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Semiempirical SCF Theory with "Scaled" Slater Orbitals

II. Molecular Calculations

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A new method is presented for the calculation of molecular properties in which the one center integrals are evaluated within their environment (scaled in the molecule) rather than carried over from atomic structures.

The procedure can be incorporated into any SCF scheme using a minimal basis set of atomic orbitals. In this paper an INDO framework was chosen to illustrate the results. Both heats of formation and bond distances for various types of molecules were found in satisfactory agreement with experiment.

Es wird eine neue Methode für die Berechnung von Moleküleigenschaften vorgeschlagen, in welcher die Einzentrenintegrale innerhalb ihrer Umgebung im Molekül bestimmt werden, statt sie von freien Atomen zu übernehmen.

Diese Methode kann bei jedem SCF Verfahren angewandt werden, das auf einer minimalen Basis von Atomorbitalen aufbaut. Zur Illustration der Ergebnisse in dieser Arbeit wird das INDO-Verfahren gewählt. Sowohl Bildungswärmen als auch Bindungsabstände von verschiedenen Molekülarten sind in guter Übereinstimmung mit den experimentellen Daten.

Une nouvelle méthode pour le calcul des propriétés moléculaires est presentée, dans laquelle les intégrales monocentriques sont evaluées dans leur environnement (ajustées à la molécule), au lieu d'être transférées du calcul atomique.

Le procédé peut être incorporé dans n'importe quel schema SCF qui utilise un «basis set» minimal.

Dans cet article, le procédé est illustré par l'utilisation d'un schema INDO.

Les chaleurs de formation et les distances de liaison pour plusieurs types de molécules sont trouvées en accord satisfaisant avec l'experience.

1. Introduction

The first semiempirical methods for the Self Consistent Field Calculation of σ bonded molecules were introduced six years ago [1]. Since then, several procedures specifically designed for the calculation of particular properties, have been proposed [2–6]. These procedures often utilize the original framework but differ from it sometimes by some minor adjustment of parameters or by some feature expecially designed to allow a specific property to be calculated, such as interaction of configuration for spectra [3].

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Although the approximations used for evaluating the various integrals are widely varied, the orbital energies and density matrices remain astonishingly similar in all these methods. A further remarkable similarity is that they consistently fail to account for ground and excited state properties consistently. Moreover, even for ground state molecules, it does not seem to be possible to obtain good values for bond distances and heats of formation simultaneously.

The total heat of formation of a molecule results from the intrinsic combination of electronic energy and core repulsions. Although the core repulsions are relatively easy to approximate and, if this is done (i.e., CNDO [4], INDO [2]), relatively good bond distances can be obtained (by minimization), the heats of formation are several orders of magnitude larger than those experimentally observed. If on the other hand, one wants to correlate the heats of formation, one has to decrease arbitrarily the core repulsion (*i.e.*, PNDO [5], MINDO [6]). By doing this, however, bond distances are usually found to be too short.

It thus appears that, at the present time, we are in possession of several powerful theoretical methods which are designed either for ground state energies, bond distances or transition energies calculations. However, one may argue that a sound method should be able to reproduce all three sets of properties. The fact that these methods do not, may mean that one is overlooking some important property which jeopardizes any new type of calculation such as the interpretation of NMR, IR or chemical reactivity data.

Numerous reasons may be invoked as responsible for such discrepancies including even the possibility that such crude methods cannot be expected to yield all these results. However, several routes which have not been investigated as yet, may still be open for improvement. One of these involves a reexamination of the "common to all semiempirical SCF methods" way of determining the one center integrals. These integrals are determined semiempirically by comparing the experimental and calculated ionization potentials of atoms. One may speculate however that such a procedure does not properly take into account the molecular environment and thus neglects the resulting expansion or contraction of the atomic orbitals on which the molecular orbitals are built. The neglect of this expansion of orbitals explains precisely the observed discrepancy between ground and excited states, and also the necessity of decreasing arbitrarily the nuclear interactions in order to obtain satisfactory bond energies.

In a previous communication [7], we have presented a new semiempirical method for the calculation of one center integrals involving scaled Slater orbitals. We now wish to present a method for the calculation of molecular properties in which the one center integrals are evaluated within their environment (scaled in the molecule) rather than treated as parameters carried over from atomic structures. The proposed method for the calculation of atomic terms might be, of course, incorporated in any numerical scheme using a minimum basis set of atomic orbitals, including an *ab initio* calculation method. In this article we are illustrating the procedure within an INDO [2] framework of approximations because of its intermediate complexity between the CNDO-type and *ab initio* type calculations. We believe with it, to gain a proper insight into the effect of using the variable exponent method to calculate molecular properties.

2. Theory

For a closed shell INDO type Hamiltonian, the elements of the Hartree-Fock matrix $F_{\alpha\beta}$ can be expressed as

$$F_{\alpha\beta} = H_{\alpha\beta} + G_{\alpha\beta}\,, \tag{1}$$

where, if $\alpha = \beta$ and the atomic orbital α is centered on atom I,

$$\left\{\begin{aligned} H_{\alpha\alpha} &= [\alpha| -\tfrac{1}{2}\Delta - V_{\mathrm{I}}|\alpha] + \sum_{\mathrm{J}(\neq \mathrm{I})} [\alpha| - V_{\mathrm{J}}|\alpha]\,,\\ G_{\alpha\alpha} &= \sum_{\gamma\in(\mathrm{I})} P_{\gamma\gamma}\{[\alpha^2|\gamma^2]^{\mathrm{I}} - \tfrac{1}{2}[\alpha\gamma|\alpha\gamma]^{\mathrm{I}}\}\\ &\quad + \sum_{\mathrm{J}(\neq \mathrm{I})}\ \sum_{\kappa\in(\mathrm{J})} P_{\kappa\kappa}[\alpha^2|\kappa^2]^{\mathrm{I},\mathrm{J}} \end{aligned}\right. \tag{2}$$

and, if $\alpha \neq \beta$,

$$\left\{\begin{aligned} H_{\alpha\beta} &= h(\alpha,\beta)\,\beta_{\alpha\beta}\,,\\ G_{\alpha\beta} &= \tfrac{1}{2}P_{\alpha\beta}\{(3[\alpha\beta|\alpha\beta]^{\mathrm{I}} - [\alpha^2|\beta^2]^{\mathrm{I}})\,\delta_{\mathrm{IJ}} - [\alpha^2|\beta^2]^{\mathrm{I},\mathrm{J}}(1-\delta_{\mathrm{IJ}})\}\,. \end{aligned}\right. \tag{3}$$

In these formulae, the Greek letters refer to atomic orbitals, the capital letters refer to atoms, the summation $\sum_{\gamma\in(\mathrm{I})}$ extends over the AO's centered on atom I, P is the charge density – bond order matrix, and δ_{IJ} is the Kronecker symbol:

$$\delta_{\mathrm{IJ}} = \begin{cases} 1, & \text{if the AO's } \alpha \text{ and } \beta \text{ belong to the same atom}\\ 0, & \text{if the AO's } \alpha \text{ and } \beta \text{ belong to two different atoms I and J}. \end{cases}$$

All other symbols are the same as those used in Paper I of this series or will be specified later on. The total molecular energy can be expressed as

$$E_{\mathrm{tot}} = \tfrac{1}{2}(\mathrm{Tr}(\boldsymbol{H} + \boldsymbol{F})\,\boldsymbol{P}) + \text{Core-Core inter. terms.} \tag{4}$$

The problem which specifically interests us here consists in deriving a procedure for the minimization of the total energy of a molecule, E_{tot}, not only with respect to the coefficients of the atomic orbitals but also to the exponents of a minimal basis set of STO functions. In this paper, the treatment will be restricted to molecules composed only of first and second row elements. Due to the space invariance requirement, it will be necessary to assign identical exponents to the various p orbitals centered on any given atom. Thus, in addition to the usual quantities that are being optimized in classical SCF theories, *i.e.*, coefficients of atomic orbitals, one (for H atom) or two (for second row atoms) additional variational parameters will have to be optimized per atom. Assuming a first order approximation to the $\boldsymbol{P}$ matrix, the optimized atomic exponents might be determined according to the variation principle by setting the corresponding partial derivatives of the total molecular energy equal to zero.

For the sake of convenience, let us use the indices μ and λ (or Λ) for the s- and p-orbitals, respectively, and let the index v refer to either kind. If I defines the specific atom, the result of the variation procedure can be expressed as the following nonlinear system of equations of the s-orbital exponents $a_{\mathrm{I}}(\mu)$ and the p-orbital exponents $a_{\mathrm{I}}(\lambda)$ of all atoms ($\mathrm{I} = \mathrm{A}, \mathrm{B}, \ldots \mathrm{K}$) composing the molecule:

$$\begin{aligned} a_{\mathrm{I}}(\mu) = K_s^{\mathrm{I}} \Bigg\{ & \frac{Z_s^{\mathrm{I}}}{N_s^{\mathrm{I}}} - \frac{1}{4} P_{\mu\mu} \frac{\partial [\mu^2|\mu^2]^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\mu)} \\ & + \left(\frac{\sum\limits_{\Lambda \in (\mathrm{I})} P_{\mu\Lambda}^2}{2 P_{\mu\mu}} - \sum_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda} \right) \frac{\partial [\mu^2|\lambda^2]^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\mu)} \\ & + \frac{1}{2} \left(\sum_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda} - \frac{3}{P_{\mu\mu}} \sum_{\Lambda \in (\mathrm{I})} P_{\mu\Lambda}^2 \right) \frac{\partial [\mu\lambda|\mu\lambda]^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\mu)} - \frac{\partial U_s^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\mu)} \Bigg\}, \end{aligned} \tag{5}$$

$$\begin{aligned} a_{\mathrm{I}}(\lambda) = K_p^{\mathrm{I}} \Bigg\{ & \frac{Z_p^{\mathrm{I}}}{2} - \frac{1}{4} \frac{\sum\limits_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda}^2}{\sum\limits_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda}} \cdot \frac{\partial [\lambda^2|\lambda^2]^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\lambda)} \\ & + \left(\frac{\sum\limits_{\Lambda \in (\mathrm{I})} P_{\mu\Lambda}^2}{2 \cdot \sum\limits_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda}} - P_{\mu\mu} \right) \frac{\partial [\lambda^2|\mu^2]^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\lambda)} \\ & + \frac{1}{2} \left(P_{\mu\mu} - \frac{3 \cdot \sum\limits_{\Lambda \in (\mathrm{I})} P_{\mu\Lambda}^2}{\sum\limits_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda}} \right) \frac{\partial [\lambda\mu|\lambda\mu]^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\lambda)} \\ & + \frac{1}{\sum\limits_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda}} \left(\frac{\sum\limits_{\Lambda < \Lambda^* \in (\mathrm{I})} \sum P_{\Lambda\Lambda^*}^2}{2} - \sum_{\Lambda < \Lambda^* \in (\mathrm{I})} \sum P_{\Lambda\Lambda} \cdot P_{\Lambda^*\Lambda^*} \right) \frac{\partial [\lambda^2|\lambda^{*2}]^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\lambda)} \\ & + \frac{1}{\sum\limits_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda}} \left(\frac{1}{2} \sum_{\Lambda < \Lambda^* \in (\mathrm{I})} \sum P_{\Lambda\Lambda} \cdot P_{\Lambda^*\Lambda^*} - \frac{3}{2} \sum_{\Lambda < \Lambda^*} \sum P_{\Lambda\Lambda^*}^2 \right) \\ & \cdot \frac{\partial [\lambda\lambda^*|\lambda\lambda^*]^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\lambda)} - \frac{\partial U_r^{\mathrm{I}}}{\partial a_{\mathrm{I}}(\lambda)} \Bigg\}, \end{aligned} \tag{6}$$

where

$$\begin{aligned} U_s^{\mathrm{I}} = \sum_{\mathrm{J}(\neq \mathrm{I})} \Bigg\{ & [\mu| - V_{\mathrm{J}}|\mu] + 2\beta_{\mathrm{IJ}} \frac{1}{P_{\mu\mu}} \sum_{\nu \in (\mathrm{J})} P_{\mu\nu} h(\mu, \nu) \\ & + [\mu^2|\mu'^2]^{\mathrm{I,J}} \left(P_{\mu'\mu'} - \frac{P_{\mu\mu'}^2}{2 \cdot P_{\mu\mu}} \right) + [\mu^2|\lambda'^2]^{\mathrm{I,J}} \\ & \cdot \left(\sum_{\Lambda' \in (\mathrm{J})} P_{\Lambda'\Lambda'} - \frac{1}{2 P_{\mu\mu}} \sum_{\Lambda' \in (\mathrm{J})} P_{\mu\Lambda'}^2 \right) \Bigg\} \end{aligned} \tag{7}$$

and

$$\begin{aligned} U_p^{\mathrm{I}} = \sum_{\mathrm{J}(\neq \mathrm{I})} \Bigg\{ & [\lambda| - V_{\mathrm{J}} |\lambda] + \frac{2\beta_{\mathrm{IJ}}}{\sum\limits_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda}} \sum_{\substack{\Lambda \in (\mathrm{I}) \\ v \in (\mathrm{J})}} P_{\Lambda v} \cdot h(\Lambda, v) \\ & + [\lambda^2 | \mu'^2]^{\mathrm{I,J}} \left(P_{\mu'\mu'} - \frac{1}{2 \cdot \sum\limits_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda}} \sum_{\Lambda \in (\mathrm{I})} P_{\Lambda\mu'}^2 \right) \\ & + [\lambda^2 | \lambda'^2]^{\mathrm{I,J}} \cdot \frac{1}{\sum\limits_{\Lambda \in (\mathrm{I})} P_{\Lambda\Lambda}} \sum_{\Lambda \in (\mathrm{I})} \sum_{\Lambda' \in (\mathrm{J})} \left(P_{\Lambda\Lambda} P_{\Lambda'\Lambda'} - \tfrac{1}{2} P_{\Lambda\Lambda'}^2 \right) \Bigg\} . \end{aligned} \tag{8}$$

Again, the notation corresponding to atomic terms is the same as in paper I.

The numerical solution of the total variation problem can be achieved by means of a double iteration procedure, based alternatively on the minimization of the total energy with respect to the linear coefficients of the STO's and to exponents.

3. Evaluation of Integrals

a. Evaluation of Atomic Integrals

In the first paper of this series [7] two alternative parameter schemes were given, differing by the fact that either the effective nuclear charges Z_s and Z_p, or the kinetic factors K_s and K_p were treated as parameters. However, in all the cases that were investigated, it was found that within a uniquely defined molecular parameter scheme, both ground state energies and charge distributions do not differ substantially when calculated according to either the first or the second parameter scheme. Parameter scheme 1 however, seems sounder from a physical point of view and will therefore be used for the discussion and further calculations.

b. Evaluation of Molecular Integrals and Terms

The Coulomb integrals $[\alpha^2|\beta^2]^{\mathrm{I,J}}$ respresenting the interaction between electrons occupying orbitals α and β localized on centers I and J, respectively, are reduced to interactions involving exclusively s atomic orbitals as in the CNDO [4] and INDO [2] methods; the only difference being that, here, the corresponding Slater exponents $a_{\mathrm{I}}(\alpha)$, and $a_{\mathrm{J}}(\beta)$ are optimized.

The two-center electron-core attraction integrals are also calculated as in the CNDO or INDO methods, *i.e.*,

$$[\alpha| V_{\mathrm{J}} |\alpha] = Z_{\mathrm{J}} [\alpha^2 | \eta^2]^{\mathrm{I,J}}, \tag{9}$$

where the α orbital with the varied orbital exponent $a_{\mathrm{I}}(\alpha)$ is centered on atom I and the s orbital η has a fixed exponent a_{av} calculated as a weighted average of the s- and p-atomic exponents a_s^0 and a_p^0, corresponding to the maximum multiplicity of atomic J, *i.e.*,

$$\begin{aligned} K &= \text{Integer}\,(Z_{\mathrm{J}} + 7/6)\,, \\ a_{\mathrm{av}} &= \frac{K \cdot a_s^0 + (Z_{\mathrm{J}} - K)\, a_p^0}{Z_{\mathrm{J}}}\,, \end{aligned} \tag{10}$$

where Z_J is the charge of the core J, equal to 1 for the H atom and equal to the atomic number diminished by 2 for all other atoms. (The numerical values of a_s^0 and a_p^0 are listed in Table 3 of Ref. [7].)

In addition, we define the total core-core interaction as

$$\text{Core-Core inter. terms} = \sum_{I<J}\sum \frac{Z_I Z_J}{R_{IJ}}. \tag{11}$$

A little longer discussion will be needed to estimate the best form of the resonance integrals corresponding to the off-diagonal terms of the ***H*** matrix defined in Eqs. (2) and (3).

Let us first assume that $h(\alpha, \beta)$ can be expressed as

$$h(\alpha, \beta) = -\{a(\alpha) + a(\beta)\}\, S_{\alpha\beta}, \tag{12}$$

where $S_{\alpha\beta}$ is the overlap integral between the corresponding STO functions having optimized exponents $a(\alpha)$ and $a(\beta)$. Such an expression accounts for the geometrical constraint appropriate to the resonance integrals and partly for the nature of orbitals as well. In addition, since all AO's localized on any given centre are orthonormal, only cofactors $\beta_{\alpha\beta}$ for AO's belonging to different atoms have to be considered. As $\beta_{\alpha\beta}$ then depends only on the type of atoms involved, it is possible to write

$$\beta_{\alpha\beta} = \beta_{IJ}.$$

The form of the cofactor β_{IJ} was estimated by comparing calculated and experimental heats of atomization of some diatomic and hydride molecules. However, since there are not enough suitable molecules for an unambiguous determination of all β_{IJ}'s, the fitting procedure was extended to several points of the Morse curves corresponding to a few of these diatomic molecules. The results are collected in Fig. 1 as a function β_{IJ} of the internuclear separation R between atoms I and J. Points corresponding to the same Morse curve are joined by a full tine.

The β-dependence on R for the hydrogen molecule was expressed analytically as

$$\beta_{HH} = F_H(R) + 0.06206, \tag{13}$$

where

$$F_H(R) = 0.12181/(R + 0.18609). \tag{14}$$

These numerical constants were chosen to fit exactly the points of the Morse curve of the H_2 molecule corresponding to the equilibrium distance and to the separations of the hydrogen nuclei of 1.0 and 2.0 a.u. The determination of the β-values for X–H bonds in polyatomic hydrides was carried out using the relationship (13) for the calculation of $H_{\mu\nu}$ elements.

From Fig. 1 it can be seen that for most types of bonds, (see however F_2) the β-values decrease with increasing bond distance along a specific pattern that seems to be describable by an expression such as:

$$\beta_{IJ}(R) = F(R) + C(Z), \tag{15}$$

where

$$\begin{aligned} Z &= Z_I, \quad \text{if} \quad Z_I \geqq Z_J, \\ Z &= Z_J, \quad \text{if} \quad Z_J \geqq Z_I, \end{aligned} \tag{16}$$

$F(R)$ can thus be treated as a common function for all atoms. The constants $C(Z)$ are atomic parameters related for each bond to that atom having from both ones the larger core charge. Two exceptions only seem to violate these rules, the F_2 molecule and the Li_2 molecule, the latter corresponding to fitted values $\beta = 0.0344$ at $R = 4.5$ a.u., $\beta = 0.0374$ at $R = 5.051$ a.u., and $\beta = 0.0393$ at $R = 5.5$ a.u.

Accordingly, two versions of expressing $\beta_{IJ}(R)$ are suggested. In the Version-I no additional specific atomic parameters are introduced at all and we set

$$\beta_{IJ}(R) = F_H(R) + 0.0955 + (Z - Z_C) \cdot 0.016, \tag{17}$$

where Z_C is the charge of the carbon core and Z is defined by means of Eq. (16). We are clearly putting here preference to the hydrocarbons because the value 0.0955 is chosen to fit heats of atomization of hydrocarbons containing one and two carbon atoms. Of course, from Fig. 1 it can be seen that the β-dependence on R given by the functions $F_H(R)$ is not steep enough, at least for all bonds shorter than 2.3 a.u.

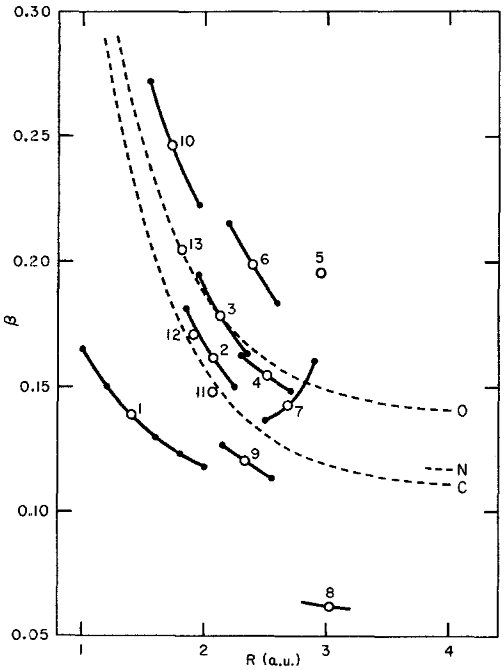

Fig. 1. β parameter as a function of internuclear distance R. Circles correspond to values matching experimental heats of atomization of corresponding molecules, full curves correspond to values fitted by means of Morse curves. (1, H_2; 2, N_2; 3, CO; 4, BeO; 5, LiF; 6, BF; 7, F_2; 8, LiH; 9, BH; 10, FH; 11, CH_4; 12, NH_3; 13, H_2O)

Alternatively, one may select a more appropriate function $F(R)$ for compounds composed of oxygen, nitrogen, carbon and hydrogen such as

$$F(R) = 1.1657 \cdot \exp(-1.5897 \cdot R) \tag{18}$$

and define in addition

$$\begin{aligned} &\mathrm{C}(4) = 0.1090 \text{ (carbon)} \\ &\mathrm{C}(5) = 0.1150 \text{ (nitrogen)} \\ &\mathrm{C}(6) = 0.1390 \text{ (oxygen)}. \end{aligned} \tag{19}$$

The β_{HH} values remain as defined via Eqs. (13) and (14). The dependences of $\beta_{\mathrm{IJ}}(R)$ vs. R defined in this way correspond to Version-II and is represented in Fig. 1 for all three cases by dashed curves. Version-II is thus limited to calculations of molecules containing only hydrogen, carbon, nitrogen and oxygen atoms.

4. Numerical Solution

Since most of the time the numerical solution of the system of equations given by Eqs. (5) and (6) does not converge when a first order iteration process is used, the Crout's [8] modification of the Newton-Raphson procedure was applied for solving the problem. The proper solution of finding the stationary value of the total energy given by Eq. (4) consisted of a double iteration procedure composed successively of one iteration step considering the $\boldsymbol{P}$ matrix as variable with the Slater exponents fixed and of the next iteration step improving the exponents with the $\boldsymbol{P}$ matrix fixed. Of course, for the second iteration step first and second derivatives with respect to Slater exponents of all kinds of integrals are needed. Whereas the expressions of one-centre terms were calculated using analytical forms of the derivatives, all two-centre terms were calculated using numerical derivation, e.g.

$$\frac{\partial f(a,b)}{\partial a} = \frac{f(a+\Delta,b) - f(a-\Delta,b)}{2\Delta}. \tag{20}$$

It was found that such a procedure yields satisfactory numerical results for the derivatives of all integrals using the value $\Delta = 0.01$. A convergence criterion was imposed upon the total energy requiring the energy difference of two successive iteration steps to be smaller than 10^{-5} a.u. In order to get faster convergence for the calculations of molecules C_2N_2 and N_2O the criterion was lowered to 5×10^{-5} a.u.

The initial $\boldsymbol{P}$ matrix was obtained by solving a secular problem in which the $F_{\mu\mu}$ terms were replaced by the average ionization potentials (Table 2, Paper I) and $F_{\mu\nu}$, $(\mu \neq \nu)$ set equal to $H_{\mu\nu}$ calculated with atomic Slater exponents (cf. Table 3 and 4, Paper I).

On several examples of molecular calculations it was verified that the iteration procedure does not depend on the way it proceeds, particularly on the order of iteration steps. In addition, the authors believe that the initial values of Slater exponents taken as atomic ones ensure that this specific solution of the nonlinear system of Eqs. (5) and (6) by means of the proposed procedure is the physically meaningful solution among all possible ones.

All calculations were performed on the UNIVAC 1108 computer using a FORTRAN V program written by the authors.

5. Experimental Data

Most experimental data of both equilibrium geometries and heats of atomization at 0° K (or dissociation energies D_0^0 and eventually other "Morse curve" parameters of diatomics) were taken from JANAF Interim Thermochemical Tables [9]. Only equilibrium geometries of molecules CHN, C_2H_2, C_2H_4, C_2H_6 [10], the heat of atomization at 0° K for ethane [11], data for diatomics LiH and the D_0^0 value for F_2 [13] were taken elsewhere.

6. Results and Discussion

The general method of calculation of ground state properties described in the previous sections has been applied to a number of diatomic and polyatomic molecules as listed in Table 2. First of all, let us stress in comparison with other existing semiempirical all-valence electron methods (CNDO [4], INDO [2], PNDO [5], MINDO [6] *et al.*) that – besides the general function $F(R)$ – only one specific parameter per atom (Version-I) was introduced to extend the atomic SCF theory with "scaled" Slater exponents to molecular structures. The parameter scheme resembles the CNDO-2 or INDO scheme, but no presumptions concerning the values of Slater exponents needed to be made.

Table 1. Equilibrium geometries of calculated polyatomic molecules (in a.u.)

Molecule		Cartesian coordinates		
		x	y	z
H_2O	O	0.0	0.0	0.0
	H1	−1.431571	−1.109440	0.0
	H2	1.431571	−1.109440	0.0
NH_3	N	0.0	0.0	0.721183
	H1	−1.534653	−0.886033	0.0
	H2	1.534653	−0.886033	0.0
	H3	0.0	1.772065	0.0
CH_4	C	0.0	0.0	0.0
	H1	1.190341	1.190341	1.190341
	H2	1.190341	−1.190341	−1.190341
	H3	−1.190341	1.190341	−1.190341
	H4	−1.190341	−1.190341	1.190341
C_2H_2	C1	0.0	0.0	0.0
	C2	2.281	0.0	0.0
	H1	−2.002	0.0	0.0
	H2	4.283	0.0	0.0
CO_2	C	0.0	0.0	0.0
	O1	0.0	0.0	2.195904
	O2	0.0	0.0	−2.195904

Table 1 (continued)

Molecule		Cartesian coordinates		
		x	*y*	*z*
C_2H_4	C1	0.0	0.0	0.0
	C2	0.0	0.0	2.551160
	H1	1.751130	0.0	-1.011015
	H2	-1.751130	0.0	-1.011015
	H3	1.751130	0.0	3.562176
	H4	-1.751130	0.0	3.562176
C_2H_6 (st.)	C1	0.0	0.0	0.0
	C2	0.0	0.0	2.915876
	H1	1.961630	0.0	-0.699148
	H2	-0.980815	1.698822	-0.699148
	H3	-0.980815	-1.698822	-0.699148
	H4	-1.961630	0.0	3.615024
	H5	0.980815	-1.698822	3.615024
	H6	0.980815	1.698822	3.615024
C_2H_6 (ecl.)	C1	0.0	0.0	0.0
	C2			2.915876
	H1	1.961630	0.0	-0.699148
	H2	-0.980815	1.698822	-0.699148
	H3	-0.980815	-1.698822	-0.699148
	H4	1.961630	0.0	3.615024
	H5	-0.980815	1.698822	3.615024
	H6	-0.980815	-1.698822	3.615024
H_2CO	C	0.0	0.0	0.0
	O	2.286613	0.0	0.0
	H1	-1.090096	1.814224	0.0
	H2	-1.090096	-1.814224	0.0
HCN	C	0.0	0.0	0.0
	N	0.0	0.0	2.187
	H	0.0	0.0	-2.0
C_2N_2	C1	0.0	0.0	0.0
	C2	0.0	0.0	2.607872
	N1	0.0	0.0	-2.186455
	N2	0.0	0.0	4.794328
N_2O	N1	0.0	0.0	0.0
	N2	0.0	0.0	2.132030
	O	0.0	0.0	4.369887
HNO	H	0.0	-1.927558	0.0
	N	0.0	0.0	0.0
	O	2.131951	0.967994	0.0
HNO_2 *cis*	H	1.804502	-0.41602	0.0
	N	0.0	2.759053	0.0
	O1	0.0	0.0	0.0
	O2	2.071661	3.681416	0.0
O_3	O1	0.0	0.0	0.0
	O2	2.415117	0.0	0.0
	O3	-1.088921	2.155700	0.0

Table 2. Heats of atomization (in a.u.)

Molecule	Exptl.	INDO	Version-I	Version-II
H_2	0.1746	0.1972	0.1746	0.1746
Li_2	0.0419	0.5037	0.1131	—
LiH	0.0942	0.2098	0.1419	—
BH	0.1300	0.3437	0.1541	—
F_2	0.0594	0.2133	0.1716	—
HF	0.2247	0.2114	0.0829	—
LiF	0.2186	−0.0756	0.1766	—
BeO	0.1723	0.1876	0.2990	0.2136
BF	0.2980	0.3744	0.2521	—
CO	0.4125	0.7043	0.4281	0.4124
N_2	0.3639	0.7279	0.4002	0.3254
H_2O	0.350	0.445	0.228	0.350
BH_3	0.345–0.414	1.081	0.464	
NH_3	0.441	0.772	0.428	0.445
CH_4	0.625	1.371	0.671	0.717
C_2H_2	0.618	1.689	0.685	0.673
C_2H_4	0.846	2.125	0.841	0.816
C_2H_6 (st.)	1.063	2.602	1.021	1.008
C_2H_6 (ecl.)		2.598	1.008	0.996
O_3	0.227	0.797	0.454	0.363
CH_2O	0.571	1.235	0.568	0.547
CHN	0.482	1.153	0.605	0.519
$(CN)_2$	0.782	2.220	—	0.756
CO_2	0.608	1.148	0.661	0.597
N_2O	0.402	1.102	0.469	0.418
HNO	0.317	0.762	—	0.391
HNO_2 *cis*	0.476	1.118	—	0.578

Heats of atomization calculated from our theory are shown in Table 2. It may be seen that the method, particularly its Version-II, works fairly well and its results compare much better to experimental values than the regular INDO-type calculations. Moreover, equilibrium distances come out very well, as can be seen from Fig. 2 and Fig. 3, where a few types of dependences of heats of formation on geometry variations are presented. These results seem to be very encouraging, since the correct energy – bond distance relationship was lacking in all semi-empirical methods described previously, unless ample parametrization is performed [14, 6].

On comparing the results of Table 3, concerning the frontier orbitals, with known experimental ionization potentials [15, 16], it may be noticed that the orbital energies of the highest occupied molecular orbital are bad estimates of the ionization potentials. This effect, of course, could have been expected, since the variation of orbital exponents might only violate the validity of the Koopmans' theorem. If correct theoretical ionization potentials were to be calculated, the exponents of the ionized state would also have to be optimized.

Due to similar reasons *i.e.*, orbital exponents variation, it is also hard to draw relevant conclusions from a conventional "population analysis" procedure based on the charges listed in Table 3. The charges cannot be assigned entirely

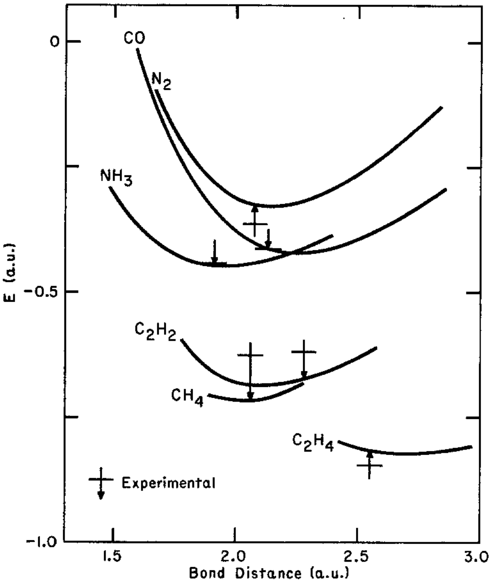

Fig. 2. Heats of atomization as functions of bond distances. Experimental values corresponding to equilibrium geometries are represented by points of intersection of horizontal and vertical lines. For molecules C_2H_2 and C_2H_4, the C–C bond is varied. In all cases of bond variation the equilibrium symmetry has been retained

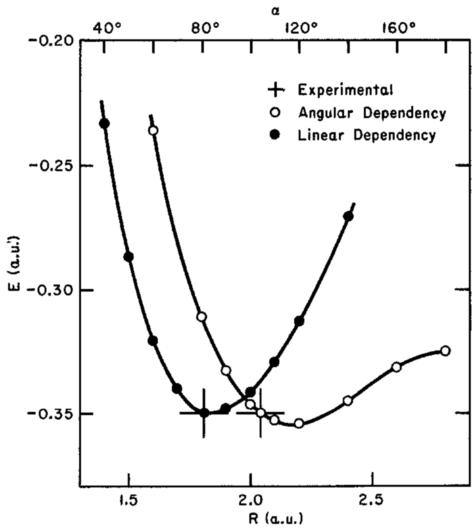

Fig. 3. Heat of atomization of water molecule plotted versus OH bond distance (at the equilibrium bond angle), A, and bond angle (at equilibrium OH bond distance), B, respectively. Experimental values are represented by points of intersection of horizontal and vertical lines

Table 3. Frontier orbital energies (in a.u.), charge densities and optimized exponents (calculated by mean of Version-II)

Molecule	ε_h	ε_l	Atom	P_{vv}				$a(s)$	$a(p)$
				s	p_x	p_y	p_z		
CO	−0.5018	0.1235	C	1.78	0.92	0.58	0.58	2.15	1.55
			O	1.82	1.48	1.42	1.42	2.12	1.95
N_2	−0.5367	0.0845	N	1.80	1.20	1.0	1.0	2.41	1.70
H_2O	−0.6132	0.3777	O	1.78	1.40	1.62	2.0	2.60	1.90
			H	0.60	—	—	—	1.28	—
NH_3	−0.5825	0.2868	N	1.61	1.40	1.40	1.79	2.17	1.58
			H	0.60	—	—	—	1.20	—
CH_4	−0.6762	0.2388	C	1.39	1.45	1.45	1.45	1.83	1.31
			H	0.56	—	—	—	1.11	—
C_2H_2	−0.5554	0.1309	C	1.28	0.95	1.0	1.0	2.11	1.50
			H	0.76	—	—	—	1.12	—
CO_2	−0.6390	0.1106	C	1.08	0.54	0.54	0.69	2.35	1.82
			O	1.88	1.73	1.73	1.23	2.65	1.92
C_2H_4	−0.4691	0.1281	C	1.25	1.08	1.0	0.98	2.09	1.55
			H	0.84	—	—	—	1.07	—
C_2H_6 (st.)	−0.4803	0.1523	C	1.205	1.103	1.103	0.992	2.061	1.57
			H	0.866	—	—	—	1.045	—
C_2H_6 (ecl.)	−0.4786	0.1544	C	1.203	1.096	1.096	0.989	2.068	1.57
			H	0.872	—	—	—	1.044	—
H_2CO	−0.4692	0.0920	C	1.22	0.86	0.98	0.62	2.18	1.62
			O	1.87	1.24	1.93	1.38	2.66	1.93
			H	0.95	—	—	—	1.06	—
HCN	−0.5787	0.0975	C	1.31	0.91	0.91	1.00	2.15	1.48
			N	1.83	1.09	1.09	1.04	2.40	1.64
			H	0.82	—	—	—	1.06	—
C_2N_2	−0.5296	0.0219	C	1.30	0.84	0.84	0.85	2.17	1.58
			N	1.84	1.16	1.16	1.02	2.36	1.64
N_2O	−0.6638	−0.0806	N1	1.86	1.30	1.30	0.79	2.40	1.68
			N2	1.41	0.90	0.90	0.87	2.53	1.77
			O	1.89	1.81	1.81	1.17	2.48	1.76
HNO	−0.4835	0.0231	H	0.85	—	—	—	1.17	—
			N	1.77	1.08	1.23	0.72	2.42	1.78
			O	1.90	1.40	1.78	1.28	2.68	1.92
HNO_2	−0.5518	0.0194	H	0.58	—	—	—	0.96	—
			N	1.88	0.90	0.67	0.55	2.58	1.95
			O1	1.85	1.56	1.57	1.93	2.60	1.88
			O2	1.90	1.45	1.67	1.52	2.62	1.96
O_3	−0.5939	−0.1209	O1	1.87	1.19	1.28	0.95	2.83	2.12
			O2	1.95	0.92	1.95	1.53	2.66	1.95
			O3	1.95	1.66	1.21	1.53	2.66	1.95

to specific centers anymore since the orbitals vary in size from molecule to molecule and the corresponding density functions may have their maxima at different distances from the nucleus. In addition, it is known from *ab initio* calculations that an energy optimization with respect to orbital exponents mostly leads to a deterioration of values of dipole moments [17].

In conclusion, we should like to express that we are aware of the fact that there might exist other better molecular parameter schemes for incorporating our basic ideas developed in Paper I, that is the proper consideration of atomic environment and atomic contributions to electron correlation. From that point of view, this paper has thus to be considered as preliminary.

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