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A Reparametrization of the CNDO Method

I. Hydrocarbons

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The empirical evaluation of the core matrix elements in the CNDO method is modified and the parameters are adjusted to give optimal values for heats of atomization, bond lengths, bond angles and force constants.

Die empirischen Ansätze der CNDO-Methode für die Core-Matrixelemente werden modifiziert und die Parameter abgeändert, um möglichst gute Werte für Bildungswärmen aus den Atomen, Bindungslängen, Valenzwinkel und Kraftkonstanten zu erhalten.

L'évaluation empirique des éléments de matrice de coeur dans la méthode CNDO et les paramètres sont modifiés en vue de donner des valeurs optimaux pour les énergies d'atomisation, les distances interatomiques, les angles de valence et les constants de force.

The semiempirical SCF MO method (CNDO) elaborated by Pople *et al.* [1] is particularly useful for studying reaction mechanisms and in fact has already been so used in some cases [2, 3, 4]. However, a general application of the method is hampered by the fact that the empirical parameters involved are apparently not yet optimized. Thus, heats of atomization, excitation energies and force constants are in most cases much too high. Equilibrium bond lengths and valence angles on the other hand are in general reasonable. A number of modifications of CNDO have already been proposed in the literature: Wiberg [5] altered the bonding parameters β_X and used a linear relationship between calculated and experimental heats of atomization. However, it is difficult to see how this can be applied to calculate energies of bimolecular chemical reactions and in particular activation energies. Clark [4] used the Wolfsberg-Helmholtz approximation for the $H_{\mu\nu}$-elements and the Mataga or Ohno formula for the γ_{AB}-elements. In addition he took different orbital exponents for s and p-orbitals. Excitation energies and dipole moments calculated with this modification are in good agreement with experiment. Equilibrium bond lengths and force constants were not considered. The parameters used by Whitehead *et al.* [6] were calibrated to fit heats of atomization, ionization potentials and dipole moments of a large number of compounds. Again, equilibrium bond lengths and force constants were not examined. Herndon *et al.* [7] reduced the empirical parameter β_X for fluorine from 35 to 14 eV in order to give the experimental N–F bondlength. It remains to be shown how this single change of an empirical parameter affects heats of atomization and bond lengths calculated of other fluorine compounds. Other changes of the empirical parameters have been proposed to improve the agreement with experiment for special properties of certain compounds [8].

It is our aim to reparametrize CNDO such that it gives at the same time good heats of atomization, equilibrium geometries and force constants. We think this is imperative if one wants to make predictions for unstable reaction intermediates and transition states whose geometries are uncertain. Moreover, it may be assumed that energy hyperplanes calculated with such a method can be used successfully to investigate reaction mechanisms, since the shape of the hyperplane may be expected to be reasonable if the derivatives of order zero, one and two at the equilibrium position are correct. Thus heats of atomization and force constants given in Tables 6 and 3 respectively were obtained at the calculated equilibrium geometry as given in Table 2, i.e. at the minimum of the energy hyperplane. Dipolemoments, ionization potentials and excitation energies will also be briefly investigated.

The modifications we propose amount to a different evaluation of the core matrix elements $H_{\mu\nu}$ for which we write[1]

$$H_{\mu\mu} = I_\mu - (Z_A - 1)\cdot\gamma_{AA} - \sum_{B\neq A} V_{AB} \qquad \mu\in A, \tag{1}$$

$$H_{\mu\nu} = \frac{1}{2}(k_A I_\mu + k_B I_\nu)\cdot S_{\mu\nu} \qquad \mu\neq\nu,\ \mu\in A,\ \nu\in B, \tag{2}$$

$$V_{AB} = Z_B[(1-\alpha)\cdot\gamma_{AB} + \alpha\sqrt{R_{AB}^2 + 1/\mu_A^2}]; \quad \alpha = 0.22. \tag{3}$$

The γ_{AB} remains the same as in CNDO/2:

$$\gamma_{AB} = (s_A s_A \mid s_B s_B).$$

Our proposal for V_{AB} (Z_B = effective nuclear charge on atom B; R_{AB} = distance between atoms A and B; μ_A cf. Table 1) is between the values proposed in CNDO/1 and CNDO/2 respectively

$$\text{CNDO/1:} \quad V_{AB} = \left\langle s_A \left| \frac{Z_B}{R_{AB}} \right| s_A \right\rangle, \tag{4}$$

$$\text{CNDO/2:} \quad V_{AB} = Z_B\cdot\gamma_{AB}. \tag{5}$$

In the vicinity of normal C–C-bondlengths (3) and (5) do not differ much. However, the first and even more so the second derivative of V_{AB} with respect to distance differ greatly. It turns out that the high force constants of CNDO/2 are due to the fact that the magnitude of the second derivative of the electronic energy is too small. Increasing values for α in (3) increase the magnitude of the second derivative. The values for k_X in (2) have only little influence on the force constants but they are of importance for the bond lengths. Therefore, values for k_X were adopted which gave correct heats of atomization. Then α in (3) was chosen to give reasonable bondlengths which at the same time led to lower force constants.

Equation (2) for the $H_{\mu\nu}$-elements ($S_{\mu\nu}$ = the overlap integral; k_A, I_μ cf. Table 1) is similar to the Wolfsberg-Helmholtz relationship. We used (2) to obtain a larger separation of σ-and π-orbitals and at the same time achieved a considerable improvement of the energy of ethylene relative to those of ethane and acetylene. However, the invariance of the theory with respect to hybridization is no longer maintained. We have shown that this invariance is not essential [9].

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[1] Our notation is the same as in Ref. [1].

The quantities I_μ are regarded as empirical parameters. The values adopted for them (Table 1) are close to valence state ionization potentials of the corresponding atoms. The orbital exponent μ_A for carbon 2*s* and 2*p* orbitals is the same as in CNDO/2 in accordance with the Slater rule, while that of hydrogen is reduced from 1.20 to 1.16. This leads to a better equilibrium distance for H_2 and increases non bonded interactions between hydrogen atoms. Thus the rotation

Table 1. *Empirical parameters for carbon and hydrogen*

	μ_X	k_X	I_s [eV]	I_p [eV]
H	1.16	0.594	− 13.6	—
C	3.25	0.987	− 20.0	− 10.0

Table 2. *Calculated equilibrium geometries*[a]

Type	compound	experimental [10]	this work	CNDO/2
H–H	H_2	0.741	0.734	0.746
C–H	methane	1.106	1.110	1.114
	ethane	1.107	1.116	1.120
	ethylene	1.084	1.105	1.112
	acetylene	1.059	1.081	1.093
	benzene	1.084	1.110	1.117
C≡C	acetylene	1.205	1.213	1.197
	propyne	1.206	1.220	1.207
	butenyne		1.222	1.208
	butadiyne	1.205	1.221	1.208
C=C	ethylene	1.332	1.342	1.311
	propene	1.353	1.351	1.322
	butadiene (*s*-trans)	1.337	1.353	1.324
	butenyne		1.353	1.322
	allene	1.312	1.330	1.305
	butatriene 1–2	1.309	1.330	1.305
	butatriene 2–3	1.284	1.312	1.298
	ethylene (dih. angle 89°)		1.369	1.334
	allene (planar)		1.352	1.315
$\mathrm{C{-}C_{arom.}}$	benzene	1.397	1.419	1.385
C–C	ethane (staggered)	1.536	1.520	1.459
	ethane (eclipsed)		1.525	1.463
	propane	1.526	1.532	1.468
	cyclopropane	1.524	1.513	1.474
	propene	1.488	1.507	1.455
	propyne	1.459	1.466	1.430
	butadiene	1.483	1.498	1.446
	butenyne		1.454	1.421
	butadiyne	1.379	1.425	1.402
C–C–H	ethane (staggered)	110.5	111.6	111.9
	propyne	110.2	110.6	111.3
C=C–H	ethylene	122.3	123.5	124.2
	allene	122	122.1	123.5
C–C–C	propane	112.4	118.1	113.8
C=C–C	propene	124.8	127.0	126.2
	butadiene (*s*-trans)	122.4	124.9	124.3

[a] Bond lengths in Å; bond angles in degrees.

barrier of ethane is increased by almost 10%. Unfortunately, this barrier is still too small (1.5 kcal/mole) as compared with the experimental barrier (2.7 kcal/mole) or the barrier obtained with CNDO/2 (2.3 kcal/mole).

In Tables 2 to 7 equilibrium geometries, force constants, charge distributions, dipole moments, heats of atomization and ionization potentials for a number of hydrocarbons as calculated by our modification are compared with experimental values and with those obtained with CNDO/2.

As can be seen from Table 2, bond lengths and bond angles obtained by the modified CNDO method deviate in general less than 2% from experimental

Table 3. *Calculated force constants*[a]

Type	compound	experimental [11]	this work	CNDO/2
H–H	H_2	5.7	9.5	10.2
C–H	methane	5.4	8.9	12.6
	acetylene	6.2	9.5	12.8
C≡C	acetylene	17.2	22.4	35.7
C=C	ethylene	10.9	14.7	25.2
	allene	9.7[b]	15.3	26.7
$C-C_{arom.}$	benzene	7.6[b]	12.9	21.7
C–C	ethane	4.6	8.5	15.5
C≡C–H	acetylene	0.21[b]	0.31	0.56
C=C–H[c]	ethylene	4.4[b]	4.1	5.9
C–C–H[d]	ethane	6.2[b]	5.9	8.2
C≡C–C	propyne	0.16[b]	0.21	0.39
C=C–C	propene	0.54[b]	0.53	0.59

[a] Values in mdyne/Å; bending force constants for type A–B–C as k_{A-B-C}/R^2_{B-C}.

[b] Values not corrected for unharmonicity.

[c] $4 \cdot k_{C-C-H} + 8 \cdot k_{H-C-H}$.

[d] $6 \cdot k_{C-C-H} + 6.2 \cdot k_{H-C-H}$.

Table 4. *Calculated charge densities for hydrogen atoms in various hydrocarbons*

Compound	Charge density on H	
	this work	CNDO/2
Methane	0.967	0.989
Ethane	0.975	1.003
Ethylene	0.962	0.990
Acetylene	0.901	0.938
Benzene	0.970	1.012

Table 5. *Calculated dipole moments*[a]

Compound	experimental [12]	this work	CNDO/2
Propane	0.08	0.03	0.00
Propene	0.35	0.50	0.44
Propyne	0.75	0.56	0.41
Butenyne		0.37	0.17

[a] Values in Debye.

values. Particularly noteworthy is the improvement in the C–C single bond length which came out too short by 0.08 Å in CNDO/2. The large shortening of C–C single bonds by neighbouring multiple bonds as observed is not yet entirely satisfactorily reproduced. Bond stretching force constants, to be sure, are still some 50% too high. However, in CNDO/2 they were from twice to three times the experimental values. Bending force constants seem to be reasonable. The dipole moments are not much different from those calculated with CNDO/2 and are in good agreement with experiment. Hydrogen atoms in hydrocarbons are slightly more positive than in CNDO/2. Ionization potentials calculated for methane and ethane using Koopman's theorem compare favorably with experimental values obtained from photoelectron spectroscopy.

The heats of atomization calculated are in general within 2% of the experimental values. There is one defect of CNDO/2 which seems to have gone un-

Table 6. *Calculated heats of atomization*[a]

Compound	experimental[b]	this work	CNDO/2
H_2	0.174	0.184	0.197
Methane	0.669	0.666	1.396
Ethane (staggered)	1.134	1.136	2.663
Ethane (eclipsed)		1.134	2.660
Ethylene	0.897	0.895	2.188
Ethylene (dih. angle 89°)		0.785	1.971
Acetylene	0.647	0.653	1.737
Propane	1.602	1.588	3.921
Cyclopropane	1.357	1.408	3.628
Propene	1.371	1.365	3.458
Propyne	1.123	1.144	3.030
Allene	1.120	1.135	3.000
Allene (planar)		1.083	2.864
Butadiene (*s*-trans)	1.614	1.592	4.255
Butenyne	1.353	1.373	3.826
Butatriene		1.364	3.808
Butadiyne	1.108	1.146	3.390
Benzene	2.183	2.149	6.290

[a] Values in atomic units (= 27.21 eV).

[b] Corrected for zero point energy.

Table 7. *Calculated ionization potentials*[a]

Compound	MO	experimental [13]	this work	CNDO/2[b]
Methane	t_2	13.6	12.9	15.1
	a_1	23.1	30.9	30.4
Ethane	e_g	10.7	10.7	11.8
	a_{1g}	10.7	11.0	14.5
	e_u	14.7	14.8	20.2
	a_{2u}	20.3	23.7	25.8
	a_{1g}	23.9	36.2	37.3

[a] Values in eV.

[b] Energy zero assumed: 3.8 eV.

noticed, as it is also present in the modified methods of Wiberg and of Sichel and Whitehead: the heat of atomization of ethylene comes out too low as compared with ethane and acetylene. As a consequence, heats of reactions involving formation or destruction of double bonds are considerably in error. As can be seen from Tables 7 and 8 we could not entirely remove this defect but achieved a definite improvement. This was chiefly accomplished by using Eq. (2). However, this also had the undesirable effect that certain bonds with high *s*-character such as the C–H bonds in cyclopropane and C–C single bonds originating from *sp*-hybridized atoms are favored too strongly. Thus heats of atomization calculated for propyne, butadiyne and cyclopropane are too high. This shows up in heats of reactions involving such compounds (cf. Table 8).

Table 8. *Calculated heats of reactions*[a]

Reaction	ΔH (0° K)		
	experimental	calculated this work	calculated CNDO/2
Hydrogenations			
Acetylene → ethylene	39.8	36.5	159
Acetylene → ethane	70.8	72.1	334
Ethylene → ethane	31.0	35.6	174
Propyne → propane	65.6	48.1	312
Propene → propane	28.0	24.8	166
Butadiyne → butadiene	81.5	49.1	295
Butenyne → butadiene	45.5	22.0	145
Isomerizations			
Allene → propyne	1.7	5.6	18.5
Butatriene → butenyne		6.0	11.4
Cyclopropane → propene	9.3	−26.8	−107
Cyclobutane → butene-(1)	7.5	−24.5	−146
Rotation barriers			
Ethylene	61.3	69.4	136
Allene		32.6	85.5
Ethane	2.8	1.5	2.3
Condensations			
2 acetylenes → butenyne	33.3	41.9	221
3 acetylenes → benzene	139.0	118.8	677
Acetylene + ethylene → butadiene	39.1	27.4	207
2 ethylenes → cyclobutane	16.5	43.7	360

[a] Values in kcal/mole.

Table 9. *Calculated excitation energies*[a]

Compound	experimental	this work	CNDO/2
Benzene	4.72	4.79	10.00
	5.76	5.13	10.34
	7.27	8.09	13.30
Butadiene	5.92	6.46	10.58

[a] Values in eV.

Results of preliminary calculations of excitation energies for *s*-trans-butadiene and benzene are listed in Table 9. All singly excited configurations from the 7 highest occupied and the seven lowest unoccupied MO's were included in the configuration interaction treatment. Although the excitation energies thus obtained are not yet quite satisfactory a definite improvement of the CNDO/2 values is clearly recognizable.

Calculations were performed on a CDC 3300 computer using a Fortran program based on Pople and Segal's CNDO/2 program. The energy minimizations were carried out in the following manner:

i) selection of a set of bond lengths and bond angles (variables) which uniquely determine the geometry of the system,

ii) evaluation of the total energy for the assumed geometry (origin),

iii) evaluation of the total energy at 2 points around the origin for each variable while keeping the other variables constant,

iv) calculation of a new origin using a parabolic extrapolation and start at ii).

This procedure was contained until the total energy was constant within 10^{-4} a.u.

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