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CNDO–S²—a semiempirical SCF MO method for transition metal organometallics

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A new semiempirical SCF MO procedure available for prediction of the transition metal compounds energy and geometry is developed. The procedure takes an explicit account of the orthogonality of the basis set in the calculation of the core-Hamiltonian elements. A new formula for the resonance integral used in CNDO-S² gives a physically correct treatment of diffuse orbital-localized orbital interaction. The parametrization for atoms H, C, N, O and Ni is presented, with one-center empirical parameters only used. The results of CNDO-S² energy and geometry calculations performed for a number of organic compounds and some nickelorganics are compared with the experimental data. The average absolute errors for the binding energies of organic compounds and nickel complexes are 6.6 kcal/mol and 9.3 kcal/mol respectively.

Key words: S^2 terms in CNDO — Transition metal compounds

1. Introduction

When developed the semiempirical ZDO methods for quantitative determination of the transition metal complexes energetics and geometry one should take into account some peculiarities of their electronic structure. To begin with, the orthogonality effects of the basis set of the atomic orbitals [1] are not expected to be small for compounds that contain atoms with a large number of valence d-electrons. Also, the interaction between localized and diffuse atomic orbitals (e.g., s- or p-metal orbitals and localized ligand orbitals) is of value for the chemical bonding in metal complexes. With that, ZDO parametrization including a large number of transition elements requires the extensive experimental data

on metal compounds energy and structure. The latter condition isn't always justified in practice.

In this paper a new semiempirical SCF MO procedure CNDO-S^2 available for prediction of the transition metal compounds energy and geometry is presented. The procedure takes an explicit account of the orthogonality of the basis set [1] in the calculation of core-Hamiltonian diagonal elements by introducing the term proportional to the square of overlap integral between the atomic orbitals involved. In this sense the procedure proposed is similar to SINDO1 [1], but contrary to [1] in CNDO-S^2 a new formula for the resonance integral is used. The new formula has been derived from the model two-orbital system [2] with interacting localized and diffuse orbitals. Since the main contribution to the binding energy of a molecule comes from the resonance terms [3] the new formula seems to lead to the better results for transition metal compounds energetics and structure. To avoid aforementioned difficulties arising in the parametrization of a large number of transition elements in CNDO-S^2 the one-center empirical parameters are adopted. This facilitates the parametrization and, in our opinion, not spoils too much the results obtained.

The parametrization including atoms H, C, N, O and Ni has been developed and CNDO-S^2 calculations of energy and geometry for a number of organic compounds and some nickel complexes have been performed. The binding energies, ionization potentials, dipole moments and equilibrium geometries calculated are compared with the experimental data.

2. Method and parametrization

To account for the orthogonality in ZDO Fockian we use the approximate formulae for the matrix elements $F_{\mu\nu}$ over the symmetrically orthogonalized basis set [4]. In the present paper for the Coulomb repulsion integrals the usual approximation [5]

$$^\lambda(\mu\nu\,|\,\sigma\tau) = \delta_{\mu\nu}\delta_{\sigma\tau}(\mu\mu\,|\,\sigma\sigma)$$

is adopted. Using the Löwdin transformation [4]

$$^\lambda H = S^{-1/2} H S^{-1/2} \tag{1}$$

and a binomial expansion of $S^{-1/2}$ to second order in the overlap integral, the core-Hamiltonian matrix elements $^\lambda H_{\mu\mu}$ and $^\lambda H_{\mu\nu}$ are given by [5]

$$^\lambda H_{\mu\mu} = H_{\mu\mu} - \sum_{\sigma \neq \mu} S_{\mu\sigma}(H_{\mu\sigma} - \tfrac{1}{2}S_{\mu\sigma}(H_{\mu\mu} + H_{\sigma\sigma}))$$
$$+ \tfrac{1}{4} \sum_{\lambda \neq \mu} S_{\mu\lambda}^2 (H_{\mu\mu} - H_{\lambda\lambda}) + O(S^3) \tag{2}$$

$$^\lambda H_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}S_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu}) + O(S^2). \tag{3}$$

The first two terms in Eq. (3) is the well-known Mulliken function $M_{\mu\nu}$ [6] which is usually approximated by

$$M = -\beta_{\mu\nu}S_{\mu\nu}, \tag{4}$$

where $\beta_{\mu\nu}$ is a resonance parameter depending on the nature of the μ and ν orbitals, $S_{\mu\nu}$ is the overlap integral. Therefore, neglecting the last term in Eq. (2) and substituting Eq. (4) into Eqs. (2) and (3) we obtain

$$^{\lambda}H^A_{\mu\mu} = H^A_{\mu\mu} + \sum_{B\neq A} \delta_{AB} \sum_{\sigma\in B} \beta_{\mu\sigma}S^2_{\mu\sigma}; \qquad \delta_{AB} = \tfrac{1}{2}(\delta_A + \delta_B) \qquad (5)$$

$$^{\lambda}H^{AB}_{\mu\nu} = -\beta_{\mu\nu}S_{\mu\nu}. \qquad (6)$$

Here δ_A and δ_B are the empirical parameters depending on the nature of the A and B atoms. The empirical parameter δ has been introduced in order to adjust the shortcomings of the approximations used in Eq. (5). For the core-Hamiltonian diagonal matrix elements calculation the usual neglect of penetration integrals is adopted. In order to preserve rotational invariance of the Eq. (5) the square of the overlap integral is averaged by

$$\overline{S^{AB2}_{\mu\nu}} = \frac{1}{N_{t_\mu}N_{t_\nu}} \sum_{r\in t_\mu} \sum_{s\in t_\nu} (S^{AB}_{rs})^2, \qquad (7)$$

where t_μ and t_ν are the types of the μ and ν atomic orbitals (s-, p- or d-AO) centered on the A and B atoms respectively, N_{t_μ} and N_{t_ν} are the amount of AOs of the type t_μ and t_ν. Substituting Eq. (7) into Eq. (5) the latter can be written as

$$^{\lambda}H^A_{\mu\mu} = H^A_{\mu\mu} + \sum_{B\neq A} \delta_{AB} \sum_{\sigma\in B} \beta_{\mu\sigma}\overline{S^{AB2}_{\mu\sigma}}. \qquad (8)$$

As mentioned in the introduction a considerable part of the metal complexes binding energy may originate from the interaction between diffuse metal valence orbitals (s- and p-type AO's) and localized ligand orbitals. So, modified expression [2] for the resonance parameter $\beta_{\mu\nu}$ entering in Eqs. (6) and (8) is used

$$\beta_{\mu\nu} = \beta_{AB}\left(2 - \frac{(I_\mu - I_\nu)^2}{(I_\mu + I_\nu)^2}\right)\frac{I_\mu I_\nu}{I_\mu + I_\nu}; \qquad \beta_{AB} = \tfrac{1}{2}(\beta_A + \beta_B), \qquad (9)$$

where I_μ is the ionization potential of the AO μ, β_A and β_B are the empirical parameters depending on the nature of the A and B atoms. This expression is an orthogonal basis analog of the so-called "weighted" formula for the off-diagonal matrix elements over the non-orthogonal basis set [17] used in extended Hückel calculations. Provided that the ionization potential I_ν is much less than another one Eq. (9) leads to

$$^{\lambda}H_{\mu\nu} \simeq I_\nu S_{\mu\nu}; \qquad I_\nu \ll I_\mu,$$

i.e. the interaction vanishes when I_ν tends to zero. If the ionization potentials are approximately equal, Eq. (9) gives the same result as that given by the conventional formula [8]

$$\beta_{\mu\nu} = \beta_{AB}(I_\mu + I_\nu)/2.$$

Using expressions (8) and (9) for the core-Hamiltonian matrix elements, the

CNDO Fockian elements are given by

$$F_{\mu\mu}^{A} = U_{\mu\mu}^{A} + \sum_{B \neq A} \delta_{AB} \sum_{\sigma \in B} \beta_{\mu\sigma} \overline{S_{\mu\sigma}^{AB2}} - \sum_{B \neq A} \sum_{\lambda \in B} (n_{\lambda} - P_{\lambda\lambda}) \gamma_{\mu\lambda}^{AB}$$

$$+ \sum_{\rho \in A} (1 - \tfrac{1}{2}\delta_{\mu\rho}) P_{\rho\rho} \gamma_{\mu\rho}^{AA} \qquad (10)$$

$$F_{\mu\sigma}^{AA} = -\tfrac{1}{2} P_{\mu\sigma} \gamma_{\mu\sigma}^{AA}$$

$$F_{\mu\nu}^{AB} = -\beta_{\mu\nu}^{AB} S_{\mu\nu}^{AB} - \tfrac{1}{2} P_{\mu\nu} \gamma_{\mu\nu}^{AB},$$

where n_{λ} represent fixed occupation numbers of the neutral atom, $U_{\mu\mu}$ is the one-center one-electron energy, $\gamma_{\mu\nu}^{AB}$ and $\gamma_{\mu\nu}^{AA}$ are the Coulomb repulsion integrals, $P_{\mu\nu}$ represent the density matrix elements, $\delta_{\mu\rho}$ is the Kronecker delta.

This expressions represent the core of the computational scheme presented that, in general, is similar to SINDO1 proposed in [1]. But our procedure is worked out to describe structural and energetic properties of transition metal complexes. Consequently, their main features are the utilization of Eq. (9) for $\beta_{\mu\nu}$, allowing for the interaction between diffuse and localized atomic orbitals, being of value for chemical bonding in metal compounds, and application of the one-center empirical parameters. Insertion of the empirical parameter δ into the orthogonality correction term entering in Eq. (8) is another important feature of CNDO-S^2.

In line with the other semiempirical treatments available for prediction of the molecular energetic and structural features [8] the well-known formulae for the bicentric Coulomb repulsion integrals $\gamma_{\mu\nu}^{AB}$ and the core-core repulsion potential V_N^{AB} are used

$$\gamma_{\mu\nu}^{AB} = (R_{AB}^2 + \tfrac{1}{4}(1/\gamma_{\mu\mu} + 1/\gamma_{\nu\nu})^2)^{-1/2} \qquad (11)$$

$$V_N^{AB} = \gamma_{\mu\nu}^{AB} + (1/R_{AB} - \gamma_{\mu\nu}^{AB}) \exp(-\alpha_{AB} R_{AB}); \qquad \alpha_{AB} = (\alpha_A + \alpha_B)/2, \qquad (12)$$

where α_A and α_B are the empirical parameters.

We shall next discuss the choice of the empirical parameters α_A, β_A and δ_A entering in Eqs. (12), (9) and (8). Different values of the parameters β_A^x and δ_A^x ($x = sp, d$) for different shells (sp- or d-shell) are used for the transition metal atoms.

The parametrization procedure is based on the fitting of calculated energetic and structural properties to observed ones for a chosen "basis set" of molecules. This is done by minimizing the sum of the squares of the weighted errors in the calculated heats of formation and geometry. To reduce the computational efforts, the calculations are carried out at the experimental geometries and the gradients of the energy with respect to the geometrical variables are taken as reference functions. A non-linear least-squares minimization procedure proposed by Powell [9] is used to fit the empirical parameters. Table 1 contains the standard molecules, the optimized values of the CNDO-S^2 parameters for elements H, C, N, O and Ni are listed in Table 2.

Table 1. Standard molecules used for parametrization

Atom	Standard molecules
H and C	H_2, CH_4, C_2H_6, C_2H_4, C_2H_2, $H_2C{=}C{=}CH_2$, $C(CH_3)_4$, △, ⬡
N	N_2, NH_3, CH_3NH_2, C_5H_5N, N_2H_4, HNO_2
O	H_2O, H_2O_2, H_2CO, O_3, CO, $HCOOH$, H_3COCH_3
Ni	Ni_2, NiH, $NiCH_2$

The values of the atomic integrals $U_{\mu\mu}^A$ and $\gamma_{\mu\nu}^{AA}$ entering in the CNDO Fockian (10) are taken from Oleari [10], with the Coulomb repulsion integrals being averaged by

$$\gamma_{\mu\nu}^{AA} = \frac{1}{N_{t_\mu} N_{t_\nu}} \sum_{r \in t_\mu} \sum_{s \in t_\nu} g_{rs}$$

where t_μ, t_ν, N_{t_μ}, N_{t_ν} are the same numbers as those entering in Eq. (7), g_{rs} are the Oleari' two-electron integrals. The orbital exponents for s- and p-orbitals of the H, C, N, O atoms are taken from [11] and those for s-, p- and d-AOs of the nickel are taken from [12]. The atomic integrals and the orbital exponents used in the calculations are listed in Table 2.

The parametrization described was used for the energy and geometry calculations for a number of organic compounds and some nickel complexes. Restricted Hartree–Fock (RHF) and spin-polarized unrestricted Hartree–Fock (UHF) calculations were carried out for both closed-shell and open-shell systems (the half-electron approximation being used for RHF open-shell calculations). The

Table 2. Atomic integrals (eV), orbital exponents (au) and binding parameters

Atom	H	C	N	O	Ni
$-U_{ss}$	13.595	52.140	71.860	97.830	96.920
$-U_{pp}$	—	40.880	58.500	78.120	78.430
$-U_{dd}$	—	—	—	—	141.570
γ_{ss}	12.848	12.230	13.590	15.420	7.960
γ_{sp}	—	10.260	11.090	12.510	6.680
γ_{pp}	—	10.050	11.820	12.810	6.400
γ_{sd}	—	—	—	—	9.970
γ_{pd}	—	—	—	—	8.390
γ_{dd}	—	—	—	—	15.410
ξ_s	1.0000	1.6083	1.9237	2.2458	1.4730
ξ_p	—	1.5679	1.9170	2.2266	1.4730
ξ_d	—	—	—	—	2.960
α_A (Å^{-1})	2.320976	1.879058	2.800834	3.723636	1.684967
β_A^{sp}	0.361913	0.756121	0.987516	1.316619	0.749434
δ_A^{sp}	0.072920	0.074500	0.334904	0.452094	0.083218
β_A^d	—	—	—	—	1.693896
δ_A^d	—	—	—	—	0.374344

molecular geometries were optimized by Davidon–Fletcher–Powell method [13] with numerically formed gradients. The ionization potentials were calculated by Koopmans' theorem.

3. Results and discussion

The CNDO-S^2 parametrization has been worked out to calculate the electronic structure and the potential energy surfaces of the organometallic systems, including the catalytic ones. Taking this into account, the parametrization for H, C, N and O atoms was first tested in the calculations of a number of organic compounds: hydrocarbons and compounds with N and O heteroatoms. Table 3 contains the heats of formation, ionization potentials dipole moments and equilibrium geometries for 53 organic molecules selected. The average absolute errors for these quantities are 6.6 kcal/mol, 0.85 eV, 0.53 Debye, 0.023 Å and 4.7 deg. respectively, that is comparable with the widely used methods MINDO/3 and MNDO [8]. Thus, an approximate account of orthogonality in core-Hamiltonian elements in combination with the CNDO pattern allows to obtain the same accuracy as that obtained by more sophisticated semiempirical methods, with the number of the empirical parameters used in CNDO-S^2 being much less than in aforementioned methods. It is interesting to point out, that the optimized values of the δ parameters entering in Eq. (8) increase in the sequence $\delta_C < \delta_N < \delta_O$ that correlates with the increase of the Fermi exchange repulsion between filled orbitals as the number of such AOs increases in the sequence C, N, O. For molecules containing unshared electron pairs CNDO-S^2 provides the results as accurate as those for molecules without lone electron pairs.

The results listed in Table 3 suggest that CNDO-S^2 overestimates ($\sim$10–15 kcal/mol) the stability of compounds containing triple bonds and that it tends to underestimate the strain energies of small rings. Such deficiencies, already having been found in MINDO/3 calculations [8], seem to be due to the overestimation of $s\sigma$-$s\sigma$ resonance interaction relative to $s\sigma$-$p\sigma$ and $p\sigma$-$p\sigma$ interactions [14]. The gross underestimation ($\sim$25 kcal/mol) of CO and N$_2$ molecular binding energies is, in our opinion, due to the fact that triple C$\equiv$O and N$\equiv$N bonds are not typical for compounds of these elements and the CNDO-S^2 parametrization is less accurate when applied to such systems.

When worked out the parametrization for nickel attention was paid to the nickel organometallics containing single Ni–C and double Ni=C bonds. Since no experimental data on the energy and structure of such compounds were available for us, the data of the GVB calculations were predominantly used to find the nickel parameters. Ni$_2$ [15], NiCH$_2$ [16] and NiH [17] were chosen as the standard molecules used in the parametrization (the experimental data on geometry and energy being used only for NiH [17]). In Table 4 results of the CNDO-S^2 calculations of binding energy and geometry for the standard molecules and NiCH$_3$, Ni(CH$_3$)$_2$, NiCO are compared with the available data. Mean absolute errors in the binding energies and equilibrium bond lengths are 9.3 kcal/mol and 0.096 Å respectively. For NiCH$_2$ the results of the RHF and spin-polarized UHF

Table 3. Heats of formation, ionization potentials, dipole moments and geometry of organic molecules: hydrocarbons and molecules with N and O heteroatoms[a]

| Molecule	ΔH_f, kcal/mol		I.P., eV		μ, Debye		Geometry, Å, deg
	CNDO-S²	exp	CNDO-S²	exp	CNDO-S²	exp	Experimental geometry in parenthesis
H_2	3.1	0.0	15.94	15.98	—	—	HH, 0.760 (0.742)
CH_4	−13.4	−17.9	13.47	14.00	—	—	CH, 1.102 (1.094)
C_2H_6	−22.7	−20.2	11.85	12.10	—	—	CH, 1.110 (1.091); CC, 1.488 (1.536); CCH, 112.3 (110.9)
C_2H_4	16.3	12.5	11.51	10.51	—	—	CH, 1.101 (1.086); CC, 1.301 (1.339); CCH, 124.7 (121.2)
C_2H_2	48.1	54.3	12.06	11.40	—	—	CH, 1.075 (1.060); CC, 1.177 (1.203)
C_3H_8	−29.5	−24.8	11.54	11.50	0.04	0.08	C¹H, 1.111 (1.094); C²H, 1.116 (1.096); CC, 1.505 (1.526); CCC, 115.5 (112.4)
C_3H_6	4.4	4.9	10.94	9.88	0.29	0.37	C¹C², 1.314 (1.336); C²C³, 1.479 (1.500); CCC, 130.3 (124.3)
C_3H_4	29.7	44.4	11.16	10.37	0.23	0.78	C¹C², 1.186 (1.206); C²C³, 1.441 (1.459)
$H_2C=C=CH_2$	38.3	45.6	10.70	10.07	—	—	CH, 1.098 (1.087); CC, 1.293 (1.308); CCH, 123.5 (120.9)
[isobutane structure]	−30.7	−32.4	11.08	11.40	0.09	0.13	CC, 1.526 (1.525); CCC, 113.6 (111.2)
[isobutylene structure]	−4.6	−4.3	10.66	9.17	0.40	—	C¹C², 1.327 (1.330); C²C³, 1.499 (1.507); C¹C²C³, 122.3 (122.4)
[butadiene structure]	32.2	26.0	10.48	9.08	—	—	C¹C², 1.315 (1.341); C²C³, 1.471 (1.463)
[butadiene structure]	32.6	28.0	10.50		0.05	—	C¹C², 1.316; C²C³, 1.471
$C(CH_3)_4$	−31.3	−40.3	11.20	11.30	—	—	CH, 1.112 (1.098); CC, 1.544 (1.570); CCH, 113.0 (112.7)
[cyclopropane structure]	−4.5	12.7	11.24	11.00	—	—	CH, 1.103 (1.089); CC, 1.493 (1.510); HCH, 117.6 (115.1)

Table 3 (continued)

Molecule	ΔH_f, kcal/mol		I.P., eV		μ, Debye		Geometry, Å, deg
	CNDO-S²	exp	CNDO-S²	exp	CNDO-S²	exp	Experimental geometry in parenthesis
(cyclopentane ring)	−33.4	−18.4	11.22	11.59	—	—	CH, 1.113 (1.114); CC, 1.530 (1.546); HCH, 103.8
(cyclohexane ring)	−43.5	−29.5	10.68	9.81	—	—	CC, 1.523 (1.536); CH, 1.117 (1.121); HCH, 103.9 (107.5); CCC, 114.3 (111.4); CCCC, 50.9 (54.9)
(cyclobutene ring)	28.1	37.5	10.45	9.43	0.01	0.13	C^1C^2, 1.331 (1.342); C^2C^3, 1.510 (1.517); C^3C^4, 1.547 (1.566); C^1H, 1.099 (1.083); C^3H, 1.110 (1.094)
(cyclopentadiene ring)	34.5	31.9	10.18	8.57	0.37	0.42	C^1C^2, 1.343 (1.342); C^2C^3, 1.511 (1.509); C^1C^5, 1.483 (1.469)
(benzene ring)	31.4	19.8	10.67	9.25	—	—	CH, 1.105 (1.084); CC, 1.397 (1.397)
(toluene ring)	21.4	12.0	10.30	8.82	0.17	0.36	C^1C^2, 1.412; C^2C^3, 1.394; C^3C^4, 1.395; C^1C^7, 1.496 (1.510)
N_2	24.1	0.0	12.78	15.60	—	—	NN, 1.098 (1.094)
NH_3	−2.8	−11.0	11.50	10.85	1.00	1.47	NH, 1.052 (1.012); HNH, 107.0 (106.7)
N_2H_4	22.4	22.8	10.51		1.02	1.90	NN, 1.474 (1.449); NH, 1.060 (1.022); HNN, 112.8 (112.0); HNNH, 86.3 (90.0)
CH_3NH_2	−5.8	−5.5	10.72	9.45	1.08	1.31	CN, 1.442 (1.474); NH, 1.053 (1.011); HNC, 111.5 (112.0); HNH, 107.4 (105.9)
$(CH_3)_2NH$	−6.8	−4.4	10.41	8.93	0.80	1.03	CN, 1.446 (1.462); NH, 1.054 (1.019); CNC, 119.4 (112.2); HNC, 110.5 (108.9)
$n\text{-}C_3H_7NH_2$	−19.5	−16.8	10.56		1.18		CN, 1.475; NH, 1.054; CNH, 110.7
$i\text{-}C_3H_7NH_2$	−18.9	−20.0	10.68		0.90		CN, 1.492; NH, 1.056; CC, 1.526; CNH, 110.5
$t\text{-}C_4H_9NH_2$	−18.9	−28.9	10.59		0.89		CN, 1.504; NH, 1.056; CC, 1.548; CNC, 109.8
CH_3CH_2CN	−1.1	12.1	11.64		1.97		C^1N, 1.133; C^1C^2, 1.453; C^2C^3, 1.508

Table 3 (continued)
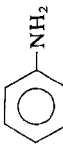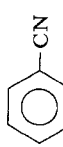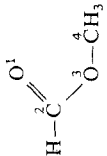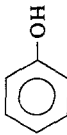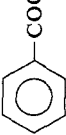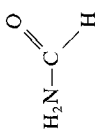
Molecule	ΔH_f, kcal/mol		I.P., eV		μ, Debye		Geometry, Å, deg
	$CNDO\text{-}S^2$	exp	$CNDO\text{-}S^2$	exp	$CNDO\text{-}S^2$	exp	Experimental geometry in parenthesis
CH_3NC	41.8	35.6	11.69		1.51	3.85	C^1N, 1.399 (1.424); C^3N, 1.150 (1.166); HC^1, 1.117 (1.101); NC^1H, 114.3 (109.1)
C_5H_5N	39.5	34.6	10.27	9.67	0.73	2.22	C^2N, 1.346 (1.338); C^2C^3, 1.401 (1.394); C^3C^4, 1.416 (1.392)
$C_6H_5NH_2$ (aniline)	34.2	20.8	9.43		1.81	1.53	CN, 1.396 (1.341); CC (avrg.), 1.404 (1.392)
C_6H_5CN (benzonitrile)	49.6	51.5	10.61		2.16		CN, 1.133; CC (avrg.), 1.401
$O_2(^1\Delta)$	18.1	22.0	11.24		—	—	OO, 1.250 (1.216)
O_3	29.6	34.2	11.53	12.75	1.68	0.53	OO, 1.289 (1.278); OOO, 123.9 (116.8)
CO	−0.5	−26.4	12.22	14.01	0.76	0.11	CO, 1.105 (1.128)
H_2O	−49.7	−57.8	12.54	12.62	2.61	1.82	OH, 0.986 (0.957); HOH, 111.2 (104.5)
H_2O_2	−44.3	−32.5	11.36		0.00		OH, 0.997 (0.950); OO, 1.476 (1.475); OOH, 106.8 (94.8); $HOOH$, 180.0 (119.8)
CH_3OCH_3	−44.4	−44.0	11.06	10.04	1.23	1.30	CO, 1.368 (1.410); COC, 123.8 (111.7)
$n\text{-}C_3H_7OH$	−63.0	−61.2	11.06		1.28		CO, 1.402; OH, 0.989; C^1C^2, 1.530; C^2C^3, 1.509
$i\text{-}C_3H_7OH$	−61.3	−65.1	10.92		1.25		CO, 1.425; OH, 0.991; CC, 1.530; CCC, 109.6
$t\text{-}C_4H_9OH$	−62.9	−74.7	10.85		1.17		CO, 1.437; OH, 0.991; CC, 1.548; CCC, 109.3
H_2CO	−30.1	−26.0	10.97	10.88	1.75	2.33	CO, 1.153 (1.208); CH, 1.125 (1.116); HCH, 101.0 (116.5)
CH_3CH_2CHO	−47.6	−45.5	10.47		1.67	1.41	C^1O^1, 1.171; C^1H, 1.339; C^1C^2, 1.509; C^2C^3, 1.508
$HCOOH$	−92.5	−90.6	11.10	11.51	2.45		CO^1, 1.174 (1.202); CO^2, 1.316 (1.343); O^2H, 0.989 (0.972); O^1CO^2, 131.3 (124.9)
CH_3COOH	−102.9	−103.3	10.88		1.67	1.74	CC, 1.528 (1.520); CO^1, 1.193 (1.214); CO^2, 1.340 (1.364); OH, 0.991 (0.970)
$\overset{O^1}{\underset{}{H{-}\overset{2}{C}}}{-}\overset{3}{O}{-}\overset{4}{C}H_3$ (methyl formate)	−87.3	−83.6	11.23	11.02	1.68	1.77	O^1C^2, 1.170 (1.200); O^3C^2, 1.322 (1.334); O^3C^4, 1.397 (1.437); $O^1C^2O^3$, 131.9 (125.9); $C^2O^3C^4$, 125.7 (114.8)

Table 3 (continued)

Molecule	ΔH_f, kcal/mol		I.P., eV		μ, Debye		Geometry, Å, deg
	CNDO-S²	exp	CNDO-S²	exp	CNDO-S²	exp	Experimental geometry in parenthesis
⬡—OH	−12.0	−23.0	9.93		1.30	1.45	C¹O, 1.357; OH, 0.990; CC (avrg.), 1.403
⬡—COOH	−59.0	−70.1	10.16		1.63		C⁷O¹, 1.190; C⁷O², 1.336; OH, 0.989; C¹C⁷, 1.542; CC (avrg.), 1.402
N₂O₄	−9.8	2.5	11.54		—	—	NN, 1.558 (1.750); NO, 1.231 (1.180); ONO, 132.2 (133.7)
HNO₂	−15.0	−18.8	10.36		2.85	1.86	NO¹, 1.215 (1.163); NO², 1.417 (1.433); OH, 0.993 (0.954); O¹NO², 119.4 (110.7)
H₂N—C(=O)—H	−40.7	−44.5	10.61		2.84	3.25	CN, 1.385 (1.376); CO, 1.176 (1.193); CH, 1.155 (1.102); NH, 1.049 (1.014)

ᵃ All experimental data were taken from [8]

Table 4. Binding energies and geometry of nickel complexes

Molecule	State	B.E., kcal/mol		Geometry, Å, deg Experimental geometry in parenthesis
		CNDO-S^2	exp	
Ni$_2$	$^3\Sigma_g^+$	71	67[a]	NiNi, 2.252(2.030)
NiH	$^2\Sigma$	88	71[b]	NiH, 1.419 (1.475)
NiCH$_2$	$^1A_1$	49	65[c]	NiC, 1.633 (1.780); CH, 1.099 NiCH, 123.2 (123.5)
NiCH$_2$	SDW	68	65[c]	NiC, 1.801 (1.780); CH, 1.095 NiCH, 122.5 (123.5)
NiCH$_3$	$^2A_1$	54	60[c]	NiC, 1.870 (1.870); CH, 1.105 NiCH, 107.2 (109.4)
Ni(CH$_3$)$_2$	$^1A_1$	54	40[d]	NiC, 1.812 (2.080); CH, 1.110 CNiC, 120.5 (94.3); HCH, 111.5
NiCO	$^1\Sigma$	15	26.5[e]	NiC, 1.906 (1.900); CO, 1.101 (1.115)

[a] Energy and geometry were taken from [15]
[b] Those were taken from [17]
[c] From [16]
[d] From [18]
[e] From [20]

calculations are listed in Table 4. The UHF spin polarized solution is in much better agreement with the results of GVB CI calculations [16] than the RHF one due to the simulation of the antiferromagnetic type correlation between the Ni=C π-bond electrons. Thus the parametrization developed allows to reproduce with reasonable accuracy the results of the elaborate *ab initio* calculations.

Calculations of the concerted elimination of ethane from dimethyl-nickel have been performed to test efficiency of the scheme presented in the chemical reactions surfaces studies. This reaction has been studied at the *ab initio* level with the correlation effects included through the contracted CI method [18]. The formation and disruption of M–C and C–C bonds are of value in many catalytic processes involving transition metals. While calculating the transition state [19] of the Ni(CH$_3$)$_2 \rightarrow$ Ni(^{1}D) + C$_2$H$_6$ reaction the saddle point were determined by varying the same geometric parameters as in [18], i.e. the Ni–C bondlengths, the Me–Ni–Me bond angle and the rocking angle α (see Fig. 1). The geometries of the CH$_3$ groups were kept fixed in the saddle point determination with the C–H
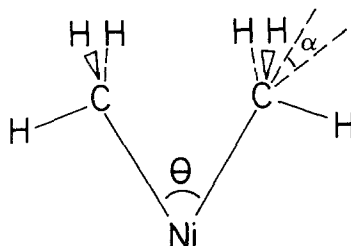
Fig. 1. Geometric parameters definitions for transition state of the reaction Ni(CH$_3$)$_2$(^{1}A$_1$) $\rightarrow$ Ni(^{1}D) + C$_2$H$_6$

Table 5. Transition state of the reaction $Ni(CH_3)_2(^1A_1) \rightarrow Ni(^1D) + C_2H_6$

	R(Ni–C), Å	R(C–C), Å	θ, deg	α, deg
ab initio[a]	2.132	2.068	58	35
CNDO–S^2	1.867	1.818	58.3	49.1

[a] From [18]

bondlengths and the H–C–H angles being the same as in the local minimum (see Table 4). The so-obtained barrier of the elimination reaction is 37 kcal/mol, being just the same as the *ab initio* value [18]. The transition state geometry obtained by CNDO–S^2 is in rather satisfactory agreement with the *ab initio* one and is listed in Table 5.

The results of our calculations performed for the organic molecules, nickel complexes and reaction $Ni(CH_3)_2 \rightarrow Ni(^1D) + C_2H_6$ shows that CNDO–S^2 procedure describes satisfactorily energetic and structural features of nickelorganic compounds. Being simple enough, the new semiempirical procedure could easily be extended on the other transition metals and would be useful in the studies of the organometallic reactions.

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