chem Phys 68:3014; Bell S (1979) J Chem Phys 69:3879
19. Shih SK, Peyerimhoff SD, Buenker RJ, Peric M (1978) Chem Phys Lett 55:206
20. Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP (1985) J Am Chem Soc 107:3902
21. Dewar MJS, Dieter KM (1986) J Am Chem Soc 108:8075
22. Bartmes JE, McIver Jr RT (1979) In: Bowers MT (ed) Gas phase ion chemistry, vol II. Academic Press, New York p 88