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A LCAO-MO-SCF METHOD FOR COMPLEX INORGANIC MOLECULES AND THE ROLE OF TWO-CENTER COULOMB INTEGRALS

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In the present status, the LCAO-MO-SCF theories for complex inorganic molecules try to overtake the rough models arising more or less from the first approach of Wolfsberg and Helmholz[1–6]. The relatively good results obtained have repressed for several years any desire for innovation; now it has been realized that these good results were rather the consequence of mutual cancellations of different errors. It has been shown that small changes in some details of the calculation may lead to worse results[7–8].

Hence more rigorous approaches to molecular orbital problems in inorganic chemistry[9–12] are attempted, and also in this new direction it seems desirable to retain relative simplicity, avoiding too cumbersome calculations. For this reason, we have worked out a general method, which we report here, where we avoid the explicit calculation of four- and three-center integrals and empirically evaluate the one-center parts of the matrix elements; in this way, the most difficult calculation left is that of two-center Coulomb integrals, since exchange integrals may be approximately expressed by means of such integrals and empirical quantities.

Notations and preliminaries

In the LCAO approximation, we have to consider molecular orbitals φ_i as linear combinations of real atomic orbitals ψ_a, *i.e.*

$$\varphi_i = \sum_a c_{ia}\psi_a \,.$$

Referring to molecular orbitals, we use the indices k, l for the totally occupied orbitals, m,n for the partly occupied orbitals, and i, j for orbitals of either set. By the indices p, q we indicate atomic orbitals belonging to the molecular orbitals φ_k, φ_l, by t, u those belonging to φ_m, φ_n's and by a, b, c, d the general atomic orbitals.

For all molecular orbitals we define a fractional occupation number f_i equal to half the number of electrons in the orbital φ_i. Of course f_k, f_l are all equal to 1.

It is useful to define:

$$P_{pq}{}^C = 2\sum_k c_{kp}c_{kq},\; P_{tu}{}^O = 2\sum_m f_m c_{mt}c_{mu},\; P_{ab}{}^T = P_{ab}{}^C + P_{ab}{}^O = 2\sum_i f_i c_{ia}c_{ib}$$

and the operators J_i, K_i, j^{ab}, k^{ab} by means of:

$$\langle \varphi_j \mid J_i \mid \varphi_j \rangle = J_{ij} = \iint \varphi_i(1)\varphi_i(1)\,\frac{1}{r_{12}}\,\varphi_j(2)\varphi_j(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

$$\langle \varphi_j \mid K_i \mid \varphi_j \rangle = K_{ij} = \iint \varphi_i(1)\varphi_j(1)\,\frac{1}{r_{12}}\,\varphi_i(2)\varphi_j(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

$$\langle \psi_c \mid \mathrm{j}^{ab} \mid \psi_d \rangle = \mathrm{j}_{cd}{}^{ab} = \iint \psi_a(1)\psi_b(1)\,\frac{1}{r_{12}}\,\psi_c(2)\psi_d(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

$$\langle \psi_c \mid \mathrm{k}^{ab} \mid \psi_d \rangle = \mathrm{k}_{cd}{}^{ab} = \iint \psi_a(1)\psi_c(1)\,\frac{1}{r_{12}}\,\psi_b(2)\psi_d(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2$$

Furthermore, we define the operators J^C, J^O, J^T, K^C, K^O, K^T, L_i, M_i, L^C, L^O, L^T:

$$J^C = \sum_k J_k \qquad K^C = \sum_k K_k$$

$$J^O = \sum_m f_m J_m \qquad K^O = \sum_m f_m K_m$$

$$J^T = J^C + J^O = \sum_i f_i J_i \qquad K^T = K^C + K^O = \sum_i f_i K_i$$

$$L_i\varphi = \langle \varphi_i \mid J^O \mid \varphi \rangle \varphi_i + \langle \varphi_i \mid \varphi \rangle J^O \varphi_i$$

$$M_i\varphi = \langle \varphi_i \mid K^O \mid \varphi \rangle \varphi_i + \langle \varphi_i \mid \varphi \rangle K^O \varphi_i$$

$$L^C = \sum_k L_k \qquad M^C = \sum_k M_k$$

$$L^O = \sum_m f_m L_m \qquad M^O = \sum_m f_m M_m$$

$$L^T = L^C + L^O = \sum_i f_i L_i \qquad M^T = M^C + M^O = \sum_i f_i M_i$$

If G is a general operator, we indicate by G_{ij} the integral $\langle \varphi_i \mid G \mid \varphi_j \rangle$, by G_{ab} the integral $\langle \psi_a \mid G \mid \psi_b \rangle$, and by S_{ab} the atomic overlap integral $\langle \psi_a \mid \psi_b \rangle$.

In the following treatment, we often apply the Mulliken type approximation to a charge distribution $\psi_a\psi_b$:

$$\psi_a(1)\psi_b(1) = \tfrac{1}{2}S_{ab}[\psi_a(1)\psi_a(1) + \psi_b(1)\psi_b(1)] \tag{1}$$

then *e.g.* for the operator j^{cc} it is:

$$\mathrm{j}_{ab}{}^{cc} = \tfrac{1}{2}S_{ab}(\mathrm{j}_{aa}{}^{cc} + \mathrm{j}_{bb}{}^{cc}) \tag{2}$$

For the operator k^{cc} we use instead this analogous approximation:

$$\mathrm{k}_{ab}{}^{cc} = \tfrac{1}{2}S_{ab}(\mathrm{k}_{aa}{}^{cc} + \mathrm{k}_{bb}{}^{cc}) \tag{3}$$

Considering the discussion given by Ruedenberg[13] for the case of ψ_a and ψ_b different only in the reference center, such an approximation can be regarded as having the same nature and limitations as approximation (1); the formal analogy between (2) and (3) will be extremely useful to get very simple formulae.

Closed shell

The self-consistent operator for a closed shell is:

$$F = H + 2J^C - K^C$$

where H is the kinetic plus core field energy operator, *i.e.*:

$$H = T - \sum_L \frac{Z_L}{r_L}$$

with Z_L equal to the effective charge of the core of the atom L and r_L to the distance of the electron from it.

Expanding the molecular orbitals as a function of atomic orbitals, we have:

$$F = H + \sum_c \sum_d P_{cd}{}^C (\mathrm{j}^{cd} - \tfrac{1}{2}\,\mathrm{k}^{cd})$$

For $\psi_c \neq \psi_d$, we apply approximations (2) and (3), and defining:

$$P_{cc}{}^{C'} = P_{cc}{}^C + \sum_{d \neq c} P_{cd}{}^C S_{cd}$$

we obtain:

$$F = H + \sum_c P_{cc}{}^{C'} (\mathrm{j}^{cc} - \tfrac{1}{2}\,\mathrm{k}^{cc})$$

Now we write F in such a way as to distinguish the contributions arising from different atoms L:

$$F = T + \sum_L V^L$$

with

$$V^L = -\frac{Z_L}{r_L} + \sum_{c \to L} P_{cc}{}^{C'} (\mathrm{j}^{cc} - \tfrac{1}{2}\,\mathrm{k}^{cc})$$

where by c → L we mean that the index c runs over all orbitals ψ_c belonging to the atom L.

Let us consider now the diagonal matrix element F_{aa}, with ψ_a belonging *e.g.* to the atom 1:

$$F_{aa} = T_{aa} + V_{aa}{}^1 + \sum_{L \neq 1} V_{aa}{}^L$$

Since for $\psi_c = \psi_a$, $j_{aa}^{cc} = k_{aa}^{cc}$, we can write:

$$T_{aa}+V_{aa}^{1} = \chi_a = T_{aa}-Z_1\langle\psi_a\left|\frac{1}{r_1}\right|\psi_a\rangle+$$
$$+\tfrac{1}{2}P_{aa}^{C'}j_{aa}^{aa} + \sum_{\substack{c\to 1\\ c\neq a}} P_{cc}^{C'}(j_{aa}^{cc}-\tfrac{1}{2}k_{aa}^{cc})$$

The one-center part χ_a can be easily evaluated if the single empirical one-centre integrals as function of the charge configuration are known, otherwise it can be regarded as the ionization energy of an electron in ψ_a for an atomic valence state which has $(1+P_{aa}^{C}/2)$ electrons in ψ_a and $P_{cc}^{C'}$ electrons in its other orbitals ψ_c; and therefore it can be empirically evaluated as such ionization energy from atomic energy levels[14]. Unfortunately, it is very difficult, on the grounds of the spectroscopic data alone, to account quantitatively for the loss of degeneracy of the atomic orbitals taking place on passing from the atomic to the molecular state; it is however likely that the error due to the equal distribution of electrons among a set of atomic (*nl*) orbitals, which are no longer degenerate in the molecular state is not very large: this was proved by explicit calculations carried out using empirical values for the single one-center integrals. Therefore we evaluate χ_a as the ionization energy for a valence state with degenerate (*nl*) orbitals[15].

Let us consider now the off-diagonal element F_{ab}, with *e.g.* ψ_a belonging to the atom 1 and ψ_b to the atom 2. Referring the eigen-function ψ_b to an atomic valence state with $P_{bb}^{C'}$ electrons in the corresponding orbital and $P_{cc}^{C'}$ in all other orbitals ψ_c, we separate V^2 into two parts:

$$V^2 = V^{2'}+2\left(1-\frac{P_{bb}^{C'}}{2}\right)(j^{bb}-\tfrac{1}{2}k^{bb})$$

with

$$V^{2'} = -\frac{Z_2}{r_2}+2(P_{bb}^{C'}-1)(j^{bb}-\tfrac{1}{2}k^{bb})+\sum_{\substack{c\to 2\\ c\neq b}} P_{cc}^{C'}(j^{cc}-\tfrac{1}{2}k^{cc})$$

hence:

$$F_{ab} = \langle\psi_a\,|\,T+V^{2'}\,|\,\psi_b\rangle+\langle\psi_a\left|2\left(1-\frac{P_{bb}^{C'}}{2}\right)(j^{bb}-\tfrac{1}{2}k^{bb})\right|\psi_b\rangle+\sum_{L\neq 2}V_{ab}^{L}$$

Considering in eigenstate the energy χ'_b of an electron in ψ_b in an atomic valence state with $P_{bb}^{C'}$ electrons in ψ_b and $P_{cc}^{C'}$ electrons in all other orbitals ψ_c, we can write $(T+V^{2'})\psi_b = \chi'_b\psi_b$; applying then approximations (1) and (3) to the remaining terms, we have:

$$F_{ab} = S_{ab}\chi'_b+\tfrac{1}{2}S_{ab}\left(1-\frac{P_{bb}^{C'}}{2}\right)(j_{aa}^{bb}+j_{bb}^{bb})+\tfrac{1}{2}S_{ab}\sum_{L\neq 2}(V_{aa}^{L}+V_{bb}^{L}) \qquad (4')$$

Analogously to (4'), we have:

$$F_{ba} = S_{ab}\chi'_a + \tfrac{1}{2}S_{ab}\left(1 - \frac{P_{aa}{}^{C'}}{2}\right)(j_{aa}{}^{aa} + j_{bb}{}^{aa}) + \tfrac{1}{2}S_{ab}\sum_{L \neq 1}(V_{aa}{}^{L} + V_{bb}{}^{L}). \qquad (4'')$$

Since F is a hermitian operator, then $F_{ab} = F_{ba}$, and the best expression of the off-diagonal element will be given by the average of (4′) and (4″):

$$\begin{aligned} F_{ab} = F_{ba} = {} & \tfrac{1}{2}S_{ab}(\chi'_a + \chi'_b) + \\ & + \tfrac{1}{4}S_{ab}\left[\left(1 - \frac{P_{bb}{}^{C'}}{2}\right)(j_{aa}{}^{bb} + j_{bb}{}^{bb}) + \left(1 - \frac{P_{aa}{}^{C'}}{2}\right)(j_{aa}{}^{aa} + j_{bb}{}^{aa})\right] + \\ & + \tfrac{1}{4}S_{ab}(V_{aa}{}^{1} + V_{bb}{}^{1} + V_{aa}{}^{2} + V_{bb}{}^{2}) + \tfrac{1}{2}S_{ab}\sum_{L \neq 1,2}(V_{aa}{}^{L} + V_{bb}{}^{L}) \end{aligned} \qquad (4)$$

In this expression, χ'_a and χ'_b are one-center terms which can be empirically evaluated, as already discussed; $j_{aa}{}^{aa}$ and $j_{bb}{}^{bb}$ are integrals which can he empirically determined as $(I_a - A_a)$ and $(I_b - A_b)$[15]; $j_{bb}{}^{aa}$ or $j_{aa}{}^{bb}$ is a two-center Coulomb integral; $V_{aa}{}^{L}$ ($L \neq 1$) and $V_{bb}{}^{L}$ ($L \neq 2$) are multi-center terms we bave already evaluated for the respective diagonal element. Finally $V_{aa}{}^{1}$ and $V_{bb}{}^{2}$ may be easily evaluated semi-empirically by subtracting the corresponding kinetic energy integrals from the quantities χ_a and χ_b already evaluated:

$$V_{aa}{}^{1} = \chi_a - T_{aa}$$
$$V_{bb}{}^{2} = \chi_b - T_{bb}$$

Moreover it should be pointed out that the evaluation of such symmetric kinetic integrals is very simple.

Another possible approximation for the off-diagonal element could be the following: let us write the operator F as $T + V$, then:

$$F_{ab} = T_{ab} + V_{ab}$$

Applying approximations (1) and (3) to V_{ab}, we have:

$$F_{ab} = T_{ab} + \tfrac{1}{2}S_{ab}(V_{aa} + V_{bb})$$

Since $F_{aa} = T_{aa} + V_{aa}$ and similarly for F_{bb}, we have:

$$V_{aa} = F_{aa} - T_{aa}$$
$$V_{bb} = F_{bb} - T_{bb}$$

then:

$$F_{ab} = T_{ab} - \tfrac{1}{2}S_{ab}(T_{aa} + T_{bb}) + \tfrac{1}{2}S_{ab}(F_{aa} + F_{bb}) \qquad (5)$$

As it can be seen from (5), if a formally analogous approximation to (2) could be applied to the term T_{ab} as well, this kind of approximation would also apply to the whole element F_{ab}. The first two terms on the right-hand side of (5) take into account this impossibility. The difference between (4) and (5) consists in the extension of the approximations (1) and (3) to the whole terms $V_{ab}{}^{1}$ and $V_{ab}{}^{2}$.

For this reason we believe that formula (4) is better; furthermore in formula (5) there is the additional analytical task of the evaluation of T_{ab}.

Open shell

Let us now consider those open-shell cases with only one open shell outside the closed shell. These can be treated as pseudo-eigenvalue problems by means of the Roothaan operator[17]:

$$F = H+2J^T-K^T-2\alpha J^O+\beta K^O+2\alpha L^T-\beta M^T$$

with $\alpha = \dfrac{1-a}{1-f_m}$ and $\beta = \dfrac{1-b}{1-f_m}$

where a and b are characteristic constants for the specific case and f_m is the fractional occupation number equal for all orbitals φ_m belonging to the only open shell present; *i.e.* f_m is equal here to the number of electrons in the open shell divided by the number of the available open-shell spin-orbitals. Let us consider the diagonal element F_{aa}, with ψ_a belonging *e.g.* to the atom 1:

$$F_{aa} = H_{aa}+2J_{aa}{}^T-K_{aa}{}^T-2\alpha J_{aa}{}^O+\beta K_{aa}{}^O+2\alpha L_{aa}{}^T-\beta M_{aa}{}^T$$

For convenience, we consider separately three contributions to this expression. The first part:

$$F'_{aa} = H_{aa}+2J_{aa}{}^T-K_{aa}{}^T$$

is formally analogous to the diagonal element of the closed shell, with the only difference that the sum is to be extended over the open shell orbitals as well; then:

$$F'_{aa} = H_{aa} + \sum_c P_{cc}{}^{T'}(\mathrm{j}_{aa}{}^{cc}-\tfrac{1}{2}\,\mathrm{k}_{aa}{}^{cc})$$

with:

$$P_{cc}{}^{T'} = P_{cc}{}^T + \sum_{d\neq c} P_{cd}{}^T S_{cd}$$

The second part is:

$$F''_{aa} = -2\alpha J_{aa}{}^O+\beta K_{aa}{}^O$$

Expanding the molecular orbitals as function of atomic orbitals, we obtain:

$$\begin{aligned} F''_{aa} &= -(2\alpha \sum_m f_m \sum_t \sum_u \mathrm{c}_{mt}\mathrm{c}_{mu}\mathrm{j}_{aa}{}^{tu}-\beta \sum_m \mathrm{f}_m \sum_t \sum_u \mathrm{c}_{mt}\mathrm{c}_{mu}\mathrm{k}_{aa}{}^{tu}) = \\ &= -(\alpha \sum_t \sum_u P_{tu}{}^O\mathrm{j}_{aa}{}^{tu}-\beta \sum_t \sum_u P_{tu}{}^O\tfrac{1}{2}\,\mathrm{k}_{aa}{}^{tu}) \end{aligned}$$

Defining an operator $B^{ab} = \alpha j^{ab} - \frac{1}{2}\beta k^{ab}$, we have:

$$F''_{aa} = -\sum_{t}\sum_{u} P_{tu}{}^{O} B_{aa}{}^{tu}$$

Applying approximations (2) and (3) to the terms with t ≠ u and defining:

$$P_{tt}{}^{O'} = P_{tt}{}^{O} + \sum_{u \neq t} P_{tu}{}^{O} S_{tu}$$

we have:

$$F''_{aa} = -\sum_{t} P_{tt}{}^{O'} B_{aa}{}^{tt}$$

Let us consider the third part:

$$\begin{aligned}
F'''_{aa} &= 2\alpha L_{aa}{}^{T} - \beta M_{aa}{}^{T} = \\
&= 2\alpha(\sum_{i} f_i \langle \psi_a | L_i | \psi_a \rangle) - \beta(\sum_{i} f_i \langle \psi_a | M_i | \psi_a \rangle) = \\
&= 2\alpha[\sum_{i} f_i(\langle \varphi_i | J^O | \psi_a \rangle \langle \psi_a | \varphi_i \rangle + \langle \varphi_i | \psi_a \rangle \langle \psi_a | J^O | \varphi_i \rangle)] - \\
&- \beta[\sum_{i} f_i(\langle \varphi_i | K^O | \psi_a \rangle \langle \psi_a | \varphi_i \rangle + \langle \varphi_i | \psi_a \rangle \langle \psi_a | K^O | \varphi_i \rangle)] = \\
&= 4\sum_{i} f_i \langle \varphi_i | \alpha J^O - \tfrac{1}{2}\beta K^O | \psi_a \rangle \langle \psi_a | \varphi_i \rangle
\end{aligned}$$

Expanding the molecular orbitals as function of atomic orbitals, we have:

$$F'''_{aa} = 4\sum_{i} f_i \sum_{c} c_{ic} \langle \psi_c | \alpha J^O - \tfrac{1}{2}\beta K^O | \psi_a \rangle \sum_{d} c_{id} \langle \psi_a | \psi_d \rangle$$

Being:

$$\langle \psi_c | \alpha J^O - \tfrac{1}{2}\beta K^O | \psi_a \rangle = \sum_{m} f_m \sum_{t}\sum_{u} c_{mt} c_{mu} B_{ca}{}^{tu}$$

we obtain after rearrangement:

$$F'''_{aa} = \sum_{d} S_{ad} \sum_{c} P_{cd}{}^{T} \sum_{t}\sum_{u} P_{tu}{}^{O} B_{ca}{}^{tu}$$

We now apply approximations (2) and (3) to the terms with t ≠ u, and obtain:

$$F'''_{aa} = \sum_{d} S_{ad} \sum_{c} P_{cd}{}^{T} \sum_{t} P_{tt}{}^{O'} B_{ca}{}^{tt}$$

Using the same approximations for the terms with c ≠ a and defining:

$$P_{ad}{}^{T'} = P_{ad}{}^{T} + \tfrac{1}{2} \sum_{c \neq a} P_{cd}{}^{T} S_{ca}$$

we get:

$$F'''_{aa} = (\sum_{d} S_{ad} P_{ad}{}^{T'}) \sum_{t} P_{tt}{}^{O'} B_{aa}{}^{tt} + \tfrac{1}{2} \sum_{d} S_{ad} \sum_{c \neq a} S_{ca} P_{cd}{}^{T} \sum_{t} P_{tt}{}^{O'} B_{cc}^{tt} \tag{6}$$

Summing the three terms F'_{aa}, F''_{aa}, F'''_{aa}, we have, apart from the last term on the right-hand side of (6):

$$F_{aa} = H_{aa} + \sum_{c} P_{cc}^{T'}(j_{aa}^{cc} - \tfrac{1}{2}\,k_{aa}^{cc}) - \sum_{t} P_{tt}^{O'}\, B_{aa}^{tt} + (\sum_{d} S_{ad}P_{ad}^{T'}) \sum_{t} P_{tt}^{O'} B_{aa}^{tt}$$

Since $P_{cc}^{O'}$ is vanishing if ψ_c does not belong to the open shell this formula can be rewritten in the following way:

$$F_{aa} = H_{aa} + \sum_{c} P_{cc}^{T'}(j_{aa}^{cc} - \tfrac{1}{2}\,k_{aa}^{cc}) - \sum_{c} P_{cc}^{O'} B_{aa}^{cc} + (\sum_{d} S_{ad}P_{ad}^{T'}) \sum_{c} P_{cc}^{O'} B_{aa}^{cc} \tag{7}$$

For ψ_c's belonging to the atom 1, we have a one-center part χ_a, which, if we do not know the single empirical one-center integrals as function of the charge configuration, may be empirically evaluated, in the case $\alpha = \beta$, under the limitations already discussed. The ionization energy of an electron in ψ_a for an atomic valence state which has $(1 + n_a(a)/2)$ electrons in ψ_a and $n_c(a)$ electrons in all other orbitals ψ_c, with $n_c(a)$ (c including a) given by:

$$n_c(a) = P_{cc}^{T'} + \alpha P_{cc}^{O'} \Big(\sum_{d} S_{ad}P_{ad}^{T'} - 1\Big)$$

Furthermore $n_c(a)$ also stands for the whole multiplying factor in (7) of the two-center terms $(j_{aa}^{cc} - \frac{1}{2}k_{aa}^{cc})$.

If $\alpha \neq \beta$, in the multi-center part, the exchange terms arising from F'' and F''' have to be multiplied by a factor β/α. With regard to the one-center part, we should have to know the single empirical one-center integrals for its evaluation, or at least the exchange ones for adding to the preceding χ_a the remaining $(\beta - \alpha)$ part of the exchange terms arising from F'' and F''', unless the approximation (1) is applied to this part (that is nullifying it), since it represents only a minor contribution to F''_{aa} and F'''_{aa}.

The last term on the right-hand side of (6) actually contains one-center integrals whose effect cannot be included into any empirical evaluation of valence state ionization energies; probably however this term can be neglected without any serious error, both because it is presumably rather small and because it should be approximately constant for all matrix elements.

With regard to the off-diagonal element F_{ab} with *e.g.* ψ_a belonging to the atom 1 and ψ_b to the atom 2, we notice that it is impossible to apply Mulliken type approximations to the terms L^T and M^T of the operator, so that a formally analogous treatment to that used for the closed shell case cannot be developed. Let us consider instead, separately, the terms $(F'_{ab} + F''_{ab})$ and F'''_{ab}. We start with F'''_{ab}:

$$F'''_{ab} = 2\alpha L_{ab}^{T} - \beta M_{ab}^{T} = 2 \sum_{i} f_i(\langle \varphi_i \,|\, \alpha J^O - \tfrac{1}{2}\beta K^O \,|\, \psi_b\rangle \langle \varphi_i \,|\, \psi_a\rangle +$$
$$+ \langle \varphi_i \,|\, \psi_b\rangle \langle \psi_a \,|\, \alpha J^O - \tfrac{1}{2}\beta K^O \,|\, \varphi_i\rangle)$$

Following an analogous treatment to that of F'''_{aa} and neglecting again a term of the same nature of the last term on the right-hand side of (6), we have:

$$F'''_{ab} = \tfrac{1}{2}\left(\sum_{d} S_{ad}P_{bd}{}^{T'}\right)\sum_{t} P_{tt}{}^{O'}B_{bb}{}^{tt} + \tfrac{1}{2}\left(\sum_{d} S_{bd}P_{ad}{}^{T'}\right)\sum_{t} P_{tt}{}^{O'}B_{aa}{}^{tt} \tag{8}$$

Bringing in now the limitation $\alpha = \beta$, we define:

$$n_c{}^{*}(b) = \tfrac{1}{2}P_{cc}{}^{O'}\alpha\sum_{d} S_{ad}P_{bd}{}^{T'} \text{ and } n_c{}^{*}(a) = \tfrac{1}{2}P_{cc}{}^{O'}\alpha\sum_{d} S_{bd}P_{ad}{}^{T'}$$

and considering that $P_{cc}{}^{O'} = 0$ if ψ_c does not belong to the open shell, we rewrite (8) in the following way:

$$F'''_{ab} = \sum_{c} n_c{}^{*}(b)\,(j_{bb}{}^{cc} - \tfrac{1}{2}\,k_{bb}{}^{cc}) + \sum_{c} n_c{}^{*}(a)\,(j_{aa}{}^{cc} - \tfrac{1}{2}\,k_{aa}{}^{cc})$$

Retaining the limitation $\alpha = \beta$, we note from (7) that $(F'_{ab} + F''_{ab})$ may be expressed as the off-diagonal element of an operator:

$$F^{*} = H + \sum_{c} n_c{}^{**}(j^{cc} - \tfrac{1}{2}\,k^{cc})$$

with

$$n_c{}^{**} = P_{cc}{}^{T'} - \alpha P_{cc}{}^{O'}$$

This operator is analogous that used for the closed shell with the only difference of $n_c{}^{**}$ replacing $P_{cc}{}^{C'}$; then, referring the eigen-functions ψ_a and ψ_b to an atomic valence state with $P_{cc}{}^{T'}$ electrons in all its orbitals ψ_c, we can write nearly analogously to (4):

$$\begin{aligned} F'_{ab} + F''_{ab} = F_{ab}{}^{*} = {} & \\ & \tfrac{1}{2}S_{ab}(\chi'_a + \chi'_b) + \tfrac{1}{4}S_{ab}\left[\left(1 - P_{bb}{}^{T'} + \frac{n_b{}^{**}}{2}\right)(j_{aa}{}^{bb} + j_{bb}{}^{bb}) + \right. \\ & \left. + \left(1 - P_{aa}{}^{T'} + \frac{n_a{}^{**}}{2}\right)\left((j_{aa}{}^{aa} + j_{bb}{}^{aa})\right)\right] + \\ & + \tfrac{1}{4}S_{ab}(V_{aa}{}^{1} + V_{bb}{}^{1} + V_{aa}{}^{2} + V_{bb}{}^{2}) + \tfrac{1}{2}S_{ab}\sum_{L \neq 1,2}(V_{aa}{}^{L} + V_{bb}{}^{L}) \end{aligned} \tag{9}$$

where

$$V^{L} = -\frac{Z_L}{r_L} + \sum_{c \to L} n_c{}^{**}(j^{cc} - \tfrac{1}{2}\,k^{cc})$$

It can be easily seen that (9) is fully analogous to (4) (with only $P_{cc}{}^{C'}$ replaced by $P_{cc}{}^{T'}$ if $n_a{}^{**}$, $n_b{}^{**}$, $n_c{}^{**}$ were equal to $P_{aa}{}^{T'}$, $P_{bb}{}^{T'}$, $P_{cc}{}^{T'}$. In (9) χ'_a and χ'_b can be empirically evaluated, as already discussed, respectively as the ionization energy of an electron in ψ_a and ψ_b for an atomic valence state which has $P_{cc}{}^{T'}$ electrons in all its orbitals ψ_c. Adding F'''_{ab} and $F_{ab}{}^{*}$, and collecting together the interaction terms referring to the same orbitals ψ_c, we have:

$$\begin{aligned}F_{ab} \approx {} & \tfrac{1}{2}S_{ab}(\chi'_a+\chi'_b)+\\ & +\tfrac{1}{4}S_{ab}\left[\left(1-P_{bb}{}^{T'}+\frac{n_b{}^{**}}{2}\right)(j_{aa}{}^{bb}+j_{bb}{}^{bb})+\right.\\ & \left.+\left(1-P_{aa}{}^{T'}+\frac{n_a{}^{**}}{2}\right)(j_{aa}{}^{aa}+j_{bb}{}^{aa})\right]+\\ & +\tfrac{1}{4}S_{ab}(V_{aa}{}^{1*}+V_{bb}{}^{1*}+V_{aa}{}^{2*}+V_{bb}{}^{2*})+\tfrac{1}{2}S_{ab}\sum_{L\neq 1,2}(V_{aa}{}^{L*}+V_{bb}{}^{L*}) \qquad (10)\end{aligned}$$

where

$$V_{cc}{}^{L*} = -Z_L\left\langle\psi_c\left|\frac{1}{r_L}\right|\psi_c\right\rangle + \sum_{c\rightarrow L} n'_c(e)\,(j_{cc}{}^{cc}-\tfrac{1}{2}\,k_{cc}{}^{cc})$$

with

$$n'_c(e) = n_c{}^{**} + \frac{4n_c{}^{*}(e)}{S_{ab}} \qquad \text{if} \qquad L = 1, 2,$$

$$n'_c(e) = n_c{}^{**} + \frac{2n_c{}^{*}(e)}{S_{ab}} \qquad \text{if} \qquad L \neq 1, 2$$

and with $\psi_c = \psi_a$ or ψ_b.

Naturally $V_{aa}{}^{1*}$ and $V_{bb}{}^{2*}$ still have to be semi-empirically evaluated adding and subtracting T_{aa} and T_{bb} in order to have:

$$V_{aa}{}^{1*} = \chi''_a - T_{aa}$$
$$V_{bb}{}^{2*} = \chi''_b - T_{bb}$$

where χ''_a and χ''_b can be empirically evaluated, respectively as the ionization energy of an electron in ψ_a and ψ_b for an atomic valence state which has $(1+n'_a(a)/2)$ and $(1+n'_b(b)/2)$ electrons in ψ_a and ψ_b, and $n'_c(a)$ and $n'_c(b)$ electrons in all other orbitals ψ_c.

The remaining terms $V_{aa}{}^{L*}$ with $L \neq 1$ and $V_{bb}{}^{L*}$ with $L \neq 2$ are linear combinations of the Coulomb and exchange integrals already met in the diagonal element but with somewhat different coefficients.

The formula (10) is again rigorously valid for $\alpha = \beta$, otherwise analogous remarks to those already discussed for the diagonal element hold.

The two-center exchange integrals, which appear in the above formulae are certainly much smaller than the corresponding Coulomb integrals, and neglecting them could not be a very bad approximation. However, by applying the approximation (1), they could be calculated in terms of empirical quantities and of two-center Coulomb integrals:

$$k_{aa}{}^{bb} = \tfrac{1}{4}S_{ab}{}^{2}(2j_{aa}{}^{bb}+j_{aa}{}^{aa}+j_{bb}{}^{bb})$$

where $j_{aa}{}^{aa}$ and $j_{bb}{}^{bb}$ may be empirically evaluated, as seen in the previous sections.

Two-center Coulomb integrals

The use of the master formulae resulting from the general treatment developed in the previous sections implies indeed as its essential requirement, the knowledge of two-center Coulomb integrals.

Exact calculation of such Coulomb integrals is actually feasible, although usually at the cost of a very large calculation effort, which increases rapidly with increasing principal quantum numbers of the involved AO's. On the other hand, LCAO-MO-SCF methods for complex inorganic molecules almost necessarily imply some other approximations (*e.g.* also the uncertainties inherent to the population analysis), which lower the accuracy of the final results, so that extreme accuracy in the calculation of the two-center Coulomb integrals becomes superfluous. We therefore worked out a method for the simplified evaluation of two-center Coulomb integrals for any principal quantum number, a method which probably does not lower the overall accuracy, and requires no more calculating effort than is needed for nuclear attraction integrals. This method is based upon replacement of one of two interacting charge distributions through an appropriate distribution of point charges; referring for instance to orbitals with nodeless radial parts, we adopt the following charge systems for the different types of charge distribution:
s : fourteen charges $-\frac{1}{14}$ e on the vertices of a tetrakishexahedron.
p: two charges $-\frac{1}{2}$ e along the axis of the orbital.
d (except d_{z^2}): four charges $-\frac{1}{4}$ e on the two appropriate axes at right angles.
d_{z^2}: two charges -0.30755 e on the z axis plus four charges -0.09623 e on the x and y axes.

All these fractional charges are supposed to lie at the same appropriate distance from the nucleus. This distance is a critical parameter of the problem: the mean orbital radius or the radius of maximum density can be a physically plausible choice for it.

This point-charge approximation will be better the narrower is the "bell" in the radial distribution curve, *i.e.* the less expanded is the orbital charge distribution; then, between the two interacting charge distributions, it will be more convenient to replace the less expanded one through point charges. This rule may have exceptions only when the distribution with the more expanded "bell" is of s-type, since we can make use of a better point-charge model for this charge distribution, because of the finer fractionation of the overall charge of the electron.

When dealing with orbitals with radial nodes, we will adopt as many sets of point charges of the above described symmetry as are the "bells" in the radial distribution curve, taking care that each set comprises the fraction of the electronic charge lying under the corresponding "bell". In this case, the point-charge approximation will be particularly good, because the single "bells" are narrower and the replacement of the point charges at the points of maximum density is safer.

Generally speaking, we can say that the method will become less accurate with increasing overlap of the two charge distributions, that is with decreasing the interatomic distance and furthermore with increasing the principal quantum numbers.

Some improvements are possible in the method. Every integral j_{aa}^{bb}, treated according to our approximation, contains the term

$$\sum_i \frac{q_{ib}}{R_{ib}}$$

where q_{ib} is a charge belonging to the system of point charges replacing the continuous charge distribution $\psi_b\psi_b$, and R_{ib} is the distance of q_{ib} from the reference center of ψ_a. It is then evident that this term is our point-charge approximation of the integral $\int\psi_b(1)1/r_{1a}\cdot\psi_b(1)\,d\tau_1$, where r_{1a} is the variable distance of the electron 1 from the reference center of ψ_a; this integral may be calculated exactly, and, as a matter of fact, is of the same type already considered in our model. So the replacement of

$$\sum_i \frac{q_{ib}}{R_{ib}}$$

by the exact value may lead to significant improvements.

Moreover it is to be remarked that all the integrals j_{aa}^{bb} contain, as the main contribution, the point-charge approximation of the integrals j_{sasa}^{bb}, where ψ_{sa} is a s-type orbital with the same radial part of ψ_a. The last integral may be evaluated following its own optimization rules, for instance by approximating the $\psi_{sa}\psi_{sa}$ distribution with point charges even if this is the more expanded one.

Although a direct comparison with exactly calculated values has only been made for some cases involving principal quantum number 2 and 3, we have worked out a fairly realistic criterion through which we extend the limits of validity of the method and the conditions for optimization to higher principal quantum numbers.

We have considered all the previously discussed aspects of our approximation, checking the limits of validity and ascertaining in detail the optimal procedures and, in contrast with the first impression of the model, we have arrived at the conclusion that this model leads to an accuracy of 1% in most cases of practical interest, *i.e.* for valence orbitals and for interatomic distances near to or larger than the usual bond distances; a more ample and detailed exposition of the method is reported elsewhere[18].

Conclusive remarks

The treatment outlined in the present paper results in a LCAO-MO-SCF method which is quite complete and yet does not imply greater analytical difficulties than the calculation of two-center Coulomb integrals for the matrix elements of both the closed and open shell; rather, by the approximation worked out for the two-center Coulomb integrals, the greatest difficulty is effectively the calculation of nuclear attraction type integrals. We have pointed out the approximations used to get this result, that is the points which could possibly be improved. The explicit knowledge of one-center Coulomb and exchange integrals would enable us to take into account some minor terms neglected in the matrix elements of the open shell, to avoid the approximation of the equal distribution of the overall electronic charge among a (nl) atomic orbital set, actually differently occupied in the molecular state, when we evaluate the atomic valence state ionization energies. Eventually we could treat more rigorously the case: $\alpha \neq \beta$.

Moreover, the approximation (1), often used in our formulae, is notoriously unsatisfactory for large distances and orbitals of different type. Occasionally better approximations[19] could be inserted in our treatment in place of (1); such replacement would be particularly simple at those points concerning some terms (V_{ab}^L) of the off-diagonal elements, *i.e.* just at those points where the reduction of multi-center to two-center integrals is more important for the final result. For the diagonal elements, where such replacement would be less immediate, the accuracy of this reduction is less important because such elements consist mainly of interactions of $(j^{cc}-\frac{1}{2}k^{cc})$ type. Approximation (3) has not got wider limitations than (1); furthermore, it acts on terms which are much smaller than those upon which approximation (1) is used. For instance, the vanishing of the k_{ab}^{cc} type terms, with ψ_a and ψ_b belonging to the same atom, always parallels the even more arbitrary vanishing of the corresponding terms j_{ab}^{cc} following from the approximation (1). Moreover, the use of approximations (1) and (3) in the one-center parts $(\chi_a, \chi'_a, \chi''_a)$ results in a commonly accepted procedure, *i.e.* in considering only the Coulomb and exchange interactions with the *symmetrical* charge distributions corresponding to the different orbitals present in the atom. The possible adoption of other approximations instead of (1) should be conveniently paralleled by an analogous substitution of (3), in order to maintain a formally analogous approximation for j_{ab}^{cc} and k_{ab}^{cc}; it could in fact also appear justified to some extent that the same type of decomposition is considered in the approximation of both the Coulomb and exchange interaction of $\psi_c\psi_c$ and $\psi_a\psi_b$.

Another possible source of error, to be discussed in future developments of this method, comes out because we include some terms arising from the use of approximations (2) and (3) in the empirically evaluated one-center parts: actually the type of correlation appropriate to these terms should be investigated as a feature of the problem of the evaluation of the integrals which are approximated by (2) and (3).

Some preliminary calculations have shown that the inclusion of two-center Coulomb interactions into the matrix elements strongly affects their values, leading sometimes to physically not very plausible values; *e.g.* for anionic coordination compounds, all matrix elements turn to be unduly high and some even positive. Such instability is however fictitious; indeed the complete treatment will necessarily require explicit consideration of the electrostatic field arising from solvent molecules placed in the second coordination sphere, in order to bring the matrix elements to physically more acceptable values. Stabilization by solvation effects is very important and cannot be disregarded. Insertion of solvation effects into the treatment presented in the preceding sections will offer no new computational difficulty.

Calculations on some inorganic complex molecules, using the general criteria outlined in this paper, are now in progress in our laboratory.

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