An Approximate Treatment of the 1s Hartree Fock Energies in Molecules

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It is found on the basis of Hartree Fock calculations that the inner shell molecular orbitals of compounds that are composed of elements of the first two rows of the periodic table, are described satisfactorily by the corresponding 1s atomic orbitals. Such molecular orbitals (MOs) may be substituted in a good approximation by the 1s atomic orbitals (AOs). The energy of the localized MOs varies according to the type of bonding in which the atom is participating. The factors influencing the energy values may be classified in two parts; 1) the interaction with the other 1s atomic orbitals and nuclii in the molecule, 2) the interaction with the valence shell electrons. Neglecting the correlation effects, both factors are considered by the calculation of the 1s orbital energies. The results are compared with ab-Initio calculations done for the same molecules.

Introduction

According to the classical representation of chemical bonding [1], the electrons of a molecule are classified in core electrons and valence electrons that participate in the bond formation. This classification was considered by Lennard-Jones [2] and Mulliken [3] on formulating the molecular orbital theory. The following configuration was formulated for the O_2 molecule;

$$(1\,s)^2(1\,s)^2(2\,s)^2(2\,s)^2(2\,p_+)^2(2\,p_-)^2(2\,p)^2 \quad \{2\,p_+, 2\,p_-\} \tag{1}$$

the $(1\,s)^2$ and $(2\,s)^2$ electrons belonging to the individual atoms [2]. Coulson could show by his SCF-treatment of methane that the contribution of the valence atomic orbitals ($2\,s_C$, $2\,p_C$ and $1\,s_H$) to the energetically lowest molecular orbitals is negligibly small [4]. He showed later that the same neglection applys for the Li_2 molecule [5]. The following conclusions could be drawn from his work;

1) $\int \Phi_{1s}^{A}\ \Phi_{1s}^{B}\, d\tau \cong 0.0$
2) $(1\,s_A\,1\,s_B, 1\,s_B\,1\,s_A) = 0.0$, the exchange integral between 2 1s AOs.
3) $(A\,\sigma, \sigma\,A) = 0.07$ eV, the exchange integral between the inner (A) and the valence shell MO (σ),
4) the Slater exponents of the 1s atomic orbitals remain constant on bond formation.

Roothaan postulated that the inner shell MOs should be almost identical to the original 1s AOs [6]. He showed that in the case of a homonuclear diatomic molecule the following formed combination,

$$\psi'_{1s} = (1/\sqrt{2})\ (\Phi_{1s} \pm \Phi_{1s}{}') \tag{2}$$

is transferable to the original 1s AOs. In fact some authors did tacitely assume that the Hartree Fock energy of the inner shell MOs should be of the same magnitude as that of the free atoms [7]. Mulligan carried out a Hartree-Fock calculation for the CO_2 molecule, neglecting all the inner-outer shell orbital mixing [8]. Comparing the so obtained ε_{1s} eigenvalues for both atoms with the corresponding ionization potentials of the free atoms [$\varepsilon_{1s}(O) = -560.0$ eV; $I_{1s}^{\text{exp.}}(O_{\text{atom}}) = 524.0$ eV; $\varepsilon_{1s}(C) = -314.0$ eV; $I_{1s}^{\text{exp.}}(C_{\text{atom}}) = 284.0$ eV], he attributed the established difference to the nonmixing of the orbitals. Sahni [9] carried out a similar calculation for the CO molecule and obtained the eigenvalues $\varepsilon_{1s}(O) = -562.7$ eV and $\varepsilon_{1s}(C) = -308.5$ eV. Ellison and Schull did two SCF calculations for the H_2O molecule, in the first calculation (I) they did not consider any inner-outer shell orbital mixing and in the second (II) a complete mixing was considered [10]. The obtained, energetically lowest MOs were,

$$\begin{array}{ll}
\text{(I)} & \psi'_{1a_1} = 1.0\ (1\,s), \\
 & \varepsilon_{1a_1} = -559.1 \text{ eV}. \\
\text{(II)} & \psi'_{1a_1} = -0.0039\,\sigma_1 + 1.002\ (1\,s) \\
 & \qquad + 0.0163\ (2\,s) \\
 & \qquad + 0.0024\ (p_z), \\
 & \varepsilon_{1a_1} = -557.3 \text{ eV}.
\end{array} \tag{3}$$

They found that the eigenvalue, $\varepsilon_{1s}(O)$, of the first calculation shows a good agreement with the ε_{1s}

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value of atomic oxygen. Discussing the Mulligan's results for the CO_2 molecule[8], they attributed the calculated deviation of $\varepsilon_{1s}(O)$ from the theoretical $\varepsilon_{1s}(O_{atom})$ to the choice of the 1s orbital function.

For the BH molecule two similar calculations were done[11]. The obtained total electronic energy of the molecule, calculated with and without orbital mixing, corresponded to -681.8 and -681.7 eV respectively. The difference is obviously small.

The application of orthogonal and localized MOs should allow an exact SCF-MO treatment without the inner-outer shell mixing of AOs. This was shown by McWeeny who demonstrated that such a SCF-MO calculation, limited to the treatment of valence electrons alone, does describe exactly the electronic state of the molecule[12-14]. Both ab Initio calculations[15] and ESCA measurements[16] yielded different orbital energies for the inner shell MOs in different hydrocarbon molecules. The calculated Hartree-Fock energies $\varepsilon_{1s}(C)$ for acetylene, cyclopropane, methane and benzene were -305.93, -304.55, -305.19 and -306.29 eV respectively. ESCA measurements gave a difference of 11.1 eV between the ionization potentials ($1s_C$) of CF_4 and CH_4. Applying a SCF technique similar to that of Mulligan[4] and Sahni[9] and utilizing the Mulliken's approximation for the calculation of the electronic interaction energies, R. Manne attempted a theoretical prediction of the ε_{1s} orbital energies of some organic molecules including S and O[17]. The so calculated spectroscopic shifts of the K_{a12} lines;

$$\Delta E = (\varepsilon_{2p} - \varepsilon_{1s})_{\text{molec.}} - (\varepsilon_{2p} - \varepsilon_{1s})_{\text{atom}} \qquad (4)$$

showed a qualitative agreement with the available experimental results.

In spite of the fundamental importance of the core approximation for the construction of approximate and semiempirical SCF-MO methods the variation of the core energy (energy of the inner shell electrons + the internuclear interaction) is treated differently in the different existing semiempirical methods[18]. The discussion of the ε_{1s} energies is neglected completely. The following chapters deal with the derivation of the core approximation from the Hartree-Fock equations and the possibility of an approximate model for the calculation of ε_{1s} energies as a function of the valence electron densities. The obtained eigenvalues are compared with those of ab Initio calculations done for the same molecules.

The Core-Valence Separation of the Hartree-Fock Problem

According to the published Hartree-Fock calculations, the energetically lowest MOs of a molecule may be described approximately by 1s AOs that are centered on the atomic nuclii[4-14]. Due to the big Slater exponents of the 1s AOs the following integral;

$$\int \Phi_{1s}\, \Phi_i \, d\tau\,, \quad i = 2\,s, \ldots, n\,l \text{ valence A0}$$

is negligibly small.

Similar to the Lykos and Parr's discussion[19] of the σ-π separability, the separation of the Hartree-Fock problem is allowed if,

1) the total wave function of the molecule (atom) is composed of two antisymmetrical products;

$$\Psi = [\Sigma\Pi]$$

$$\text{similarly} \qquad \Psi = [\Psi_{\text{core}}\, \Psi_{\text{valence}}]\,. \qquad (5)$$

Ψ_{core} and Ψ_{valence} being antisymmetrical;

2) $\int \Psi^2_{\text{core}}\, d\tau\, d\sigma = 1\,,$
and $\int \Psi^2_{\text{valence}} d\tau\, d\sigma = 1\,,$ (6)

i.e. each subproduct is normalized by itself.

3) Ψ_{core} and Ψ_{valence} include no common spin orbitals.

The introduction of the core MOs' localization causes the satisfaction of the first condition by the core-valence seperation. Both wave functions then, Ψ_{core} and Ψ_{valence}, describe antisymmetrical Slater determinants of the dimension $(2\,N \times 2\,N)$ and $(n \times n)$ respectively.

$$\Psi_{\text{core}} = |\, \Phi^{A}_{1s}\ (i)\, \overline{\Phi^{A}_{1s}}\ (i) \ldots \Phi^{N}_{1s}\ (i)\, \overline{\Phi^{N}_{1s}}\ (i)| \qquad (7)$$

(A. . . .N are atoms with nuclear charge >2).

$$\text{and} \qquad \Psi_{\text{valence}} = |\, \psi_a(k)\, \overline{\psi_a(k)} \ldots \psi_{n/2}(k)\, \psi_{n/2}(k)\,| \qquad (8)$$

(n = number of the valence electrons).
Condition 2 is satisfied through the multiplication of both subproducts by the normalization factors $1/\sqrt{2\,N!}$ and $1/\sqrt{n!}$.

To satisfy condition 3 it is essential to orthogonalize all the localized and nonlocalized MOs relative to each other[12-14]. However since we are interested mainly in the 1s orbital energies of the molecule and in an approximate and mathematically convenient procedure for its calculation, we shall avoid the orthogonalization process. The 1s MO energies are to be calculated then as functions of the electron densities obtained from valence shell MO calculations.

The Calculation of the Hartree-Fock Energy of 1s Molecular Orbitals in Closed Shell Molecules, an ab Initio Study

We represent the inner shell MOs with the letters *p*, *q*, . . . and the valence shell MOs with *u*, *v*, *w*. From the general equation for the energy of a MO,

$$\varepsilon_t = \Sigma_i \Sigma_j a_{t,i} a_{t,j} H_{ij}^{\mathrm{C}} + \Sigma_i \Sigma_j \Sigma_k \Sigma_l P_{kl} \\ a_{t,i} a_{t,j} [(i\,j, k\,l) - \tfrac{1}{2}(i\,k, j\,l)] \qquad (9)$$

it follows that the Hartree-Fock energy of a 1 s MO is given by the equation,

$$\varepsilon_{1\mathrm{s}} = \Sigma_i \Sigma_j a_{1\mathrm{s},i} a_{1\mathrm{s},j} H_{\mathrm{ij}}^{\mathrm{C}} + \Sigma_i \Sigma_j \Sigma_k \Sigma_l P_{kl} \\ a_{1\mathrm{s},i} a_{1\mathrm{s},j} [(i\,j, k\,l) - \tfrac{1}{2}(i\,k, j\,l)]\,. \qquad (10)$$

The concentration of $\Phi_{1\mathrm{s}}$ on the AO *p* compells the following relation

$$a_{1\mathrm{s},p} = 1 \quad \text{and} \quad a_{1\mathrm{s},q} = 0 \quad \text{for} \quad p \neq q \qquad (11)$$

and

$$\varepsilon_{1\mathrm{s},p} = H_{pp}^{\mathrm{C}} + \Sigma_k \Sigma_l P_{kl} \\ [(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)]\,. \qquad (12)$$

H_{pp}^{C} = sum of the kinetic and potential energies of the electron occupying the orbital *p* in the field of all nuclii in the molecule.

$$H_{pp}^{\mathrm{C}} = \int \Phi_p(i) | -\Delta/2 + Z_p/r_{ip} | \Phi_p(i)\,\mathrm{d}\tau \\ + \int \Phi_p(i) | \Sigma_{\mathrm{K} \neq \mathrm{P}} Z_{\mathrm{K}}/R_{\mathrm{K}} | \Phi_p(i)\,\mathrm{d}\tau \qquad (13)$$

$$= E_p^{\mathrm{atom}} + \Sigma_{\mathrm{K} \neq \mathrm{P}} Z_{\mathrm{K}}/R_{\mathrm{K}}\,, \qquad (14)$$

E_p^{atom} = core hamiltonian energy of a pseudo Helium atom with the nuclear charge $Z_p^{\,+}$,

$\Sigma_{\mathrm{K} \neq \mathrm{P}} Z_{\mathrm{K}}/R_{\mathrm{K}}$ = the potential energy of an electron occupying the orbital *p* in the field of the other nuclii (K ≠ P).

There are two terms in the electronic interaction function *(T)* of Eq. (12); a) the term for the interaction with the electrons in the other 1 s MOs; b) that for the interaction with the electrons occupying the valence shell MOs.

$$T = \Sigma_k \Sigma_l P_{kl} [(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)] \qquad (15)$$

$$= 2\, \Sigma_{\mathrm{MO}}^{\mathrm{occ}} \Sigma_k \Sigma_l a_{\mathrm{MO},k} a_{\mathrm{MO},l} \\ [(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)]\,, \qquad (16)$$

MO = occupied molecular orbitals.

Separating both interaction terms we obtain;

$$T = 2\, \Sigma_q^{\,\mathrm{N}} \Sigma_k \Sigma_l a_{q,k} a_{q,l} [(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)] \\ + 2\, \Sigma_u^{\,n/2} \Sigma_k \Sigma_l a_{u,k} a_{u,l} [(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)] \qquad (17)$$

considering Eq. (11),

$$T = 2\, \Sigma_q^{\,\mathrm{N}} a_q^{\,2} [(p\,p, q\,q) - \tfrac{1}{2}(p\,q, p\,q)] \\ + \Sigma_k \Sigma_l P_{\mathrm{kl}}^{\mathrm{valence}} [(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)] \qquad (18)$$

similarly,

$$T = 2\, \Sigma_{q \neq p}^{\mathrm{N}} a_q^{\,2} [(p\,p, q\,q) - \tfrac{1}{2}(p\,q, p\,q)] \\ + 2\, a_p^{\,2} [(p\,p, p\,p) - \tfrac{1}{2}(p\,p, p\,p)] \qquad (19) \\ + \Sigma_k \Sigma_l P_{\mathrm{kl}}^{\mathrm{valence}} [(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)]\,.$$

We define then the Hartree-Fock energy of the MO *p* (≡ AO *p*) as follows;

$$\varepsilon_p = E_p^{\mathrm{atom}} + \Sigma_{\mathrm{K} \neq \mathrm{P}} Z_{\mathrm{K}}/R_{\mathrm{K}} + (p\,p, p\,p) \\ + 2\, \Sigma_{g \neq p} [(p\,p, q\,q) - \tfrac{1}{2}(p\,q, p\,q)] \\ + \Sigma_k \Sigma_l P_{\mathrm{kl}}^{\mathrm{valence}} [(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)]\,. \qquad (20)$$

Defining the entity $\varepsilon_p^{\mathrm{atom.}}$

$$\varepsilon_p^{\mathrm{atom.}} = E_p^{\mathrm{atom.}} + (p\,p, p\,p)\,, \qquad (21)$$

as the Hartree-Fock energy of a pseudo-Helium atom with the nuclear charge $Z_p^{\,+}$ and substituting it in Eq. (20) we obtain,

$$\varepsilon_p = \varepsilon_p^{\mathrm{atom.}} + 2\, \Sigma_{q \neq p}^{\mathrm{N}} [(p\,p, q\,q) - \tfrac{1}{2}(p\,q, p\,q)] \\ + \Sigma_{\mathrm{K} \neq \mathrm{P}} Z_{\mathrm{K}}/R_{\mathrm{K}} + \Sigma_k \Sigma_l P_{kl}^{\mathrm{valence}} \qquad (22) \\ [(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)]\,.$$

Thus we have simplified the calculation of ε_p by the calculation of two separate terms, A – the term for the interaction with the other core electrons and nuclii; B – the term for the interaction with the valence electrons. As it shall be shown later, the introduction of the pseudo Helium atom term $\varepsilon_p^{\mathrm{atom}}$ proofs to be very helpful in reducing the labor of the ε_p calculation. The values of $\varepsilon_p^{\mathrm{atom}}$ are obtainable from the Hartree-Fock calculations for the corresponding ions $[\mathrm{El}^{(Z-2)+}]$. Such calculations were done by Preuss [20] applying 4 Gaussians for the 1 s AO. The calculated values and the corresponding 1 center repulsion integrals (1 s², 1 s²) are tabulated in Table 1.

The influence of Term A on ε_p is expressed by the following equation,

$$\varepsilon_p{}' = \varepsilon_p^{\mathrm{atom}} + 2\, \Sigma_{q \neq p}^{\mathrm{N}} [(p\,p, q\,q) - \tfrac{1}{2}(p\,q, q\,p)] \\ + \Sigma_{\mathrm{K} \neq \mathrm{P}} Z_{\mathrm{K}}/R_{\mathrm{K}} \qquad (23) \\ = \varepsilon_p^{\mathrm{atom}} + \mathrm{A}$$

$= \varepsilon_p -$ the interaction energy with the valence electrons.

Table 1. Calculated $\varepsilon_{1s}^{\text{atom}}$ and (1s^2, 1s^2) energies of the ions El$^{(Z-2)+}$ (at. units).

Ion	$\varepsilon_p^{\text{atom}}$	(1s1s, 1s1s)
Li$^+$	−2.784925	1.6515294
Be^{2+}	−.478240	1.2848861
B^{3+}	−9.522169	2.899299
C^{4+}	−14.388083	3.5232718
N^{5+}	−20.252016	4.147404
O^{6+}	−27.114043	4.7716609
F^{7+}	−34.974159	5.3960358

Table 2. ε_p' energies obtained from ab initio calculations and from the application of Eq. (24) for the ions $C^{4+}-C^{4+}$ and $C^{4+}-O^{6+}$.

Bondlength (at. U.)	ε_p (Harthree-Fock)	ε_p [Eq. (24)]	$\Delta\varepsilon_p$
$C^{4+}-C^{4+}$			
2.2	16.20676	16.2062648	.0005
2.6	15.926530	15.9265445	−.00001
3.0	15.721382	15.7214163	−.00004
3.2	15.638049	15.6380830	−.00004
3.6	15.499160	15.49919411	−.00003
3.8	15.440681	15.44071458	−.00003
4.0	15.340430	15.34046395	−.00003
4.6	15.257614	15.25764822	−.00004
5.0	15.157280	15.15731377	−.00003
6.0	15.054716	15.0547967	−.00003
7.0	14.959478	14.95951157	−.00004
$C^{4+}-O^{6+}$			
C-energy			
2.2	17.1153557	17.115322	.000034
2.6	16.695775	16.695741	.000034
3.0	16.388083	16.388049	.000034
3.4	16.152788	16.152755	.000033
3.8	15.967030	15.966996	.000034
4.0	15.888083	15.888049	.000034
4.4	15.715172	15.7151685	.000035
4.8	15.638083	15.638049	.000034
5.0	15.588083	15.588049	.000034
6.0	15.388083	15.388049	.000034
6.4	15.325583	15.325549	.000034
7.6	15.177557	15.177523	.000034
8.0	15.138083	15.138049	.000034
12.0	14.888083	14.888049	.000034
O-energy			
2.2	28.932225	28.932225	.0
2.4	28.780710	28.780710	.0
3.0	28.447376	28.447376	.0
3.4	28.290514	28.290514	.0
3.8	28.166675	28.166675	.0
4.0	28.114043	28.114043	.0
4.4	28.023134	28.023134	.0
4.8	27.947376	27.947376	.0
5.0	27.914043	27.914043	.0
6.0	27.780710	27.780710	.0
6.8	27.702278	27.702278	.0
7.6	27.640359	27.640359	.0
8.0	27.614043	27.614043	.0

The value for the exchange integral $(p\,q, q\,p)$ is negligibly small due to the small overlap between different 1 s AOs [5]. The remaining terms of Eq. (23), $(p\,p, q\,q)$, resemble the repulsion between different 1 s AOs. These may be approximated by the corresponding Coulomb repulsion (e^2/R_{p-q}) between the centers of charge. The definition of ε_p' is then reduced to the following equation;

$$\varepsilon_p' = \varepsilon_p^{\text{atom}} + \Sigma_{\text{K} \neq \text{P}} (Z_{\text{K}} - 2)/R_{\text{K}} . \tag{24}$$

Table 2 shows the ε_p' values for the ions $C^{4+}-C^{4+}$ and $C^{4+}-O^{6+}$, including only two 1 s electrons on each atom, obtained from the application of Eq. (24) and from the ab initio calculations.

The agreement between the results of both methods is excellent, it confirms our recent assumptions indeed. The mean deviation between both values is 0.00003 at. units = 18 cal/mol.

The total core energy of a molecule is defined as the sum of all core electronic energies plus the internuclear repulsion energy.

$$\begin{aligned} E_{\text{total}}^{\text{core}} = {} & 2\,\Sigma_p\,\varepsilon_p' - \Sigma_p (p\,p, p\,p) \\ & - \Sigma_p\,\Sigma_q\, 2\,(p\,p, q\,q) + \underset{\text{K}<\text{M}}{\Sigma\,\Sigma}\, Z_{\text{K}}\, Z_{\text{M}}/R_{\text{KM}} \end{aligned} \tag{25}$$

or,

$$\begin{aligned} E_{\text{total}}^{\text{core}} = {} & 2\,\Sigma_p\,\varepsilon_p - \Sigma_p (p\,p, p\,p) \\ & + \underset{\text{K}<\text{M}}{\Sigma\,\Sigma}\, (Z_{\text{K}} - 2)\,(Z_{\text{M}} - 2)/R_{\text{KM}} \end{aligned} \tag{26}$$

according to the point charge model. Table 3 shows the values of $E_{\text{total}}^{\text{core}}$ for $C^{4+}-C^{4+}$ and $C^{4+}-O^{6+}$, calculated according to the Hartree-Fock (ab Initio) method and to the point charge model (26). The values of $2\,\varepsilon_p - (p\,p, p\,p)$ used in Eq. (26) are those of Reference [20]. Again the agreement between the results of both methods is excellent and the accuracy of the point charge model is sufficient for chemical purposes.

Relatively more complicated is the interaction of the 1 s electrons with the valence electrons. The corresponding interaction term is,

$$B = \Sigma_k\,\Sigma_l\, P_{kl}^{\text{valence}} [\,(p\,p, k\,l) - \tfrac{1}{2}(p\,k, p\,l)\,] . \tag{27}$$

The straight forward method for the evaluation of this function is the theoretical calculation of all its coulomb and exchange integrals, e. g. according to the Roothaan's scheme [21], and the adoption of the elements of a bond order matrix P_{kl}^{valence} from a suitable Hartree-Fock treatment of the valence electrons. Such work is a subject of present research in our laboratory and shall be referred to in subsequent reports. Instead we shall discuss a simplified model for the calculation of the function (27).

Table 3. $E_{\text{total}}^{\text{core}}$ calculated according tho the Hartree-Fock and the point charge model (in at. units).

Bondlength	$E_{\text{total}}^{\text{core}}$ (Hartree-Fock)	$E_{\text{total}}^{\text{core}}$ [Eq. (26)]
$C^{4+}-C^{4+}$		
2.2	−57.326227	−57.326227
2.6	−58.445108	−58.445108
3.0	−59.265620	−59.265620
3.4	−59.893071	−59.893071
3.8	−60.388427	−60.388428
4.0	−60.598954	−60.598800
4.4	−60.96259	−60.96245
4.8	−61.2656205	−61.265470
5.0	−61.3989538	−61.398800
5.4	−61.6359908	−61.63584
6.0	−61.9322871	−61.93213
7.0	−62.3132395	−62.31309
$C^{4+}-O^{6+}$		
2.2	−80.39013	−80.39011
2.6	−82.06845	−80.06843
3.0	−83.29922	−83.29920
3.4	−84.24040	−84.24038
3.8	−84.98343	−84.98341
4.0	−84.29922	−85.29920
4.4	−85.84468	−85.84465
4.8	−86.29922	−86.29920
5.0	−86.49922	−86.49920
6.0	−87.29922	−87.29920
6.4	−87.54922	−87.54920
6.8	−87.76981	−87.76979
8.0	−88.29922	−88.29922
10.0	−89.07700	−89.07698
12.0	−89.29922	−89.29920

An Approximate Model for the Calculation of the Hartree-Fock Energy of 1s MOs in Closed Shell Molecules

The suggested model is similar to the INDO treatment of valence electrons [18]. We neglect all the four and three orbital exchange and repulsion integrals of the type $(p\,j, q\,k)$ and $(p\,p, k\,l)$ ... etc. and the two centers, two orbitals exchange integrals too. The one center integrals of the type $(p\,k, k\,p)$ are retained. Function B is then reduced to the following expression;

$$ {}^{\mathrm{R}}B = \Sigma_k^{\mathrm{R}}\, q_{kk}^{\text{valence}}\left[(p\,p, k\,k) - \tfrac{1}{2}(p\,k, p\,k)\right] + \Sigma_k^{\mathrm{S}}\, q_{kk}^{\text{valence}}\,(p\,p, k\,k)\,, \tag{28} $$

R, S = atoms.

Evaluation of the one center interaction integrals

Average values of the interaction terms

$$ [(p\,p, k\,k) - \tfrac{1}{2}(p\,k, p\,k)] $$

are obtainable from the Hartree-Fock calculations for the free ions $\mathrm{El}^{(Z-2)+}$, $\mathrm{El}^{(Z-4)+}$, ... El^{0}. According to the applied model, the Hartree-Fock energy of the 1 s electrons in a free ion $\mathrm{El}^{(Z-n)+}$ is defined as,

$$ \begin{aligned} \varepsilon_p^{\text{ion}} &= \varepsilon_k^{\text{atom}} + \Sigma_k^{\text{valence}} q_k (p\,p, k\,k) \\ &\quad - \tfrac{1}{2}\Sigma_k\, q_k (p\,k, p\,k) = \varepsilon_p^{\text{atom}} \\ &\quad + \Sigma_k^{\text{valence}} q_k (J_{pk} + K_{pk})\,. \end{aligned} \tag{29} $$

For $k = 2\,s$ and $q_k = 2$ the corresponding term is,

$$ (J_{pk} + K_{pk}) = \tfrac{1}{2}\{\varepsilon_p^{\text{ion}}[\mathrm{El}^{(Z-4)+}] - \varepsilon_p^{\text{atom}}\} \tag{30} $$

where $\mathrm{El}^{(Z-4)+}$ = the ion of element El having $2 \times 2\,s$ electrons only. Similarly we obtain for $k = 2\,p$ the following term,

$$ (J_{p,k} + K_{p,k}) = \tfrac{1}{2}\{\varepsilon_p^{\text{ion}}\ [\mathrm{El}^{(Z-6)+}] - \varepsilon_p^{\text{ion}}\,[\mathrm{El}^{(Z-4)+}]\}\,. \tag{31} $$

To determine the average values of the integrals $(J_{pk} + K_{pk})$ for C and O atoms we have carried out Hartree-Fock calculations for the ions El^{n+} $(n = 0, \ldots, Z-2)$ and determined the required $\varepsilon_p^{\text{ion}}$ values. Table 4 includes our calculation results. The reported calculations were done using a 5 s 6 p Gaussian basis.

Table 4. The calculated Hartree-Fock energies of the inner shell electrons ($\varepsilon_p^{\text{ion}}$) of the C and O ions and the derived average values of the one center interaction terms $(J_{pk}+K_{pk})$.

Ion	$\varepsilon_p^{\text{ion}}$	$\Delta\varepsilon_p^{\text{ion}}$	$(J_{1s,k}+K_{1s,k})$	k
C^{4+}	−14.388083	—	—	—
C^{2+}	−12.637227	1.750856	.875428	2s
C^{0}	−11.261914	1.375313	.687656	2p
C^{2-}	−10.178633	1.083281	.541642	2p′
O^{6+}	−27.114043	—	—	—
O^{4+}	−24.560333	2.553710	1.276855	2s
O^{2+}	−22.317260	2.243073	1.1215365	2p
O^{0}	−20.490048	1.827212	.913606	2p′
O^{2-}	−18.895426	1.594622	.797311	2p″

Calculation of the 2 center repulsion integrals

In our present treatment the 2 center repulsion integrals are evaluated by means of a modified Klopman-Ohno formula [18],

$$ (p\,p, k\,k) = \{.53\,\sqrt{R^2 + [1/(p\,p, p\,p) + 1/(k\,k, k\,k)]^2}\}^{-1}\,, \tag{32} $$

R = the distance between the two nuclii,

(pp, pp), (kk, kk) = one center repulsion integrals. The required values of the one center repulsion integrals $(2\,p^2, 2\,p^2)$ and $(2\,s^2, 2\,s^2)$ are calculated from the corresponding Slater-Condon parameters[22]. The values of F^0 and F^2 parameters (at. units) are tabulated in Table 5.

Table 6 shows the calculated Hartree-Fock energies (ε_{1s}) for some closed shell ions compared with the energies obtained from the application of our approximate model. The applied valence electron densities were taken from the ab Initio calculations for the same ions. The interatomic distances are 2.0 at. units (C = O) and 2.35 at. units (C – C). The agreement between the values of both methods is very encouraging specially on recognizing that the applied values of the interaction terms were not functions of the valence electron densities. It should be noticed too that the electron densities were calculated from the occupation of Gaussian functions rather than atomic orbitals.

Table 5. Values of the one center repulsion integrals (at. units).

F^0	F^2	(2p′, 2p²)	Element
.472173	—	—	H
.318924	.130459	.33797	B
.507624	.173761	.435426	C
.445008	.219122	.480068	N
.49989	.266468	.54511	O
.575614	.315873	.626154	F

Table 6. Values of the 1s orbital energies calculated according to the Hartree-Fock method and the approximate model described in the present work.

Molecule	ε_{1s}(34)	ε_{1s}(H–F)	$\Delta\varepsilon_{1s}$	Dev.%
$C^{4+}-O^{6+}$	28.932225	28.932225	0.0	0.0
$C^{3+}-O^{5+}$	26.638570	26.722138	–.083568	–.32
$C^{2+}+O^{4+}$	24.825214	24.628788	.196426	.80
$C^{+}-O^{3+}$	23.037520	23.093969	–.056459	–.25
$C-O^{2+}$	21.413587	21.824969	–.411382	–1.89
$C-O$	19.916223	20.784152	–.867929	–4.18
ε_{1s}(C) energy				
$C^{4+}+O^{6+}$	17.115355	17.115322	.000033	0.0
$C^{3+}-O^{5+}$	16.094070	16.059543	.034527	.25
$C^{2+}-O^{4+}$	14.750991	14.989428	–.238437	–1.50
$C^{+}+O^{3+}$	13.398408	13.78325	–.384842	–2.65
$C-O^{2+}$	11.963967	12.561377	–.597410	–4.39
$C-O$	10.459698	10.604558	–.825912	–.55
$C^{4+}-C^{4+}$	16.2062648	16.20676	–.0005	0.0
$C^{3+}-C^{3+}$	14.755647	14.624239	.131408	1.11
$C^{2+}-C^{2+}$	13.431291	13.431291	.081176	.87
$C^{+}-C^{+}$	12.270002	12.380158	–.110156	–.57
$C-C$	10.934567	11.414541	–.479974	–3.59

ε_{1s} energies of neutral molecules

Due to the success of the preceding theoretical treatment, we have tried the calculation of the 1s orbital energies of the neutral organic molecules, CH_4 and CO, using experimental bond distances, 2.13 at. units (C = O) and 2.066 at. units (C – H). The interaction energies ($J_{1s,2s}+K_{1s,2s}$) and ($J_{1s,2p}+K_{1s,2p}$) were set equal. The valence electron densities were taken from a CNDO calculation. The obtained ε_{1s} energies compared with the Hartree-Fock orbital energies are,

	ε_{1s} (approximate)	ε_{1s} (Hartree-Fock)
CH_4	–11.506753	–11.21879 [15]
CO_2	–11.559130	–11.36051 [23]
		–11.39129 [24]

The relatively good agreement between the results of the two methods suggests the possibility of extending the approximate method to the treatment of other molecules. Such work is being carried out presently at our laboratory.

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