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"Universal" CNDO/2 Method (CNDO/2-U)

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The Pople–Santry–Segal CNDO/2 method and the modified CNDO/2 version worked out recently by Clack for transition-metal complexes have been extended to the full periodic table.

Key words: Extended CNDO/2 method – Full periodic table – "Fictitious atoms" – Compact formalism.

1. Introduction

The CNDO/2 method proposed in 1965 and 1966 by Pople, Santry and Segal [1–5] marked the beginning of the development and the application in molecular physics and theoretical chemistry of semi-empirical methods taking into account all valence electrons. This method is strongly advised when we are interested in the variation of a physico-chemical property along a series of molecules; it also allows quantitative prediction, for a number of physico-chemical properties, provided that the parameters used are correctly chosen.

The parametrization of Pople et al. is only extended over the atoms of the three first periods of Mendeleiev's periodic table. Various authors [6–22] tried to improve and extend Pople's parametrization. The following significant point arises from our bibliographical study: there is no parametrization of the kind CNDO-INDO extended to the whole periodic table. The Pople–Santry–Segal CNDO/2 method and the modified CNDO/2 version worked out recently by Clack [12–16] for transition-metal complexes have been extended to the full periodic table. Our research is based on the following idea: if we consider a molecule *MX* and if *X* goes through the periodic table when *M* remains fixed the physico-chemical properties of MX tend to vary in close relation with the variation of the X atomic properties.

2. Formalism and Parametrization of the Method

1. Notion of Fictitious Atoms

In many electrons problems, the Hamiltonian can usually be written in the form:

$$H(1, 2, \ldots, n) = \sum_{\mu=1}^{n} h(\mu) + \sum_{\mu>\nu}^{n} \frac{e^2}{r_{\mu\nu}} \tag{1a}$$

where n is the number of electrons in the system and $h(\mu)$ is the hamiltonian operator for the μth electron moving in the field of the nuclei alone, it is given by:

$$h(\mu) = -\frac{\hbar^2}{2m}\Delta(\mu) - \sum_{s=1}^{N} V_s(\mu) \tag{1b}$$

N is the number of atoms and $V_s(\mu)$ is the potential due to the nucleus S.

The Hartree–Fock–Roothaan (HFR) equations [2, 3] are:

$$F \cdot C_k = e_k \cdot S \cdot C_k \tag{2a}$$

with

$$F_{rs} = h_{rs} + \sum_t \sum_u p_{tu}(\langle\Phi_r^*\Phi_s|\Phi_t\Phi_u^*\rangle - \tfrac{1}{2} \cdot \langle\Phi_r^*\Phi_t|\Phi_s\Phi_u^*\rangle) \tag{2b}$$

The neglect of differential overlap (NDO) approximation introduced by R. G. Parr [24] can be expressed by:

$$\Phi_r^*(\mu)\Phi_s(\mu)\, d\tau_\mu = \delta_{rs}\Phi_r^*(\mu)\Phi_s(\mu)\, d\tau_\mu \tag{3}$$

After using NDO approximation, Eqs. (2) become:

$$F \cdot C_k = e_k \cdot C_k \tag{4a}$$

$$F_{rr} = h_{rr} - \tfrac{1}{2} \cdot p_{rr} \cdot \gamma_{rr} + \sum_{t \neq r} p_{tt} \cdot \gamma_{rt} \tag{4b}$$

$$F_{rs} = h_{rs} - \tfrac{1}{2} \cdot p_{sr} \cdot \gamma_{rs} \tag{4c}$$

where

$$\gamma_{rs} = \langle\Phi_r^*(\mu) \cdot \Phi_r(\mu)|\Phi_s^*(\nu) \cdot \Phi_s(\nu)\rangle. \tag{4d}$$

Eqs. (4) are not invariant with respect to an arbitrary rotation of the local set of coordinate axes, this is due to the NDO approximation. For this reason, Pople [1, 2] introduced in the CNDO/2 method the following approximations:

$$\text{for every AO } \Phi_r \text{ of } R \text{ atom, } \gamma_{r(R)r(R)} = \gamma_{RR} \tag{5a}$$

$$\text{for every AO } \Phi_r \text{ of } R \text{ atom and every AO } \Phi_s \text{ of } S \text{ atom, } \gamma_{r(R)s(S)} = \gamma_{RS}. \tag{5b}$$

The CNDO/2 method proposed by Pople et al. is only extended over the atoms of the three first periods.

The latter approximations are no longer justified for a transitional element T which is characterised by the presence of subshells of different quantum numbers $(n-1)d$ and $ns\,np\,nd$. For this reason, we have distinguished level $(n-1)d$ electrons from level n electrons. If $T_{(n-1)}$ and T_n stand for levels $(n-1)d$ and n respectively, we shall have three Coulomb repulsion integrals in this case:

$$\gamma_{T_{(n-1)}T_{(n-1)}}; \qquad \gamma_{T_{(n-1)}T_n} \quad \text{and} \quad \gamma_{T_nT_n}.$$

On the other hand, the potential created by a transitional element:

$$V_T(\mu) = Z_T \cdot \frac{e^2}{r_T(\mu)} \tag{6a}$$

where Z_T is the number of valence electrons of a T atom (transitional element), can be decomposed in two parts $V_{T_{(n-1)}}$ and V_{T_n} because:

$$Z_T = Z_{T_{(n-1)}} + Z_{T_n} \tag{6b}$$

then,

$$V_T(\mu) = V_{T_{(n-1)}}(\mu) + V_{T_n}(\mu). \tag{6c}$$

If Φ_r represents an AO of an atom R belonging to the "$s-p$ block" one obtains from Eq. (6c):

$$\langle\Phi_r^*|V_T|\Phi_r\rangle = \langle\Phi_r^*|V_{T_{(n-1)}}|\Phi_r\rangle + \langle\Phi_r^*|V_{T_n}|\Phi_r\rangle. \tag{7a}$$

The approximation procedure of Pople and Segal [2] to calculate this type of integrals can be extended for the transitional elements:

$$\langle\Phi_r^*|V_{T_{(n-1)}}|\Phi_r\rangle = Z_{T_{(n-1)}} \cdot \gamma_{RT_{(n-1)}} \tag{7b}$$

and

$$\langle\Phi_r^*|V_{T_n}|\Phi_r\rangle = Z_{T_n} \cdot \gamma_{RT_n}. \tag{7c}$$

In our model, integrals of the type $\langle\Phi_r^*|V_S|\Phi_r\rangle$ can have six different forms. The reason is that S can be an element of the "$s-p$ block" or a transitional element; whereas Φ_r can be either an AO of an element of the "$s-p$ block" or an AO of levels T_n or $T_{(n-1)}$.

First of all we have reformulated [25] the CNDO/2 equations with the above formalism. This formalism which consists of introducing transitional elements affects the forms of the CNDO/2 equations, therefore an important modification of the computational program is needed. Indeed, using our formalism we have obtained three possible forms for F_{rr} and ten for F_{rs}. Our equations differ from those of Pople in that they contain additional terms of interaction between $(n-1)d$ electrons and $(ns\,np\,nd)$ electrons.

As an example to illustrate this point, if we consider an AO Φ_r of an atom R belonging to "$s-p$ block", the corresponding F_{rr} is:

$$F_{rr} = F_{rr}^1 + F_{rr}^2 \tag{8a}$$

$$F^1_{rr} = \chi_{rr} + ((Q_R - Z_R) - \tfrac{1}{2}(p_{rr} - 1)) \cdot \gamma_{RR} + \sum_{S \neq R} (Q_S - Z_S) \cdot \gamma_{RS} \tag{8b}$$

$$F^2_{rr} = \sum_{T_n} (Q_{T_n} - Z_{T_n}) \cdot \gamma_{RT_n} + \sum_{T_{(n-1)}} (Q_{T_{(n-1)}} - Z_{T_{(n-1)}}) \cdot \gamma_{RT_{(n-1)}}. \tag{8c}$$

F^1_{rr} is the well known term in the method of Pople, F^2_{rr} is due to the introduction of transitional elements. On the other hand, if we consider two AOs Φ_r and Φ_s belonging to T_n and $T_{(n-1)}$ respectively, the corresponding F_{rs} would be:

$$F_{rs} = -\tfrac{1}{2} \cdot p_{sr} \cdot \gamma_{T_n T_{(n-1)}} \tag{8d}$$

$\gamma_{T_n T_{(n-1)}}$ expresses the interaction between $(n-1)d$ electrons and $(ns\, np\, nd)$ electrons of the same transitional element T.

Then, in order to avoid this important modification of the program, a careful examination of the reformulated CNDO/2 equations shows that we can maintain, even for the transitional elements, the CNDO/2 equations of Pople provided that we consider a transitional atom T as a superposition of two fictitious atoms $T_{(n-1)}$ and T_n with the same space coordinates. $T_{(n-1)}$ and T_n will provide the basis with $(n-1)d$ AOs and $(ns\, np\, nd)$ AOs respectively.

One can point out that the energy of repulsion between cores is simply:

$$\frac{Z_R Z_T}{d_{RT}} \cdot e^2 = \left(\frac{Z_R Z_{T_{(n-1)}}}{d_{RT}} + \frac{Z_R Z_{T_n}}{d_{RT}} \right) \cdot e^2 \tag{9a}$$

The total energy of repulsion between cores will be expressed by:

$$E_N = \sum_{\substack{R \neq S \\ d_{RS} \neq 0}} \frac{Z_R Z_S}{d_{RS}} \cdot e^2. \tag{9b}$$

In the previous equation, $d_{RS} \neq 0$ expresses the fact that we must not take into account the energy of repulsion between two cores with the same coordinates, for example T_{n-1} and T_n.

This formalism can be extended to the Lanthanides, we shall have three fictitious atoms, $T_{(n-2)}$, $T_{(n-1)}$ and T_n for $(n-2)f$, $(n-1)d$ and $ns\, np$ AOs respectively.

2.2. Choice of the Base

We have used a basis formed by a set of real Slater type atomic orbitals (STO) defined [26–29] by the usual form:

$$\Phi_{n^*,l,m}(r, \theta, \phi) = R_{n^*}(r) \cdot \Theta_{l,m}(\theta) \cdot \Phi_m(\phi). \tag{10}$$

These AOs are expressed, for the fourth and sixth periods [30], with the aid of fractional effective quantum numbers n^*:

n^* is equal to 3.7 and 4.2 for the 4th and 6th periods respectively. If we use a_0, the Bohr radius, as the unit of length, the radial function will have the following form:

$$R_n(r) = N_n \cdot r^{n^*-1} \cdot e^{-\xi r} \tag{11a}$$

where n is the number of the period, N_n the normalization constant and ξ the orbital exponent.

For the fourth period: $R_4(r) = N_4 \cdot r^{2.7} \cdot e^{-\xi r}$. (11b)

Unfortunately the presence of fractional quantum numbers introduces an additional difficulty: one must use gamma function $\Gamma(z)$, which is a numerical function, to compute overlap and Coulomb integrals; this difficulty is not insurmountable but we have preferred to extend the procedure of interpolation proposed by J. M. Sichel and M. A. Whitehead [6] for the radial functions of the fourth and sixth periods. According to this interpolation procedure, $R_4(r)$ and $R_6(r)$ are given by:

$$\bar{R}_4(r) = \bar{N}_4 \cdot (0.3r^2 + 0.7r^3) \cdot \exp\left(-\frac{Z^*}{3.7} \cdot r\right) \tag{12a}$$

$$\bar{R}_6(r) = \bar{N}_6 \cdot (0.8r^3 + 0.2r^4) \cdot \exp\left(-\frac{Z^*}{4.2} \cdot r\right) \tag{12b}$$

where Z^* is the effective nuclear charge.

$\bar{N}_4$ and $\bar{N}_6$ normalization constants have been calculated and are given by:

$$\bar{N}_4 = \left(\frac{128.0\xi^9}{6!\,(0.09\xi^2 + 1.47\xi + 6.86)}\right)^{1/2} \tag{13a}$$

$$\bar{N}_6 = \left(\frac{0.01269\xi^{11}}{0.64\xi^2 + 1.44\xi + 0.9}\right)^{1/2}. \tag{13b}$$

The radial functions $\bar{R}_4(r)$, $R_4(r)$, $\bar{R}_6(r)$ and $R_6(r)$ have been plotted [25], these plots show that each interpolated radial function is practically equivalent to its own corresponding non-interpolated one.

Since the radial functions are interpolated for the fourth and sixth periods' atoms, the AOs $\bar{\Phi}_{4r}$ and $\bar{\Phi}_{6r}$ of the fourth and sixth periods' atoms will also be interpolated:

$$\bar{\Phi}_{4r} = 0.3\,\frac{\bar{N}_{4r}}{N_{3r}}\,\Phi_{3r} + 0.7\,\frac{\bar{N}_{4r}}{N_{4r}}\,\Phi_{4r} \tag{14a}$$

$$\bar{\Phi}_{6r} = 0.8\,\frac{\bar{N}_{6r}}{N_{4r}}\,\Phi_{4r} + 0.2\,\frac{\bar{N}_{6r}}{N_{5r}}\,\Phi_{5r} \tag{14b}$$

where Φ_{3r}, Φ_{4r} and Φ_{5r} stand for AOs with integer quantum numbers; N_{3r}, N_{4r} and N_{5r} stand for normalization constants corresponding to these AOs respectively.

In the general case we have:

$$\bar{\Phi}_r = \sum_{k=1}^{2} a_{kr} \cdot \Phi_r \tag{14c}$$

thus, overlap integrals

$$S_{rs} = \langle \bar{\Phi}_r^* / \bar{\Phi}_s \rangle \tag{15a}$$

and Coulomb integrals:

$$\gamma_{RS} = \left\langle \bar{\Phi}_r^2 \middle/ \frac{e^2}{r_{\mu\nu}} \middle/ \bar{\Phi}_s^2 \right\rangle \tag{15b}$$

using AOs pertaining to atoms of the fourth or sixth periods can be expressed as:

$$S_{rs} = \sum_{k=1}^{2} \sum_{l=1}^{2} a_{kr} \cdot a_{ls} \cdot \langle \Phi_{kr}^* / \Phi_{ls} \rangle \tag{16}$$

$$\gamma_{RS} = \sum_{k=1}^{2} \sum_{l=1}^{2} \sum_{p=1}^{2} \sum_{q=1}^{2} a_{kr} \cdot a_{lr} \cdot a_{ps} \cdot a_{qs} \cdot \langle \Phi_{kr} \Phi_{lr} / \Phi_{ps} \Phi_{qs} \rangle . \tag{17}$$

The previous formulas are general. Indeed, if an AO is non-interpolated, one of the coefficients a_{kr} will be equal to zero, the other one will be equal to one.

We have established [31] a general program to compute these integrals.

3.1. *Determination of the Parameters β_R^0 and χ_{rr}*

The parametrization of Pople is only extended over the atoms of the three first periods. For atoms pertaining to the other periods, we have to determine the atomic parameters β_R^0 and Mulliken's electronegativities χ_{rr}.

For every atom $R(ns-np-nd)$ of the "$s-p$ block" we need the atomic parameter β_R^0 and (χ_{ss}, χ_{pp}) if we use a basis $ns-np$ and $(\chi_{ss}, \chi_{pp}, \chi_{dd})$ if nd AOs are taken into account.

For a transitional atom $T((n-1)d-ns-np-nd)$ we have used two atomic parameters $\beta_{T_{(n-1)}}^0$ and $\beta_{T_n}^0$ corresponding to $((n-1)d)$ electrons and $(ns-np-nd)$ electrons respectively. Otherwise, in addition of χ_{ss}, χ_{pp} and χ_{dd} of the $(ns-np-nd)$ AOs, we have evaluated χ_{dd} Mulliken's electronegativity corresponding to the subshell $(n-1)d$.

A careful examination of the numerical values of the parameters proposed by Pople for the three first periods led us to make the following remarks: the β_R^0 parameters vary with a parallel relation to Pauling's electronegativity (χ_R) and decrease when the principal quantum number n_R increase.

It is reasonable to suppose that the above-mentioned variation can be extended to the full periodic table.

The variable $\frac{\chi_R}{1+a.n_R}$ enable us to express, simply, the dependence of β_R^0 on χ_R and n_R. We have expressed β_R^0 by means of a polynomial formula:

$$\beta_R^0 = -\sum_{k=0}^{N} A_k \cdot \left(\frac{\chi_R}{1+a \cdot n_R} \right)^k \tag{18}$$

We have used the χ_R electronegativities proposed by A. L. Allred and E. G. Rochow [32]. The numerical coefficients of Eq. (18) have been determined by parabolic fitting to the β_R^0 values proposed by Pople et al. for the elements of the second and third periods; also, the best agreement was found when k degree is equal to two. The polynomial obtained is:

$$\beta_R^0 = -(3.323 + 6.187X + 1.561X^2) \tag{19}$$

where X stands for $\chi_R/(1+0.15n_R)$.

The values obtained, by means of Eq. (19), for $\beta_{T_{3d}}^0$ of transition elements of the fourth period are systematically underestimated. However,the ratio between $\beta_{T_{3d}}^0$ used by Clack et al. [12] and $\beta_{T_{3d}}^0$ evaluated by means of Eq. (19) remains approximately constant throughout of the fourth period transition elements. The average of this ratio is equal to 1.380; it is therefore possible to reproduce, with a sufficient precision, the $\beta_{T_{3d}}^0$ proposed by Clack using the formula:

$$\beta_{T_{(n-1)d}}^0 = -1.380(3.323 + 6.187Y + 1.561Y^2) \tag{20}$$

where Y stands for $\chi_R/(1+0.15(n-1))$. We have supposed that the previous formula remains available for $\beta_{T_{(n-1)d}}^0$ of the other transition periods.

The β_{4s}^0 can be obtained by:

$$\beta_{T_{4s}}^0 = \rho_T\left(\frac{4s}{3d}\right) \cdot \beta_{T_{3d}}^0 \tag{21a}$$

where:

$$\rho_T\left(\frac{4s}{3d}\right) = \frac{\beta_{T_{4s}}^0(\text{Clack})}{\beta_{T_{3d}}^0(\text{Clack})}. \tag{21b}$$

If we suppose, and that seems reasonable, that ρ_T remains approximately constant throughout the same column of the periodic table's "d-block", we have then obtained a general procedure to evaluate the $\beta_{T_{(n-1)d}}^0$ and $\beta_{T_{ns}}^0$ of all transition elements.

A similar, but more involved procedure has been established for the calculation of χ_{rr} parameters of any element.

For the atoms of the periodic table's "$s-p$ block", the χ_{rr} may be expressed by means of very simple formulas:

$$\chi_{ss} = -4.7307 + 7.5093\chi_R + 0.3423\chi_R^2 \tag{22a}$$

$$\chi_{pp} = 0.39649\chi_{ss} \tag{22b}$$

$$\chi_{dd} = 0.03622\chi_{ss} \tag{22c}$$

where the values 0.39649 and 0.03622 are the average of the ratios obtained from the values used by Pople et al. for the second and third period elements.

Similar formulas are used for χ_{rr} of transitional's elements from Clack's parameters:

for T_n

$$\chi_{ss} = 0.43101(-4.7307 + 7.5093\chi_T + 0.3423\chi_T^2) \tag{23a}$$

and

$$\chi_{pp} = 0.23681\chi_{ss} \tag{23b}$$

Table 1. Bond lengths (R_0 in Å), force constants (k in dynes/cm), atomisation energies (E_A in eV) and ionisation potentials of homo-nuclear diatomic molecules. Results obtained by means of CNDO/2-U

	I		III		IV		V		VI		VII	
	H_2											
R_0	0.75	0.74										
k	10.40	5.70										
E_A	5.37	4.48										
I	20.82	15.43										
	Li_2		B_2		C_2		N_2		O_2		F_2	
R_0	2.18	2.67	1.23	1.59	1.14	1.31	1.14	1.10	1.13	1.21	1.12	1.42
K	0.82	0.25	24.18	3.50	36.46	12.20	49.88	23.00	50.12	11.80	46.86	4.50
E_A	14.71	1.08	27.26	2.99	27.13	6.50	25.35	9.75	17.23	5.11	14.33	1.56
I	14.09	4.96	16.67		17.53	12.00	18.51	15.58	14.86	12.08	19.19	15.70
	Na_2		Al_2		Si_2		P_2		S_2		Cl_2	
R_0	2.83	3.08	1.88		1.87	2.25	1.90	1.89	1.90	1.89	1.89	1.99
K	0.47		6.06		9.65		13.19		15.14		13.97	3.80
E_A	12.65	0.75	16.16		16.64	3.25	16.37	5.03	11.57	3.60	9.86	2.47
I	11.95		11.43		11.05		12.77		10.23	9.60	23.43	11.50
	K_2		Ga_2		Ge_2		As_2		Se_2		Br_2	
R_0	4.41	3.92	1.94		2.03		2.14		2.21	2.15	2.25	2.28
K	0.15		4.72		7.78		9.81		11.44		10.72	2.40
E_A	12.23	0.51	17.69	1.52	18.26	2.82	18.26	3.94	11.85	2.82	8.01	1.97
I			13.03		12.84		12.07		8.76		10.97	10.71
	Rb_2		In_2		Sn_2		Sb_2		Te_s		I_2	
R_0	4.85		2.16		2.34		2.44		2.53	2.59	2.57	2.67
K	0.11		3.89		5.17		6.73		6.22		6.07	1.70
E_A	11.44	0.47	13.10		13.36	1.99	12.66	2.99	7.64	2.30	5.53	1.54
I	9.58		9.98		10.17		9.50		7.41	8.50	9.12	9.65
	Cs_2		Tl_2		Pb_2		Bi_2		Po_2		At_2	
R_0	6.00		2.56		2.71		2.87		2.89		2.97	
K	0.07		2.58		3.36		4.24		3.81		5.79	
E_A	10.87	0.45	12.12		11.36	1.00	10.87	1.70	5.97		3.79	
I	8.65		9.20		8.63		8.08				7.91	

On the right experimental data are given by G. Herzberg (Ref. [33]); Ionisation potentials of S_2 and Te_2 are measured by Photoelectron spectroscopy (Ref. [34]).

for T_{n-1}

$$\chi_{dd} = 1.27044\chi_{ss}. \tag{23c}$$

3. Results and Discussion

Our CNDO/2-U method has been applied to a set of molecules pertaining to verious class. This set includes 52 diatomic molecules, 42 small polyatomic moecules and 10 transition metal complexes. In all we have studied 104 molecular species. In each case the energy has been fully minimised with respect to molecular geometry.

Table 2. Results for some heteronuclear diatomic molecules by means of CNDO/2-U

A

	Bond lengths (Å)		Dissociation energies (eV)		Ionisation potentials (eV)		Dipole moments (D)	
AB	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.
LiH	1.57	1.60	5.86	2.50	13.17	6.50	6.17	5.88
NaH	2.09	1.89	1.75	2.04	9.48		6.83	
KH	3.19	2.24	0.77	1.89	7.46		9.76	
RbH	3.51	2.37	0.22	1.70	6.76		10.92	
FH	1.00	0.92	6.69	5.90	21.12	16.06	1.87	1.83
ClH	1.38	1.27	3.61	4.50	15.26	12.72	1.73	1.08
BrH	1.47	1.41	6.79	3.80	12.98	11.68	1.46	0.82
IH	1.63	1.61	4.72	3.09	10.71	10.41	0.67	0.44

For experimental bond lengths and experimental dissociation energies see Refs. [33, 35, 36, 37] and [38].

Experimental ionisation potentials: for LiH see Ref. [39] and for hydracids see Refs. [34] and [40].

Experimental dipole moments see Refs.: [33, 37, 38, 39, 41] and [42].

B

	Bond lengths		Force const. (mdyn/Å)		Dissociation energies (eV)		Dipole moments (D)		C_A
AB	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.	CNDO
CO	1.22	1.13	42.09	19.02	21.96	11.09	0.56	1.37	+0.09
SiO	1.79	1.51	14.23	9.24	20.05	8.02	0.08	3.10	+0.02
GeO	1.95	1.65	7.78		4.52	6.81		3.28	+0.35
SnO	2.25	1.84	0.66		1.46	5.72	3.83	4.32	+0.36
PbO	2.36	1.92	5.74		−2.13	4.08		4.64	+0.34
CS	1.54	1.53	17.25	8.49	20.29	7.18	0.64	1.96	−0.06
CSe	1.71	1.66	17.50		18.80	4.99			−0.08
SiS	1.97	1.93	9.71		15.30	6.42	0.28	1.73	+0.13

C_A atomic charge of atom A.

Experimental dipole moments: see Ref. [44].

Other experimental data: the same references which for Table 2A.

3.1. Diatomic molecules

Table 1 presents the CNDO/2-U results obtained for all the homonuclear diatomic molecules of the "$s-p$ block" of the periodic table. Under consideration of this table, generally, the theoretical results, obtained with our method, reproduce quite well the experimental variation, according to Z, of the three physicochemical properties k, I and R_0. Atomisation energies E_A are overestimated but the CNDO/2 results are also overestimated for this property.

The Table 2 presents the results obtained for some heteronuclear diatomic molecules and led us to make the following remarks, if one of the molecule's atoms goes through a column of the periodic table, in the direction of increasing Z, bond lengths increase while force constants, atomisation energies and ionization potentials decrease. Let us notice that dipole moments are reproduced quite well, CNDO/2-U is able to give as CNDO/2 reasonable atomic charges.

3.2. Small Polyatomic Molecules

The AX_2 linear molecules results are presented in Table 3 and the AX_3 and AX_4 centrosymmetrical molecules in Table 4. The measured bond lengths progress in the way of the increasing atomic numbers when the X atom goes through a class of the periodic table. This variation is well reproduced by means of CNDO/2-U.

Table 5 presents the results obtained for AX_2 angular molecules and AX_3 pyramidal molecules. For this species of molecules, the energy depends on two independent structural parameters: the bond length AX and the angle XAX.

Table 3. AX_2 linear molecules by means of CNDO/2-U

AX_2	Bond lengths AX(Å) CNDO	Exp.	Atomisation energies (eV) CNDO	Exp.	C_X CNDO
BeF_2	1.66	1.43	10.80	13.16	−0.351
$BeCl_2$	1.70	1.77	30.10	9.66	−0.028
$BeBr_2$	1.91	1.90	32.70	8.26	+0.089
BeI_2	2.02	2.12	28.20	6.60	+0.183
MgF_2	1.44	1.77	0.50	11.22	−0.532
$MgCl_2$	2.40	2.18	15.10	8.86	−0.295
$MgBr_2$	2.46	2.34	18.60	7.52	−0.139
MgI_2	2.56		16.60		0.000
CaF_2	4.02	2.02	4.90	11.63	−0.664
SrF_2	4.38	2.10	5.10	11.40	−0.697
BaF_2	5.40	2.17	5.80	11.83	−0.705
$ZnBr_2$	2.44	2.24	19.00		+0.047
$CdBr_2$	2.70		15.00		−0.115
$HgBr_2$	3.24	2.41	9.20		−0.229

C_X: atomic charge of X.
Experimental data see Refs. [35, 37, 38] and [43].

Table 4. AX_3 and AX_4 centrosymmetric molecules

A

	Bond lengths AX (Å)		Atomisation energies (eV)		C_X
AX_3	CNDO	Exp.	CNDO	Exp.	CNDO
BH_3	1.18	1.14	29.60	11.56	−0.068
BF_3	1.44	1.29	29.30	20.03	−0.242
BCl_3	1.72	1.74	45.70	14.17	−0.085
BBr_3	1.90	1.87	43.60	11.70	−0.029
BI_3	2.04	2.03	35.10	8.41	+0.031
$AlCl_3$	2.26	2.06	26.60	13.22	−0.242
$GaCl_3$	2.34	2.09	26.00	11.29	−0.181
$InCl_3$	2.58	2.46	20.20	9.59	−0.315

Experimental data see Refs. [27] and [43].
C_X: atomic charge of atom X.

B

	Bond lengths AX (Å)		Atomisation energies (eV)		C_X
AX_4	CNDO	Exp.	CNDO	Exp.	CNDO
CH_4	1.12	1.09	37.70	17.24	+0.011
SiH_4	1.54	1.48	25.50	13.42	−0.109
GeH_4	1.62	1.53	25.00	11.99	−0.061
SnH_4	1.84	1.70	18.70	10.48	−0.165
SiF_4	1.94	1.54	11.60	23.41	−0.343
$SiCl_4$	2.20	2.02	36.30	15.78	−0.219
$SiBr_4$	2.32	2.15	37.50	12.83	−0.155
SiI_4	2.50	2.43	30.40	9.71	−0.068
CCl_4	1.72	1.76	49.10	13.56	−0.089
$SiCl_4$	2.16	2.02	36.50	15.78	−0.224
$GeCl_4$	2.30	2.08	34.80	14.04	−0.211
$SnCl_4$	2.48	2.30	27.70	13.18	−0.292
$PbCl_4$	2.82	2.43	20.30	10.33	−0.365

Experimental data see Refs. [35. 37. 38] and [43].
C_X: see Table 4A.

We notice that the angle of valence HAH is clearly reduced when we go from atom A of the second period to the atom A of the third, fourth and fifth periods. This "closing" of the angle of valence, constitutes the most notable fact related to the geometries of the molecules AH_n. Therefore we are satisfied to notice that this fact is well reproduced by the results of CNDO/2-U.

3.3. *Transition Metal Complexes*

For a transitional element T of the type $T((n-1)d-ns-nd)$, the AOs np are empty, we have examined [25] the importance of their inclusion in the base

Table 5. AX_2 angular molecules and AX_3 pyramidal molecules

	d_{AX} (Å)		$\theta_{X\hat{A}X}$ (°)		E_A (eV)		I (eV)		$\mu(D)$		k_{AX}		$k_{X\hat{A}X}$	
AX_n	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.
OH_2	1.03	0.96	103	105	14.32	9.61	17.8	12.6	2.10	1.84	27.4	7.8	0.7	0.7
SH_2	1.36	1.33	99	92	13.95	7.62	13.1	10.5	2.70	0.92	22.9	4.1	0.5	0.5
SeH_2	1.52	1.47	95	91	14.06	6.34	11.8	9.9	1.80	0.62	17.1	3.2	0.5	0.3
TeH_2	1.68	1.66	94	90	9.52	5.46	9.7	9.1	2.00		10.8		0.1	
NH_3	1.08	1.02	104	107	24.22	12.15	16.5	10.9	2.20	1.47	43.9	6.4	1.8	0.4
PH_3	1.46	1.42	97	94	19.51	9.98	13.4	10.5	2.70	0.55	24.5	3.1	1.3	0.3
AsH_3	1.58	1.51	93	92	19.50	9.22	12.5	10.4	3.10	0.15	11.1		1.1	

Experimental data: Bond lengths d_{AX} and angle $\theta_{X\hat{A}X}$ see Refs. [35, 36, 37] and [38].
Atomisation energy E_A see Refs. [35, 37] and [43].
Dipole moment μ see Refs. [37, 41] and [42].
Force Constants k_{AX} and $k_{X\hat{A}X}$ see Refs. [33] and [34].
Ionisation Potentials I see Refs. [34] and [40].
The force constants k_{AX} are in 10^5 mdyn. $Å^{-1}$.
The force constants $k_{X\hat{A}X}$ are given in 10^5 mdyn. $Å^{-1}$ Rad^{-2}.

Table 6. Results for some complexes

	d_{MX} (Å)		E_c (eV)		I (eV)		k_{MX}		W_{MX}	C_M	C_X	C_O
	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.	CNDO	Exp.	CNDO	CNDO	CNDO	CNDO
$ZrCl_4$	3.43	2.32	2.5		10.35				0.618	+2.460	−0.615	
OsF_6	2.68	1.83	0.4		9.96		35.8		0.645	+3.077	−0.513	
$Ni(CO)_4$	1.91	1.82	194.8	8.15	3.64	8.28	26.5		0.489	+0.250	+0.023	−0.086
$Cr(CO)_6$	2.22	1.91	40.2	14.31	6.46	8.03	3.5	2.08	0.217	−0.183	+0.099	−0.068
$Mo(CO)_6$	2.49	2.06	19.9	8.06	7.65	8.13	4.3	1.96	0.373	−0.392	+0.160	−0.094
$W(CO)_6$	2.51	2.06	14.4	5.20	8.25	8.18	7.6	2.36	0.459	−0.554	+0.188	−0.096
MnO_4^-	1.61	1.59	67.1		1.88		41.5		0.869	+1.376	−0.593	
NiF_6^{4-}	2.11	2.00	176.7		11.18		9.5		0.160	+1.341	−0.887	
$FeCl_4^{2-}T_d$	2.38	2.27	138.6		1.28		16.2		0.285	+1.252	−0.804	
$FeCl_4^{2-}D_{4h}$	2.32	2.27	137.6		0.85		29.2		0.280	+1.228	−0.807	

d_{MX} distance Metal-X, Experimental data see Refs. [38, 45, 46, 47].
E_c complexation energy, Experimental data see Ref. [48].
I ionisation potential, Experimental data see Ref. [48].
k_{MX} force constant in 10^5 mdyn. Å^{-1}, see Ref. [49].
W_{MX} Wiberg's index.
C_M, C_X and C_O are atomic charges of metal, X and O.

LCAO. This study led us to conclude that a reduced base $((n-1)d-ns)$ for a transitional element provides better results.

Clack et al. used Burns' exponents. A comparative study of Slater's and Burns' exponents led us to select Burns' ones. Thus, for a study of fundamental state of the complexes, by means of CNDO/2-U, we have used Burns' base, including only the AOs $(n-1)d-ns$ from the transitional elements.

On Table 6 we have mentioned the results obtained for some complexes. We have applied CNDO/2-U for two conformations of $FeCl_4^{2-}$. This complex is tetrahedral (T_d group), but we have also examined a hypothetical square planar conformation (D_{4h} group). The results obtained for the two conformations by using the experimental length of the bond Fe–Cl indicate for the tetrahedral shape a larger stability than the one for the planar shape. Qualitatively the result remains the same one if we optimise the length of the bond Fe–Cl for the two conformations of $FeCl_4^{--}$. This result seems interesting; it shows that CNDO/2-U method, used carefully can be fruitful for some questions relating to the relative stabilities of the transition metals complexes even if the atomization's energies, as in CNDO/2 method, are over estimated.

4. Conclusions

Our CNDO/2-U procedure has been applied to a set of molecules pertaining to various classes. This set includes 52 diatomic molecules, 42 small polyatomic molecules and 10 transition metal complexes. In each case the energy has been fully minimised with respect to molecular geometry. CNDO/2-U method is successful in predicting equilibrium bond lengths, bond angles and dipole moments but stretching force constants, binding energies and ionization potentials are too high. As a result of our calculations, it appears that CNDO/2-U possesses both the merits and the failures of Pople–Santry–Segal CNDO/2 method. Last we can say that CNDO/2-U method reproduces quite well, the periodicity of the various kinds of physicochemical properties.

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