Semiempirical SCF Theory with "Scaled" Slater Orbitals

I. Atoms

G. KLOPMAN and R. POLÁK[*]

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, USA

A self consistent quantum mechanical treatment of atomic structures is presented. The method which is suitable for molecular calculations involves the optimization (scaling) of exponents of a minimal basis set of Slater orbitals and accounts semiempirically for electron correlation.

The calculation of successive ionization potentials as well as that of promotional energies lead to results in satisfactory agreement with experiment.

Es wird ein selbstkonsistentes quantenmechanisches Verfahren für Atomstrukturen entwickelt, das auch für Moleküle geeignet ist, und eine Optimierung ("scaling") der Exponenten von Slater-orbitalen in einem minimalen Satz der Basisvektoren sowie eine semiempirische Berücksichtigung der Elektronenkorrelation beinhaltet.

Die berechneten Ionisierungs- und Anregungsenergien stimmen gut mit den experimentellen Werten überein.

Un traitement quantique self consistent des structures atomiques est décrit. La méthode qui est aussi valable pour le calcul des molécules introduit l'optimalisation (scaling) des exposents d'un "minimal basis set" d'orbitales de Slater et prend en considération la correlation électronique d'une manière semi empirique.

Le calcul des potentiels d'ionisations successifs ainsi que celui des énergies de promotion conduit a des résultats en accord satisfaisant avec l'expérience.

The various integrals appearing in "all valence electrons" methods may conveniently be classified in three categories depending on how many centers they involve.

a) The one center integrals include the core attraction integral, the electron repulsion and exchange integrals and the kinetic term.

b) The two center integrals consist of core or penetration integrals, resonance integrals, electron repulsion and various types of exchange integrals.

c) The three and four center integrals, which are sometimes approximated in terms of two center integrals but often completely neglected.

The purpose of this paper is to present a critical discussion of the various factors affecting the one center integrals and a consistent method for evaluating them in complex atomic structures.

A semiempirical method designed for the "accurate" calculation of the energies of atomic structure would probably be welcomed but have only a relatively minor interest unless it may be inserted into a more sophisticated molecular model.

* Present address: Institute of Physical Chemistry, Czechoslovak Academy of Science, Machova ul 7, Praha 2, Czechoslovakia.

Our objective therefore was to develop a theory of atomic structure for the specific purpose of including it into a molecular program. Part I of this series deals with the atomic procedure and Part II describes the subsequent molecular method.

1. Introduction

Most so called "all valence electrons" methods [1] make use of almost identical approximations for evaluating the one center "atomic terms". They consist essentially in determining from the known atomic spectra a set of parameters representing the various one center integrals [2] or "experimental" Slater-Condon parameters [3]. The values of these parameters are such that, when used in the appropriate atomic theory, they reproduce both valence state ionization potentials and electron affinities. The main difference between the various available produres is, in addition to the type of parameters used, the way in which the bary-centers [2] of the atomic states are chosen, i.e. the definition of the valence state.

Unfortunately, none of these methods give satisfactory values for partly ionized atoms and the atomic parameters are apparently valid only within the range in which they have been determined. The reason for this failure can almost certainly be attributed to the relative contraction of the atomic orbitals upon ionization and it was shown that if such modification of orbital size is taken, even empirically, into account [4] the results can be greatly improved. This fact underlines the importance of the environment upon the magnitude of the various integrals and casts some doubts about the adequacy of the common practice of incorporating atomic parameters into molecular programs without any further modification [5, 6].

It seems thus reasonable to investigate the importance of orbital size variation in isolated atoms and, if an appropriate method can be found to handle the problem, include it into molecular SCF calculations. The resulting program would allow us to estimate the appropriate atomic integrals within their molecular environment.

Two alternate routes are available to us for such improvement. One consists in the widely used method of expanding the basis set. This procedure, however, presents numerous problems when incorporated into a semiempirical molecular framework by increasing the number of disposable parameters. In addition, it does not guarantee that the atomic functions contributing most to the atomic structure remain preponderant in the molecular combinations.

Another solution can be attained by allowing the orbitals exponents to vary freely, so as to minimize the total energy. By successive iterations, self consistent "scaled" exponents can then be obtained that reflect the change in orbital size due to the atomic environment. The advantage of such a scheme is that it does not, in principle, require additional parameters when it is incorporated into a molecular program.

We thus choose to follow the latter procedure and found that the minimization of the total energy with respect to each of these exponents can be carried out in a simple and efficient way.

2. Theory

The problem thus consists in developing a semiempirical theory of atomic structure including the variation of exponents of a minimal basis set of Slater orbitals. The theory should be suitable for use in SCF LCAO MO treatment of molecules. As given below, it deals specifically with first and second row elements assuming that only valence electrons are explicitly taken into account. Since our final objective is the calculation of molecular quantities we will reduce the total atomic energy expression to the averaged form, or barycenter, which corresponds to the weighted mean of all the multiplets in the given configuration (m, n) of m s-electrons and np-electrons [7].

$$
\begin{aligned}
E(m, n) = {} & m \left\{ \frac{a^2}{K_s} - \frac{Z_s}{N_s} a \right\} + n \left\{ \frac{b^2}{K_p} - \frac{Z_p}{N_p} b \right\} \\
& + 1/2\, m(m-1)\, [s_a^2 | s_a^2] + m \cdot n \{ [s_a^2 | p_b^2] - 1/2\, [s_a p_b | s_a p_b] \} \\
& + 1/2\, n(n-1)\, [px_b^2 | py_b^2] .
\end{aligned}
\tag{1}
$$

The first two brackets in Eq. (1) contain one-electron terms consisting of both kinetic energy and core attraction contributions. They are expressed in terms of:

  — Slater exponents a and b corresponding to s and p atomic orbitals, respectively,

  — kinetic factors K's theoretically equal to 2., 6., and 2. for the atomic orbitals $(1s)$, $(2s)$ and $(2p)$, respectively,

  — effective charges Z's, and,

  — principal quantum numbers N's.

The notation of the two-electron integrals assumes that orbitals being functions of the same electron are on one side of the bracket. Their value can be expressed in the usual manner in terms of Slater-Condon parameters [8] as follows

$$
\langle s_a^2 | s_b^2 \rangle = \langle s_a^2 | p_b^2 \rangle = F^0
$$

$$
\langle px_a^2 | px_b^2 \rangle = F^0 + \frac{4}{25} F^2
$$

$$
\langle px_a^2 | py_a^2 \rangle = F^0 - \frac{2}{25} F^2
\tag{2}
$$

$$
\langle px_a py_b | px_a py_b \rangle = \frac{3}{25} F^2
$$

$$
\langle 2s_a px_b | 2s_a px_b \rangle = \frac{1}{3} G^1
$$

The condition for optimization of the energy expression (1) with respect to the Slater exponents a and b

$$
\frac{\partial E(m, n)}{\partial a} = \frac{\partial E(m, n)}{\partial b} = 0
\tag{3}
$$

leads to the system of equations

$$a = 0.5 \cdot K_S \left\{ \frac{Z_S}{N_S} + 0.5(1-m) \cdot A + n \left(0.5 \frac{\partial}{\partial a} [s_a p_b | s_a p_b] - \frac{\partial}{\partial a} [s_a^2 | p_b^2] \right) \right\}$$

$$b = 0.25 \cdot K_p \left\{ Z_p + (1-n) B + m \left(\frac{\partial}{\partial b} [s_a p_b | s_a p_b] - 2 \frac{\partial}{\partial b} [p_b^2 | s_a^2] \right) \right\} \tag{4}$$

where A and B are numerical constants related to two-electron integrals involving STO's [9] as follows

$$[s_a^2 | s_a^2]_{\text{theor}} = aA$$

$$[p_{xb}^2 | p_{yb}^2]_{\text{theor}} = bB \tag{5}$$

A being equal to 0.625 and 0.363281 in case of (1s) and (2s) orbitals respectively and B to 0.349219.

Of course, even such variational procedure with theoretical integrals does not bring the calculated energy values satisfactorily close to experimental ones and, therefore, an additional introduction of parameters is necessary. The corrections may affect one and two-electrons integrals because of the following reasons.

One Electron Integrals

The theoretical value of the kinetic factor K_s corresponding to a 2s Slater orbital is equal to 6 and thus very large in comparison with that of the 2s hydrogen-like functions where it is equal to 2.; it is the only case among the atomic orbitals of the considered limited basis set where such a discrepancy arises. However, since STO's may be considered as one-electron eigenfunctions [10] of a central field problem with the potential given by

$$V(r) = -\frac{Z_{\text{eff}}}{r} + \frac{n^*(n^*-1)}{2r^2} \tag{6}$$

where Z_{eff} and n^* are the effective nuclear charge and effective principal quantum number, respectively, a term depending on the square of the Slater exponent should be naturally added. Furthermore, if a screening model is adopted, the effective charges Z_s and Z_p should not necessarily be equal in Eq. (1). Accordingly, two sets of parameters can and were left free for the fitting procedure. Either K_s and K_p (with theoretical values for $Z_s = Z_p$) or Z_s and Z_p (assuming that $K_s = K_p = 2$) will be fitted.

Two-Electrons Integrals

Many kinds of semiempirical theories show that the theoretical values of the one-center electron-electron repulsion terms are overestimated [11]. It seems evident that the main reason for the discrepancy is due to electron correlations and that the electron correlation is not satisfactorily accounted for even in the calculation of one-center electron Coulomb interaction integrals. In order to correct for this, we followed a procedure analogous to that proposed by Clementi [12] that consists in introducing the "Coulomb hole" as in the following way.

Table 1. *Correlation energies as function of orbital size for the $1s^2$-isoelectronic series*[a]

Element	E_{Corr}^{eV}
He	-1.14
Li$^+$	-1.18
Be^{2+}	-1.19
B^{3+}	-1.20
C^{4+}	-1.20

[a] Fröman, A.: Rev. mod. Physics **32**, 317 (1960).

In the calculations of the regular electron-electron Coulomb interaction integral, both electron distributions are considered as unaffected by each other. This situation does not reflect correctly the physical situation when the electrons are located in the same space region. For the sake of simplicity let us assume that we are dealing with a couple of electrons occupying each a spherically symmetric space corresponding to Slater type orbitals ($N_a S_a$) and ($N_b S_b$), respectively. The Coulomb energy corresponding to the interaction of two electronic fractions occupying each the spherical shell defined by means of the radii $R(1-\delta)$ and $R(1+\delta)$ (δ being a free parameter) is given by

$$I(R) = C' \int_{R(1-\delta)}^{R(1+\delta)} r_1^{2N_a} e^{-2ar_1} dr_2 \left[\frac{1}{r_1} \int_{r_1(1-\delta)}^{r_1} r_2^{2N_b} \cdot e^{-2br_2} dr_2 + \int_{r_1}^{r_1(1+\delta)} r_2^{2N_b-1} e^{-2br_2} dr_2 \right] \quad (7)$$

$$= 4\delta^2 \cdot C \cdot e^{-2(a+b)R} \cdot R^{2(N_a+N_b)+1}$$

where

$$C = \frac{(2a)^{2N_a+1}(2b)^{2N_b+1}}{(2N_a)!\,(2N_b)!}. \quad (8)$$

It may be expected that the sum of all these situations expressed as

$$\text{Corr} = \int_0^\infty I(R)\,dR = 4\delta^2 \frac{[2(N_a+N_b)+1]!}{(2N_a)!\,(2N_b)!} \cdot \frac{a^{2N_a+1}b^{2N_b+1}}{(a+b)^{2(N_a+N_b+1)}} \quad (9)$$

is a measure of the quantity by which the atomic two-electron integrals could be corrected

$$\langle aa/bb \rangle = \langle aa/bb \rangle_{\text{theor}} - \text{Corr}. \quad (10)$$

For the case where one deals with interactions of electron belonging to the same shell i.e.: $N_a = N_b = N$, this expression reduces to

$$\text{Corr} = 4\delta^2 \frac{(4N+1)!}{(2N)!\,(2N)!} \frac{(ab)^{2N+1}}{(a+b)^{2(2N+1)}} \quad (11)$$

and by setting $(a-b)/(a+b) = \tau$ one finally obtains

$$\text{Corr} = \frac{1}{2^{4N}} \delta^2 \frac{(4N+1)!}{(2N!)^2} (1-\tau^2)^{2N+1} \quad (12)$$

$$= f^0 (1-\tau^2)^{2N+1} \quad (13)$$

where f^0 may be considered to a first approximation as being a constant for any given atomic shell irrespective of its occupancy and orbital exponents. The Slater Condon parameter F^0 then becomes

$$F^0 = \langle s_a s_a | s_b s_b \rangle = \langle s_a s_a | s_b s_b \rangle_{\text{theor}} - f^0 (1 - \tau^2)^{2N+1} . \tag{14}$$

Apparently the function 13 has interesting limit properties. First, if the size of both orbitals is equal $(a = b, \tau^2 = 0)$, the correction is a constant one and does not depend on the size of the orbitals; secondly, the bigger the difference between the sizes of the two orbitals, the smaller the correction term is. The latter conclusion corresponds to what intuitively one would have predicted for the correlation of electrons belonging to orbitals of increasingly different sizes. The former one, perhaps somewhat more surprising, can however be verified for $1s^2$ isoelectronic series where the correlation energy is found to be practically independent of the size of the $1s$ orbital (Table 1). Finally, let us assume that a similar correction scheme can also be applied to the other components of the integrals in our calculation

$$\left.\begin{aligned} F^0_{(a,b)} &= F^0_{(a,b)\text{theor}} - f^0 (1 - \tau^2)^{2N+1} \\ F^2_{(a,b)} &= F^2_{(a,b)\text{theor}} - f^2 (1 - \tau^2)^{2N+1} \\ G^1_{(a,b)} &= G^1_{(a,b)\text{theor}} - g^1 (1 - \tau^2)^{2N+1} \end{aligned}\right\} \tag{15}$$

so that, combining Eq. (2) and (15), the expression for the various integrals becomes

$$\left.\begin{aligned} [(1s)^2 | (1s)^2]_I &= F^0_{(a,a)\text{theor}} - f^0_I \\ [(2s)^2 | (2s)^2]_I &= F^0_{(a,a)\text{theor}} - f^0_I \\ [(p_x)^2 | (p_x)^2]_I &= F^0_{(a,a)\text{theor}} - f^0_I + \frac{4}{25} [F^2_{(a,a)\text{theor}} - f^2_I] \\ [(p_x)^2 | (p_y)^2]_I &= F^0_{(a,a)\text{theor}} - f^0_I - \frac{2}{25} [F^2_{(a,a)\text{theor}} - f^2_I] \\ [(p_x)(p_y) | (p_x)(p_y)]_I &= \frac{3}{25} [F^2_{(a,a)\text{theor}} - f^2_I] \\ [(2s_a)^2 | (p_b)^2]_I &= F^0_{(a,b)\text{theor}} - f^0_I (1 - \tau^2)^5 \\ [(2s_a)(p_b) | (2s_a)(p_b)]_I &= \frac{1}{3} [G^1_{(a,b)\text{theor}} - g^1_I (1 - \tau^2)^5] \end{aligned}\right\} \tag{16}$$

where f^0_I, f^2_I and g_I are parameters to be adjusted for each specific atom I.

3. Calculation of Derivatives of One-Center Coulomb Integrals

The minimization of the atomic energy with respect to the orbital exponents requires the calculation of first derivatives of one-center Coulomb integrals and, if the second order iteration process for the solution of the system of Eqs. (4) is used, even the calculation of corresponding second derivatives. We found that a convenient method of performing these calculations can be made based on the following observations.

The one-center Coulomb Integrals $I(a, b)$ can be expressed in the product form [9]

$$I(a, b) = \xi \cdot G(\tau) \tag{17}$$

$G(\tau)$ being an even function in τ and

$$\xi = \frac{1}{2}(a + b)$$
$$\tau = \frac{a - b}{a + b}, \tag{18}$$

it is convenient to use the relations

$$\frac{\partial I}{\partial a} = \frac{1}{2}\left[(1 - \tau)\frac{dG(\tau)}{d\tau} - G(\tau)\right], \tag{19}$$

where $dG(\tau)/d\tau$ is an odd function of τ. Because of (17), (18) and (19), one finally also obtains:

$$I = a\frac{\partial I}{\partial a} + b\frac{\partial I}{\partial b}. \tag{20}$$

In this interesting equation, representing the Coulomb repulsion between two electrons, $\partial I/\partial a$ can be interpreted as the screening of the electron in orbital of exponent a by that in orbital of exponent b and $\partial I/\partial b$ as the screening of the electron in orbital b by that in a. The relationship is apparently general and valid irrespective of the type of orbitals involved. Furthermore, when the Coulomb integral is evaluated via the associated Legendre polynomial method.

$$F^k = N a^{3+\nu} b^{3+\mu} \int\limits_0^\infty \int\limits_0^\infty \frac{r_<^k}{r_>^{k+1}} e^{-2ar_1} e^{-2br_2} r_1^{2+\nu} r_2^{2+\mu} dr_1 dr_2 \tag{21}$$

where N is a normalization constant, ν and μ depend on the type of orbitals and k on the Legendre polynomial term,

$$\begin{aligned} F^k = N a^{3+\nu} b^{3+\mu} &\left[\int\limits_0^\infty e^{-2ar_1} r_1^{\nu-k+1} dr_1 \int\limits_0^{r_1} e^{-2br_2} r_2^{\mu+k+2} dr_2 \right.\\ &\left.+ \int\limits_0^\infty e^{-2ar_1} r_1^{\nu+k+2} dr_1 \int\limits_{r_1}^\infty e^{-2br_2} r_2^{\mu-k+1} dr_2\right] \end{aligned} \tag{22}$$

$$= N a^{3+\nu} b^{3+\mu}[\alpha + \beta]. \tag{23}$$

It was found that

$$\frac{\partial F^k}{\partial a} = N a^{2+\nu} b^{3+\mu} \alpha$$
$$\frac{\partial F^k}{\partial b} = N a^{3+\nu} b^{2+\mu} \beta. \tag{24}$$

In other terms, in the process of calculating F^k, its derivative with respect to a and b are normally evaluated and can be stored for use in the minimization

procedure. Finally the second derivatives can be obtained, when necessary, by the following equations:

$$\frac{\partial^2 I}{\partial a^2} = \frac{1}{4\xi} (1 - \tau)^2 \frac{d^2 G(\tau)}{d\tau^2}$$

$$\frac{\partial^2 I}{\partial a \partial b} = \frac{1}{4\xi} (\tau^2 - 1) \frac{d^2 G(\tau)}{d\tau^2}. \tag{25}$$

4. Calibration of Parameters and Results

The most important energy properties which should be reproduced by calculation are the ionization potentials of both s- and p-electrons, and the electron affinity. The experimental data [13, 14, 3] have, of course, to be corrected to transitions between average states; These have been computed and are collected in Table 2. The corresponding corrections to electron affinities were determined by isoelectronic extrapolation [15].

In addition to the above, the term splitting corresponding to individual electron configurations of neutral atoms should be reproduced as closely as possible. This can be achieved by fitting values of the Slater-Condon parameters F^2_{exp} and G^1_{exp} [16, 8] determined from the experimentally observed splittings.

$$f^2 = F^2_{theor} - F^2_{exp} \tag{26}$$

where

$$F^2_{theor} = \frac{25}{6} \{ [(p_x)^2 | (p_x)^2]_{th} - [(p_x)^2 | (p_y)^2]_{th} \} \tag{27}$$

and

$$g^1 = (G^1_{theor} - G^1_{exp})(1 - \tau^2)^5 \tag{28}$$

where

$$G^1_{theor} = 3[(2s_a)(p_b)/(2s_a)(p_b)]_{theor}. \tag{29}$$

The following properties have thus been fitted exactly for each atom.

1. Energy necessary to remove a p electron from the neutral atom (transition between barycenters).

Table 2. *"Experimental" transition energies (in a.u.) for first and second row elements*

Atom	T $(m_1, n_1) - (m_2, n_2)$	E	T	E	T	E
H	(1, 0) − (0, 0)	0.5000	(2, 0) − (1, 0)	0.0276		
Li	(1, 0) − (0, 0)	0.1982	(0, 1) − (0, 0)	0.1302	(2, 0) − (1, 0)	0.0301
Be	(2, 0) − (1, 0)	0.3426	(1, 1) − (1, 0)	0.2190	(2, 1) − (2, 0)	−0.0070
B	(2, 1) − (1, 1)	0.5162	(2, 1) − (2, 0)	0.3049	(2, 2) − (2, 1)	0.0011
C	(2, 2) − (1, 2)	0.7143	(2, 2) − (2, 1)	0.3920	(2, 3) − (2, 2)	0.0175
N	(2, 3) − (1, 3)	0.9400	(2, 3) − (2, 2)	0.4849	(2, 4) − (2, 3)	0.0617
O	(2, 4) − (1, 4)	1.1898	(2, 4) − (2, 3)	0.5823	(2, 5) − (2, 4)	0.0882
F	(2, 5) − (1, 5)	1.4764	(2, 5) − (2, 4)	0.6856	(2, 6) − (2, 5)	0.1286

2. Energy necessary to remove an s electron from the neutral atom (transition between barycenters).

3. Energy gained by adding an electron to the neutral atom (transition between barycenters).

In addition, the g^1 parameter was fitted via Eq. (28).

Two alternative parameter schemes have been followed. The first one uses theoretical values for Z_s and Z_p assuming complete screening by inner electrons. The parameters here were chosen to be K_s, K_p, f_I^0 and g_I^1. The second one assumed constant values for $K_s = K_p = 2$ and determines Z_s, Z_p, f_I^0 and ϑ_I^1. In both cases, satisfactory values for f_I^2 were obtained by setting

$$f_I^2 = f_I^0 \cdot x \tag{30}$$

where x was found satisfactorily constant for all atoms under investigation and equal to 1.3293 for the first scheme and 1.5734 for the second one. The procedure consist in determining the value of the parameters that fit exactly the above energy criteria. The orbital exponents are optimized separately for every atomic electron configuration (m, n) but the values of F_{theor}^2 and G_{theor}^1 are calculated using the exponents obtained for the electronic configuration corresponding to the ground state. No experimental data being available for the p orbital of Li, its g^1 term was arbitrarily set equal to 0. In the case of Beryllium the g^1 term was determined by extrapolation from the higher elements. For Li and Be, the optimized p exponents are those which were obtained from the calculation of the first excited state.

Table 3. *Parameter scheme* 1

Atom	K_s	K_p	f_I^0	g_I	G.S. energy (a.u.)	exp-s	exp-p
H	2.0		0.05494		$-$ 0.5	1.0	
Li	3.1712	2.0832	0.06760	0	$-$ 0.1982	0.793	
Be	3.10198	2.23250	0.079379	0.158757	$-$ 1.1181	1.269	
B	2.90671	2.29276	0.061739	0.123972	$-$ 2.8972	1.762	1.222
C	2.69493	2.18108	0.062439	0.129135	$-$ 5.8029	2.168	1.514
N	2.46072	2.01729	0.067781	0.104988	$-$ 9.8589	2.443	1.741
O	2.36219	1.97437	0.069712	0.088401	$-$15.6940	2.791	2.031
F	2.26770	1.92086	0.073332	0.054714	$-$23.3323	3.094	2.297

Table 4. *Parameter scheme* 2

Atom	Z_s	Z_p	f_I^0	g_I	G.S. energy (a.u.)	exp-s	exp-p
H	1.0		0.05494		$-$ 0.5	1.0	
Li	1.2592	1.0206	0.02763	0	$-$ 0.1982	0.630	
Be	2.37426	2.06071	0.036229	0.108687	$-$ 1.0472	1.005	
B	3.42020	3.06592	0.034802	0.098034	$-$ 2.6759	1.396	1.151
C	4.42748	4.03767	0.043516	0.109296	$-$ 5.4484	1.766	1.464
N	5.35137	4.92844	0.063792	0.100488	$-$ 9.4525	2.085	1.742
O	6.33525	5.89373	0.071209	0.090036	$-$15.2332	2.436	2.052
F	7.28917	6.83005	0.082568	0.065736	$-$22.9098	2.766	2.349

Table 5. *Comparison of experimental and calculated atomic energies (in a.u.) (Parameter scheme 1 was used throughout the calculations)*

Config. (m, n)	(1, 0)	(2, 0)	(2, 1)	(2, 2)	(2, 3)	(2, 4)	(2, 5)	(2, 6)	(1, e)	Separation of the average and lowest term energy
Atom Exp. energy Calc. energy										
Be										
e = 1	−0.6692 −0.7755	− 1.0118 − 1.1181	− 1.0048 − 1.1111						− 0.8882 − 0.9945	—
B										
e = 1	−1.3939 −1.6350	− 2.3184 − 2.5878	− 2.6233 − 2.8927	− 2.6244 − 2.8938					− 2.1071 − 2.3765	— —
C										
e = 2	−2.3701 −2.6949	− 4.1295 − 4.5177	− 5.0255 − 5.3890	− 5.4175 − 5.7810	− 5.4350 − 5.7985				− 4.7032 − 5.0667	0.0220 0.0220
N										
e = 3	−3.5973 −3.8449	− 6.4444 − 6.6807	− 8.1872 − 8.2962	− 9.2425 − 9.2942	− 9.7274 − 9.7811	− 9.7891 − 9.8428			− 8.7874 − 8.8411	0.0832 0.0777
O										
e = 4	−5.0757 −5.3149	− 9.2616 − 9.4513	− 12.1054 − 12.0658	− 14.0814 − 13.9123	− 15.3014 − 15.0799	− 15.8837 − 15.6622	− 15.9719 − 15.7504		− 14.6939 − 14.4724	0.0342 0.0317
F										
e = 5	−6.8055 −6.9448	− 12.5810 − 12.5587	− 16.7771 − 16.3595	− 19.9302 − 19.2493	− 22.1406 − 21.3162	− 23.5287 − 22.6467	− 24.2143 − 23.3323	− 24.3429 − 23.4609	− 22.7379 − 21.8559	— —

In both schemes, good convergence was obtained and the parameters which were found to produce the best results are given in Table 3 for Scheme 1 and Table 4 for Scheme 2. These tables list also the calculated total energies and optimized exponents for the atomic ground states. Both schemes lead to satisfactory calculations of total energies of the various oxidized states of the atoms although Scheme 1 seems to provide slightly better values. Scheme 1 in contrast to Scheme 2 leads to reasonably constant values for the f_1^0 terms and this agrees better with our initial appraisal of the correlation effect. Scheme 1 was thus adopted for further calculations.

The "average" energies for all electronic configurations of the atoms calculated with scheme 1 are compared to the "experimental" ones in Table 5. The electron configuration $(1s)^2$ is considered to define the zero energy level and the relevant "experimental" values to which they correspond were determined from Ref. [13] and [16]. The table also includes the energy separation between the barycenter and the lowest term state of the neutral atom. As can be seen from this table, the agreement between the calculated and experimental energies seem reasonable. A more appropriate evaluation of the method can be made as in Table 6, where its results for successive ionization potentials of fluorine are compared to other ones reported in the literature.

From the comparison, it is clear that our results including exponents variation are far superior to the previous ones and this, in spite of the fact that the number of parameters does not exceed that of the other methods. The only other method that gave equivalent results is the 5 parameter procedure (column 4, Table 6) which took empirically also into consideration the orbital size variation. Unfortunately, that method was not general enough to be used in molecular calculations as it accounts for orbital size variation produced only by the atomic electronic occupancy and not be eventual neighbors.

Table 6. *Successive ionization potentials of fluorine (in e.V.)*

Ionization process (between barycenters)	Klopman[a] 4 Par. PNDO (1964)	Pople and Segal[b] 3 Par. CNDO (1965)	Klopman[c] 5 Par. (1965)	Oleari et al.[d] 6 Par. (1966)	Sichel and Whitehead[e] 4 Par. (1967)	This work 4 Par.	exp.[f]
$s^2 p^6 \to s^2 p^5$	3.48	− 1.76	3.48	3.82	3.55	3.48	3.48
$s^2 p^5 \to s^2 p^4$	18.66	23.92	18.66	18.73	18.61	18.66	18.66
$s^2 p^4 \to s^2 p^3$	33.8	—	36.9	33.4	37.7	36.2	37.8
$s^2 p^3 \to s^2 p^2$	49.0	—	58.1	48.8	47.7	56.2	60.2
$s^2 p^2 \to s^2 p$	64.2	—	82.2	63.5	63.8	78.6	85.8
$s^2 p \to s^2$	79.4	—	111.8	78.4	78.83	103.4	114.2
$s^2 \to s$	114.2	—	159.3	114.0	114.5	152.8	157.2
$s \to -$	130.2	—	193.6	131.0	129.5	189.0	185.2

[a] Ref. [2].
[b] Calculated from data in Ref. [5].
[c] Ref. [4].
[d] Oleari, L., DiSipo, L., DeMichelis, G.: Molecular Physics **10**, 97 (1966).
[e] Sichel, J. M., Whitehead, M. A.: Theoret. chim. Acta (Berl.) 7, 32 (1967).
[f] Ref. [13].

Obviously the discrepancy observed between the calculated and experimental ionization potentials of atoms in a high oxydation state is not of paramount importance in molecular calculations of essentially neutral molecules.

But the very fact that such a discrepancy is found suggests that the method which produces it does not properly take into account the atomic environment and may thus lead to erroneous results even for the evaluation of atomic integrals of essentially "neutral" atoms in molecules. Such a discrepancy could probably be taken properly into account by using the variable exponent method described above to calculate atomic terms in molecules.

References

1. Klopman, G., O'Leary, B.: Fortschr. der chem. Forschung, XX, 445 (1970); Jaffé, H. H.: Acc. Chem. Res. **2**, 136 (1969).
2. Klopman, G.: J. Amer. chem. Soc. **86**, 1463 (1964).
3. Hinze, J., Jaffé, H. H.: J. Amer. chem. Soc. **84**, 540 (1962).
4. Klopman, G.: J. chem. Physics **43**, 5124 (1965).
5. Pople, J. A., Segal, G. A.: J. chem. Physics **43**, 136 (1965).
6. Dewar, M. J. S., Klopman, G.: J. Amer. chem. Soc. **89**, 3089 (1967).
7. Slater, J. C.: Quantum theory of atomic structure, Vol. I, p. 322. New York: McGraw-Hill Book Company 1960.
8. Pople, J. A., Beveridge, D. L., Dobosh, P. A.: J. chem. Physics **47**, 2026 (1967).
9. Roothaan, C. C. J.: J. chem. Physics **19**, 1445 (1951).
10. Pilar, F. L.: Elementary quantum chemistry, p. 193. New York: McGraw-Hill Book Company 1968.
11. Sinanoğlu, O., Wiberg, K. B.: Sigma molecular orbital theory, p. 394 and loc. cit. New Haven: Yale University Press 1970.
12. Clementi, E.: IBM Journal of Research and Development **9**, 2 (1965).
13. Moore, C. E.: National Bureau of Standards (U. S.), Circ. No. 467 (1969).
14. Edlen, B.: J. chem. Physics **33**, 98 (1960).
15. Pople, J. A., Segal, G. A.: J. chem. Physics **44**, 3289 (1966).
16. Ref. [7], p. 339.

Prof. Gilles Klopman
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106, USA