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New Developments in CNDO Molecular Orbital Theory

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A CNDO-level all-valence electron method is presented which yields both good heats of formation and good bond distances for hydrocarbon molecules. The success stems from a careful analysis of the total energy of molecular systems. A new versatile formula is also proposed for the computation of Coulomb integrals.

Key words: CNDO molecular orbital theory

1. Introduction

In a recent review article on the semi-empirical all-valence-electron method, Klopman [1] wrote of "the painful dilemma of having to choose between a method that gives good heats of formation and poor bond distances, or poor heats of formation and good bond distances.... Its solution, if it can be found, would probably be the most important contribution in the field of semi-empirical calculation of large molecules".

The widely accepted CNDO/2 method does not meet the challenge at all as will be shown later. The MINDO/3 method may be regarded as one of the closest solutions presently available to the problem. The method contains a large number of parameters and *ad hoc* conventions, and is a far cry from the original concept of the semi-empirical theory as proposed by Pariser and Parr, and Pople. Rather, the present authors are tempted to regard the approach typified by the MINDO/3 as a *pseudo*-quantum-mechanical model exquisitely built to simulate closely certain selected aspects of real molecular systems. Within the safe range of the applicability, such a method can be very useful and attractive for experimental chemists. It is to be remembered, however, that through a calculation by the method one is looking into a model world which would hopefully behave just like a real world for one's chosen interest.

The Pariser-Parr-Pople (PPP) method was designed for the planar π-electron system. Many serious attempts were made to justify theoretically the daring approximations and semi-empirical arguments on which the PPP method was based. Probably the most important issue was the justification of the so-called zero differential overlap approximation in the *two-electron* energy integrals. The introduction of this sweeping approximation was actually dictated by an imperative that the number of *two-electron* integrals must be reduced drastically.

In any large scale molecular energy calculation, the cost of evaluating the one-electron part is negligible compared with that of the evaluation of the two-electron part. It is very important, however, to realize that the one-electron part is essentially negative and the two-electron part is positive and the total electronic energy rests on a delicate balance between these two parts which are opposite in sign. Thus, if some alteration or simplification is applied to the two-electron part of the total energy, the one-electron part must also be doctored very carefully, a consideration singularly missing in most of the theoretical discussions on the zero differential overlap approximation.

In the present work, we shall first introduce a new formula for coulomb integrals which is flexible enough to simulate continuously from the rigorous formulas of Roothaan to the approximate formula of Ohno and, with a particular choice of the parameters, reduces itself to the formula of Mataga-Nishimoto. Then, we shall proceed to present an all-valence-electron method at the CNDO-level. One of the new features of the method is the way in which the one-electron part of the Hartree-Fock operator is parametrized so that the flexibility needed to accomplish the required delicate balance between the one-electron part and the two-electron part is greater than those in previous CNDO methods.

In the last two sections, some numerical results will be described and discussed. The calculations were made for CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_4, C_3H_8, C_4H_{10}, and C_6H_6. We have succeeded to meet the challenge mentioned at the beginning of the present section quite reasonably at the level of the CNDO approximation.

2. Klondike Formula

There are several different formulas commonly used for the computation of Coulomb integrals in semi-empirical molecular orbital calculations. People have more or less settled for Ohno's formula or Mataga-Nishimoto's formula in the case of the π-electron approximation (PPP method). In the development of all-valence-electron approximations the situation has been far from settled; some explicitly prefer using Roothaan's theoretical formula, while others carry over their habit acquired in the π-electron method to the new stage and use either Ohno's or Mataga-Nishimoto's formula.

From the discussion presented in the preceeding section it has become clear that the choice of the formula for the computation of Coulomb integrals constitutes an important part of the semi-empirical adjustment of the individual method it would be convenient if we could have a suitably parametrized formula which would cover continuously the results of Roothaan's, Ohno's, and Mataga-Nishimoto's formulas. We have succeeded in devising such a new artificial formula for Coulomb integrals and utilizing it in our present work. This we call the Klondike formula, which has the following form

$$(\mu\mu|\nu\nu) = \frac{1}{R+A} \quad \text{(in a.u.)}$$

where R is the distance between the reference site of the atomic function μ and that of ν.

$$A = (a_\mu e^{\kappa_\mu R} + a_\nu e^{\kappa_\nu R})^{-1} \quad \kappa_\mu, \kappa_\nu > 0$$

where κ_μ and κ_ν are the Klondike parameters for μ and ν centers respectively. In the present work we have restricted our considerations to the case $\kappa_\mu = \kappa_\nu = \kappa$ but our computer program accommodates the general case. When $\kappa = 0$, the above formula becomes identical with Mataga-Nishimoto's formula. The value of a_μ can be determined in the following way; when $R = 0$

$$(\mu\mu|\nu\nu) = A^{-1} = a_\mu + a_\nu .$$

If the two atomic orbitals are identical,

$$(\mu\mu|\mu\mu) = 2a_\mu .$$

In Roothaan's method the value of $(\mu\mu|\mu\mu)$ is determined by the choice of the atomic function. In Ohno's and Mataga-Nishimoto's method $(\mu\mu|\mu\mu)$ is set to a certain empirical value, usually $I_\mu - A_\mu$, where I_μ is the ionization potential and A_μ the electron affinity referring to the atomic "state" μ. Thus

$$a_\mu = \tfrac{1}{2}(I_\mu - A_\mu) .$$

In Tables 1 and 2 the following quantities are presented in order to compare the Klondike formula with Ohno's formula (Table 1) and with Roothaan's (Table 2).

$$\Gamma_{1s1s} = ((1s)_\mu (1s)_\mu | (1s)_\nu (1s)_\nu) ,$$
$$\Gamma_{2s2s} = ((2s)_\mu (2s)_\mu | (2s)_\nu (2s)_\nu) ,$$
$$\Gamma_{2s1s} = ((2s)_\mu (2s)_\mu | (1s)_\nu (1s)_\nu) .$$

In Table 1 the Klondike parameter is taken as $\kappa = 0.4$ and in Table 2 $\kappa = 0.8$. The orbitals are $(1s) \sim \exp(-1.2r)$ and $(2s) \sim r\exp(-1.8r)$. The values of $(I - A)$

Table 1. Klondike ($\kappa = 0.4$) and Ohno

Γ_{1s1s}			Γ_{2s2s}		Γ_{2s1s}	
R[a]	Ohno	Klondike	Ohno	Klondike	Ohno	Klondike
0.5	0.45988	0.44791	0.38856	0.38957	0.42443	0.41928
1.0	0.42725	0.41347	0.36827	0.37143	0.39837	0.39318
1.5	0.38552	0.37574	0.34053	0.34656	0.36391	0.36185
2.0	0.34344	0.33888	0.31048	0.31904	0.32789	0.32954
2.5	0.30531	0.30502	0.28146	0.29165	0.29423	0.29877
3.0	0.27238	0.27492	0.25504	0.26593	0.26443	0.27075
3.5	0.24450	0.24864	0.23172	0.24257	0.23870	0.24583
4.0	0.22098	0.22587	0.21141	0.22174	0.21667	0.22397
4.5	0.20110	0.20619	0.19381	0.20336	0.19783	0.20489
5.0	0.18418	0.18916	0.17856	0.18721	0.18166	0.18827

[a] (In a.u.).

Table 2. Klondike ($\kappa = 0.8$) and Roothaan

	Γ_{1s1s}		Γ_{2s2s}		Γ_{2s1s}	
R[a]	Roothaan	Klondike	Roothaan	Klondike	Roothaan	Klondike
0.5	0.71631	0.71748	0.57671	0.61120	0.63011	0.66646
1.0	0.63550	0.62535	0.53943	0.56768	0.58077	0.59857
1.5	0.54140	0.52588	0.48678	0.49739	0.51307	0.51294
2.0	0.45505	0.44068	0.42838	0.42695	0.44238	0.43453
2.5	0.38376	0.37307	0.37226	0.36638	0.37868	0.37010
3.0	0.32750	0.32041	0.32303	0.31708	0.32563	0.31894
3.5	0.28364	0.27925	0.28205	0.27754	0.28299	0.27849
4.0	0.24927	0.24665	0.24875	0.24576	0.24906	0.24625
4.5	0.22197	0.22044	0.22181	0.21996	0.22190	0.22023
5.0	0.19991	0.19903	0.19987	0.19877	0.19989	0.19891

[a] (In a.u.).

are 12.858 eV for (1*s*) and 10.778 eV for (2*s*). It is evidently shown that the Klondike formula exhibits a comfortable flexibility, which could be useful in the future development of the all-valence-electron method: In the original CNDO and INDO methods Roothaan's formula is used, while the MINDO and others adopt various formulas similar to Ohno's or Mataga's. Furthermore there are indications that in the CI (configuration interaction) calculations of the excited states of molecules we might have to make a choice even between Ohno's and Mataga's. It is to be mentioned that a somewhat similar formula was once proposed by Hinze [2].

3. A New Parametrization of All-Valence-Electron Theory

In all-valence-electron methods at the level of the CNDO approximation a particular choice of parameters may predict certain properties of molecules in good agreement with experiment but use of the same parameters may cause other calculated properties to disagree with the experimental values. One of the most serious examples is the dilemma between good bond lengths and good heat of formation as mentioned in the Introduction. In the following, we have made an attempt to parametrize the theory in order to obtain good correlation between energies and bond lengths of some typical hydrocarbons such as methane, ethane, propane, butane, ethylene, allene, acetylene and benzene.

In the SCF-LCAO-MO theory the molecular orbitals are determined by the equation

$$\mathbb{F}\mathbb{C} = \mathbb{S}\mathbb{C}\mathbb{E}$$

where $\mathbb{F}$ is the Fock matrix, $\mathbb{C}$ the matrix of the molecular orbital coefficients, $\mathbb{E}$ the eigenvalue matrix of orbital energies, and $\mathbb{S}$ the overlap integral matrix. These conventions are so well established that they do not call for any detailed elaborations.

The elements of the Fock matrix may be split up into two parts

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu}$$

where

$$H_{\mu\nu} = \int \mu(1)\left[-\tfrac{1}{2}\Delta - \sum_{\mathrm{A}} V_{\mathrm{A}}\right]\nu(1)\,dV_1 = \left\langle \mu \right| -\tfrac{1}{2}\Delta - \sum_{\mathrm{A}} V_{\mathrm{A}} \left| \nu \right\rangle$$

(one-electron part)

and

$$G_{\mu\nu} = \sum_{\lambda,\sigma} P_{\lambda\sigma}[(\mu\nu|\lambda\sigma) - \tfrac{1}{2}(\mu\sigma|\nu\lambda)]$$

(two-electron part).

Here

$$P_{\lambda\sigma} = 2\sum_{i}^{\mathrm{occ}} C_{\lambda i} C_{\sigma i}$$

and

$$(\mu\nu|\lambda\sigma) = \int\int \mu(1)\,\nu(1)\left(\frac{1}{r_{12}}\right)\lambda(2)\,\sigma(2)\,dV_1\,dV_2\,.$$

Under the zero differential overlap (ZDO) approximation all two-electron integrals $(\mu\nu|\lambda\gamma)$ are zero unless $\mu=\nu$ and $\lambda=\sigma$. The surviving integrals $(\mu\mu|\lambda\lambda)$ may be written as $\gamma_{\mu\nu}$ and further are assumed to depend on the atoms A and B to which μ and λ belong respectively and not on the type of orbitals. This is a common practice in the CNDO method in order to secure the invariance requirements.

Under the ZDO approximation the two-electron matrix elements become

$$G_{\mu\mu} = \sum_{\lambda} P_{\lambda\lambda}(\mu\mu|\lambda\lambda) - \tfrac{1}{2} P_{\mu\mu}(\mu\mu|\mu\mu)$$
$$G_{\mu\nu} = \tfrac{1}{2} P_{\mu\nu}(\mu\mu|\nu\nu) \quad (\mu \neq \nu)$$

where the summation is over all basis functions. The one-electron part calls for a closer examination. The matrix elements may be written as

$$\begin{aligned} H_{\mu\mu} &= \langle\mu| -\tfrac{1}{2}\Delta - V_{\mathrm{A}}|\mu\rangle - \sum_{\mathrm{B}\neq\mathrm{A}} \langle\mu|V_{\mathrm{B}}|\mu\rangle \\ &= U_{\mu} - \sum_{\mathrm{B}\neq\mathrm{A}} \langle\mu|V_{\mathrm{B}}|\mu\rangle \\ H_{\mu\nu} &= \langle\mu| -\tfrac{1}{2}\Delta - V_{\mathrm{A}} - V_{\mathrm{B}}|\nu\rangle - \sum_{\mathrm{C}\neq\mathrm{A,B}} \langle\mu|V_{\mathrm{C}}|\nu\rangle \end{aligned}$$

(μ on A, and ν on B).

It is to be noted that if appropriate expressions are given to $\{V_A\}$ the one-electron part can be computed explicitly, the only expensive part being the three center integrals $(\mu|V_C|\nu)$. In the present work, however, we try to parametrize the one-electron part. The primary reason is that we attempt necessary adjustments to the drastic approximations in the two-electron part. Any change in the positive energy contribution from the two-electron part must definitely be counterbalanced by the negative contribution from the one-electron part. In order to incorporate this feature into the formula we introduce the approximation,

$$\langle\mu|V_B|\mu\rangle = Z_B(1-\lambda e^{-\omega R_{AB}})\Gamma_{AB}.$$

Here Γ_{AB} is the electron repulsion integral which is typical in the CNDO/2 method and Z_B is the screened nuclear charge. λ and ω are regarded as global parameters in the present work.

One finds a precedent of this kind of formula in the work of Fischer and Kollmar [3];

$$\langle\mu|V_B|\mu\rangle = Z_B(1-\alpha)\Gamma_{AB} + \alpha\sqrt{R_{AB}^2 + 1/\mu_A^2}$$

where α is taken to be 0.22 and μ_A is an orbital exponent. Although it was shown that the above formula works very well when R_{AB} is small, it has obviously unacceptable asymptotic behaviour when $R_{AB} \to \infty$.

Now we have

$$H_{\mu\mu} = U_\mu - \sum_{B \neq A} Z_B(1-\lambda e^{-\omega R_{AB}})\Gamma_{AB}.$$

In the present work U_μ will be regarded as an adjustable parameter. Next, we drop the three-center integrals

$$-\sum_{C \neq A,B} \langle\mu|V_C|\nu\rangle$$

in $H_{\mu\nu}$ because the corresponding three-center two-electron integrals, say $(\mu\nu|\sigma_C\sigma_C)$, are also dropped under the ZDO approximation. $H_{\mu\nu}$ is now parametrized as

$$H_{\mu\nu} = \tfrac{1}{2}(\beta_\mu + \beta_\mu) S_{\mu\nu}.$$

The overlap integral here is not set to be zero; instead we calculate them using chosen set of Slater-type orbitals, which are to be used when one employs the Roothaan formula for the Coulomb integrals $(\mu\mu|\nu\nu)$. In the Klondike formula we have the parameters a_μ and κ.

Our computer program accommodates the following specifications;

Atomic orbitals. ($1s$, $2p_x$, $2p_y$, $2p_z$) for H, ($2s$, $2p_x$, $2p_y$, $2p_z$) for (Li–F), and ($3s$, $3p_x$, $3p_y$, $3p_z$) for (Na–Cl), with the orbital exponents (ζ_s, ζ_{px}, ζ_{py}, ζ_{pz}).

Atomic parameters. Z (effective nuclear charge), U_s, U_{px}, U_{py}, U_{pz}, β_s, β_{px}, β_{py}, β_{pz}.

Klondike formula. a_s, a_{px}, a_{py}, a_{pz}, and κ. $(\mu|V_B|\mu)$: λ, ω.

The parameters, κ, λ, ω could be individual "atomic" parameters but in the present work these are used as global parameters.

It should be obvious that the parametrization of the present computational program is a very flexible one. If we are to observe both the coordinate and hybridization invariance for a general molecular geometry we have rather strict restrictions,

$$U_s = U_{px} = U_{py} = U_{pz}, \qquad \beta_s = \beta_{px} = \beta_{py} = \beta_{pz},$$
$$a_s = a_{px} = a_{py} = a_{pz}, \quad \text{and} \quad \zeta_s = \zeta_{px} = \zeta_{py} = \zeta_{pz},$$

but in the present work only the coordinate invariance is observed. Then we have the following adjustable parameters,

$$U_s, U_{px} = U_{py} = U_{pz}, \qquad \beta_s, \beta_{px} = \beta_{py} = \beta_{pz},$$
$$a_s, a_{px} = a_{py} = a_{pz},$$
$$\zeta_s, \text{ and } \zeta_{px} = \zeta_{py} = \zeta_{pz}.$$

There are, of course, a vast number of planar molecules, for which we have

$$U_s, U_{px} = U_{py}, U_{pz}, \qquad \beta_s, \beta_{px} = \beta_{py}, \beta_{pz},$$
$$a_s, a_{px} = a_{py}, a_{pz}, \qquad \zeta_s, \zeta_{px} = \zeta_{py}, \text{ and } \zeta_{pz}.$$

Although we have not exploited this possibility it could be very useful to establish a link between the PPP theory and the CNDO-type theory by introducing the parametrization suggested above.

4. Applications

In the present work we have limited ourselves to hydrocarbons and we have used mostly the $1s$ orbital only for hydrogen. We have tested the effect of inclusion of $2p_x$, $2p_y$, and $2p_z$ orbitals on hydrogen in the case of benzene because we have a reference work by Ermler and Kern [4]. As is expected their effect is negligible in the ground state properties but for excited states with considerable Rydberg character the inclusion could be useful as Salahub and Sandorfy [5] demonstrated.

In the following CNDOR implies the calculation in which Roothaan's explicit theoretical formulas for coulomb integrals are used as is the case in the CNDO/2 method. On the other hand CNDOK means that we have used the Klondike formula with $\kappa = 0.4$ which would simulate Ohno's formula for the Coulomb integral. In Table 3 the values of parameters are compared among CNDO/2, CNDOR, and CNDOK.

Ionization potentials I and electron affinities A when necessary are the same as in the CNDO/2 method.

5. Heat of Atomization

For comparison with experimental values we have calculated heats of atomization in the following way: In general the energy of "atom" in the $s^m p^n$

Table 3. Parameter values

β in eV	CNDO/2	CNDOR	CNDOK
$\beta_{H,1s}$	9.0	9.0	9.0
$\beta_{C,2s}$	21.0	21.0	17.0
$\beta_{C,2p}$	21.0	17.5	17.0
U in eV			
$U_{H,1s}$	17.38	17.06	13.06
$U_{C,2s}$	70.2713	70.8399	51.774
$U_{C,2p}$	61.7923	62.5203	43.295
ζ			
$\zeta_{H,1s}$	1.2	1.16	1.2
$\zeta_{C,2s} = \zeta_{C,2p}$	1.625	1.8	1.8
Z			
$Z_{H,1s}$	1	1	1
$Z_{C,2s} = Z_{C,2p}$	4	4	4
λ, ω			
$\lambda_H = \lambda_C$	0	0.136	-0.343
$\omega_H = \omega_C$	0	0.75 a.u.$^{-1}$	0.45 a.u.$^{-1}$

electronic configuration is assumed to be given (in a.u.),

$$E(s^m p^n) = mU_s + nU_p + \tfrac{1}{2}(m+n)(m+n-1)(ss|pp),$$
$$(ss|pp) = \tfrac{1}{2}[(ss|ss) + (pp|pp)],$$
$$(ss|ss) = \tfrac{93}{256}\zeta_s, \quad (pp|pp) = \tfrac{93}{256}\zeta_p.$$

Thus, from Table 4 we have in CNDO/2

$$E(\mathrm{H}) = -0.63874 \text{ a.u.}$$
$$E(\mathrm{C}) = -5.8789 \text{ a.u.}$$

Table 4. Comparison of calculated and observed heats of atomization (in a.u.)

	ΔH_{atom}			
Molecule	CNDO/2	CNDOR	CNDOK	Observed [a]
CH_4	1.3954	0.6961	0.7204	0.6693
C_2H_2	1.7336	0.6781	0.6267	0.6478
C_2H_4	2.1825	0.9294	0.9397	0.8979
C_2H_6	2.6571	1.1857	1.2757	1.1350
C_3H_4	2.9920	1.1898	1.1705	1.1254
C_3H_8	3.8951	1.6559	1.7245	1.6033
C_4H_{10}	5.1466	2.1273	2.3203	2.0736
C_6H_6	6.2791	2.1682	2.4000	2.1847

[a] From Wiberg, K.B.: J. Am. Chem. Soc. **90**, 59 (1968).

and in CNDOR

$$E(\mathrm{H}) = -0.62698 \text{ a.u.}$$
$$E(\mathrm{C}) = -5.8789 \text{ a.u.}$$

The above approach is in line with Wiberg [6], one of our reference work. However, in our CNDOK calculation we have decided to use a straightforward value for E(H), -0.5 a.u. This choice is *not* made on the ground of better overall results. The heat of atomization is given by the formula,

$$\Delta H_{\text{atom}} = (\text{Number of "C" atoms}) \times E(\mathrm{C}) + (\text{Number of "H" atoms}) \times E(\mathrm{H}) - E_T$$

where E_T is the total energy obtained from the computer program.

Table 4 shows the results. In both CNDOR and CNDOK agreement with experiment is not really perfect but acceptable while CNDO/2 yields too large values.

6. Bond Lengths

The calculation of the molecular total energies was done by varying the C–C and C–H bonds keeping basic molecular symmetry intact. The calculated bond lengths corresponding the lowest total energy are shown in Table 5. It is seen that CNDOR is somewhat inferior to CNDO/2 especially as for C–H bond lengths. In the table some C–H bonds are missing mainly for economy reasons. The C–H bond lengths were held fixed at the observed values.

Table 5. Comparison of calculated and observed bond lengths (in Å)

Molecule	Bond	CNDO/2	CNDOR	CNDOK	Observed[a]
CH_4	C-H	1.124	1.174	1.224	1.106
C_2H_2	C≡C	1.205	1.239	1.339	1.205
	C-H	1.059	1.203	1.203	1.059
C_2H_4	C=C	1.356	1.356	1.339	1.332
	C-H	1.115	1.130	1.203	1.084
C_2H_6	C-C	1.406	1.506	1.500	1.536
	C-H	1.128	1.228	1.232	1.107
C_3H_4	C=C	1.312	1.342	1.455	1.312
	C-H	1.082	1.220	1.240	1.084
C_3H_8	C-C	1.513	1.526	1.685	1.526
	C-H	1.090	1.190	-	1.090
C_4H_{10}	C-C	1.513	1.540	1.640	1.539
	C-H	1.090	1.190	-	1.10
C_6H_6	C-C	1.397	1.423	1.565	1.397

[a] Interatomic distances, Chem. Soc. (London) Special Publ. No. 18 (1965).

7. Orbital Energies

Table 6 contains two representative studies on the occupied orbital energies of the molecules. First it is shown that the orbital energies calculated by CNDOR are in good agreement with those of Ermler and Kern [4] who recently performed an ab initio Hartree-Fock-Roothaan calculation of good accuracy. For comparison we have also included in the table the orbital energies calculated by CNDO/2. It is to be noted that the CNDO/2 ordering of the E_{1u} and πA_{2u} does not agree with that of Kern whereas our result from CNDOR agrees with it. Similar results are also found in the case of ethylene: the orbital energies and the ordering calculated by CNDOR are superior to those from CNDO/2 when compared with the results of Moskowitz and Harrison [7].

8. Discussion

In view of the results presented here, we may conclude that good theoretical values for heats of formation can be obtained through the proper parametrization

Table 6. Orbital energies (in a.u.)

C_6H_6 : (D_{6h} symmetry)

	CNDO/2	CNDOR	Kern[a]
A_{1g}	-1.8728	-1.3996	-1.1487
E_{1u}	-1.3872	-1.1098	-1.0138
E_{2g}	-1.1098	-0.8482	-0.8230
A_{1g}	-1.0632	-0.7571	-0.7081
B_{1u}	-0.8590	-0.5975	-0.6427
B_{2u}	-0.7896	-0.5439	-0.6187
E_{1u}	-0.6966	-0.5204	-0.5872
πA_{2u}	-0.7193	-0.5056	-0.4979
E_{2g}	-0.5156	-0.3949	-0.4946
πE_{1g}	-0.5104	-0.2890	-0.3337

C_2H_4 : (D_{2h} symmetry)

	CNDO/2	CNDOR	Moskowitz & Harrison[b]
A_g	-1.4061	-1.2094	-1.0581
B_{3u}	-1.0054	-0.8540	-0.8063
B_{2u}	-0.8973	-0.6747	-0.6601
A_g	-0.7147	-0.5624	-0.5829
B_{1g}	-0.5748	-0.4784	-0.5175
πB_{1u}	-0.5836	-0.3873	-0.3815

[a] Ermler, W. C., Kern, C. W.: J. Chem. Phys. **58**, 3458 (1973).

[b] Moskowitz, J. W., Harrison, M. C.: J. Chem. Phys. **42**, 1726 (1965).

of a CNDO-level semi-empirical theory. The essential point we have brought forward is the importance of the balance between the one-electron (negative) and the two-electron energy (positive). The use of the ZDO approximation was, to some extent, justified by introducing the notion of the orthogonalized atomic orbitals in the PPP theory but it seems to be difficult to maintain the same logic and subsequent justification in the all valence-electron theory. However we keep it as a necessary evil in order to make the calculations feasible for large molecules. Under the ZDO approximation many terms in the energy formula are eliminated. If there arises any appreciable unbalance due to the effect of these neglected terms between the one- and two-electron parts, then we are bound to have a poor total energy value. It is our opinion that this has been the case with most of the methods thus far proposed by various authors. We have attempted to maintain the balance by introducing two parameters, λ and ω, in the one-electron part of the diagonal energy matrix elements. The effectiveness of the balancing mechanism introduced here has aptly been demonstrated by showing that it could adjust itself to cope with the two widely different formulas for electron repulsion integrals (Roothaan's and Klondike with $\kappa = 0.4$) with the results of more or less equal quality.

The introduction of a flexible two-electron energy integral formula, Klondike formula, should also be viewed from wider scope than actually shown in the present work. Considering that there still remains a considerable amount of the flexibility in the method we can be hopeful about the simultaneous prediction of a variety of molecular properties including both ground and excited states.

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