

# LCVO-MO EMPIRICAL APPROXIMATE QUANTUMCHEMICAL METHOD FOR MANY ELECTRON SYSTEMS I

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## Introduction

Up to now, partly *ab initio* (*a priori*) all electron methods, partly all valence electron methods (CNDO, INDO, MINDO, PCILO, EHT etc.) have been used for the investigation of bond structure. For studying the molecular structure of organosilicon compounds, calculations have been carried out mainly by CNDO/2 method and to a lesser degree by *ab initio* method. The latter has been less widely extended because of its large computer time demand while the CNDO/2 method does not give reasonable results either in sp or in spd approximation. The role of d orbitals is entirely neglected in sp approximation and taken excessively into account in spd approximation. Naturally, this problem refers not only to silicon but to any element in the 3rd, 4th and 5th rows. Of course the difficulty ever grows for increasing atomic numbers.

To eliminate the mentioned shortcomings a more sensitive quantum-chemical calculation method has been developed, requiring greater attention, the so-called LCVO-MO (*linear combination of valence orbitals — molecular orbitals*) method.

## Basic principles of the LCVO-MO method

The method formally is a stricter alternative of the CNDO/2 method by CLARK [1]. It is known that CLARK modified the original CNDO/2 method by the following way: he calculated the electron repulsion integrals according to OHNO [2], the shielding factors according to BURNS' [3] and the resonance integrals by the WOLFSBERG—HELMHOLZ formula [4]. The ionization energies and electron affinities were chosen according to SICHEL and WHITEHEAD [5]. Assuming a fixed configuration, the CNDO/2—CLARK method provides the excitation energies of electron transition and the corresponding oscillator strengths in addition to the orbital energies and other usual quantities. CLARK carried out calculation [6] by this method, among others, for cyclopropane, ethylene oxide and ethylamine.

Starting from the principles of CNDO/2 — CLARK method, the LCVO—MO method is featured by the following.

1. It takes only the valence electrons of the system into account. The electrons on closed atomic shells and part of the atomic nucleus are omitted and their effect only approximated.

2. In contrary to the *ab initio* and the generally used approximate methods, the starting base functions are related to valence orbitals (VO) rather than to atomic orbitals (AO). The VO base functions are mostly hybrid functions based on the geometry of molecules in question, e. g.:

$$\varphi_p = \frac{1}{(1 + a^2 + b^2)^{1/2}} [s + ap_x + bp_y + cp_z],$$

where  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  are AO eigenfunctions,  $a$ ,  $b$  and  $c$  are hybridization factors.

Consequently, the values of ionization energies and electron affinities in the HARTREE—FOCK matrix elements are calculated according to HINZE and JAFFE [7] on the basis of a given valence state.

3. Using the ZDO (zero differential overlap) condition, part of the necessary integrals are neglected. The rest of the integrals — with the exception of overlap integrals — are empirically calculated:

a) For the calculation of one-center electron repulsion integrals  $\gamma_{pp}$ , PARISER's method [8] was used:

$$\gamma_{pp} = I_p - A_p \quad (1)$$

where  $I_p$  is the ionization energy,  $A_p$  is the electron affinity.

b) The two-center electron repulsion integrals  $\gamma_{pq}$  were taken according to OHNO [2]:

$$\gamma_{pq} = \frac{14.397}{(a_{pq}^2 + R_{pq}^2)^{1/2}} [\text{eV}] \quad (2)$$

where

$$a_{pq} = \frac{28.794}{\gamma_{pp} + \gamma_{qq}}$$

and  $R$  is the bond distance.

c) The resonance integrals  $\beta_{pq}$  were calculated by WOLFSBERG—HELMHOLZ formula [4]:

$$\beta_{pq} = 1/2 K(I_p + I_q) S_{pq},$$

where  $K$  is a proportionality factor and  $S_{pq}$  is the overlap integral.

The overlap integrals were calculated from SLATER (STO) functions. The orbital exponent was given according to BURNS' rules [3], for hydrogen the  $\zeta = 1.2$  value was chosen, similarly to the CNDO/2 method.

4. Assuming fixed configuration, the electronic transition energies and the oscillator strengths can also be calculated using the configurational interaction (CI) method.

### Formalism of LCVO-MO approximation

The eigenvalue problem for a molecule (consisting of A, B, C... atoms,  $\omega$  centers and containing  $N$  valence electrons,  $n$  valence orbitals) can be written as:

$$\hat{H}(1, 2, \dots, N) \Delta(N) = E(1, 2, \dots, N) \Delta(N) \quad (4)$$

where  $\Delta(N)$  is a determinant wave function.

The Hamiltonian operator in (4) can be separated to one-electron Hamiltonian operators:

$$\hat{H}(1, 2, \dots, N) = \sum_{i=1}^N \hat{H}_i = \sum_{i=1}^N \hat{H}_0(i) + \sum_{\substack{i,j \\ i \neq j}}^N \frac{e^2}{r_{ij}} \quad (5)$$

where  $\frac{e^2}{r_{ij}}$  is the repulsion potential between electrons and  $H_0(i)$  is the core Hamiltonian operator. The latter can be specified:

$$\hat{H}_0(i) = \hat{T}(i) + \hat{V}_A(i) + \sum_{B \neq A} \hat{V}_B(i) \quad (6)$$

where  $\hat{T}(i)$  is the kinetic energy operator related to electron  $i$ ,  $V_A(i)$  and  $V_B(i)$  are potential energies from atoms A and B, respectively.

The MO eigenfunction relating to electron  $i$  in quantum state  $k$  is a linear combination of valence orbitals:

$$\Psi_k(i) = \sum_{p=1}^n c_{kp} \varphi_p(i). \quad (7)$$

The wave function  $\varphi_p(i)$  can be either VO function or hybrid function, i. e. SLATER type orbital function (AO). For example, in ethylene three  $sp^2$  trigonal hybrid wave functions and one  $p\pi$  atomic wave function belong to a carbon atom. The exact HARTREE-FOCK eigenvalue equation:

$$\mathbf{F}c_k = \varepsilon_k \mathbf{S}c_k. \quad (8)$$

Neglecting the overlap integrals  $\mathbf{S}$  becomes unity matrix:

$$\mathbf{F}c_k = \varepsilon_k c_k. \quad (9)$$

The elements of FOCK matrix in Eq. (8):

$$F_{pq} = I_{pq} + \sum_{r,s=1}^n P_{rs} \left( \langle pr | qs \rangle - \frac{1}{2} \langle pr | sq \rangle \right) \quad (10)$$

where

$$P_{rs} = 2 \sum_{k=1}^{N/2} c_{kr} \cdot c_{ks}, \quad (11)$$

$$I_{pq} = \langle \varphi_p | \hat{H}_0 | \varphi_q \rangle, \quad (12)$$

$\langle pr | qs \rangle$  and  $\langle pr | sq \rangle$  are electronic repulsion integrals.

1. Let  $p = q$ ,

$$\begin{aligned} \text{then} \quad F_{pp} &= I_{pp} + 1/2 q_p \langle pp | pp \rangle + \sum_{\alpha \neq p} q_\alpha \langle p_\alpha | p_\alpha \rangle + \\ &+ \sum_{B \neq A} \sum_{\beta} q_\beta \langle p_\beta | p_\beta \rangle \end{aligned} \quad (13)$$

and

$$\begin{aligned} p, \alpha &\in A \\ \beta &\in B \end{aligned}$$

where

$$P_p = q_{pp}, \quad q_\alpha = P_{p\alpha}, \quad q_\beta = P_{p\beta}$$

2. If  $p \neq q$ , that is, orbitals  $p$  and  $q$  belong to two different atoms, then

$$F_{pq} = I_{pq} - 1/2 P_{pq} \langle pq | pq \rangle \quad (14)$$

$$\begin{aligned} p &\in A \\ q &\in B \end{aligned}$$

Naturally, if two orbitals marked by  $p$  and  $q$  are on the same atom, then Eq. (14) becomes:

$$F_{pq}^A = -1/2 P_{pq} \langle pq | pq \rangle \text{ and } p, q \in A, \quad (15)$$

since

$$I_{pq} = 0.$$

On the basis of Eq. (7)  $I_{pp}$  can be written as:

$$I_{pp} = \langle \varphi_p | \hat{H}_0 | \varphi_p \rangle = \int \varphi_p \left( \hat{T}(i) + \hat{V}_A + \sum_{B \neq A} \hat{V}_B \right) \varphi_p d\tau =$$

$$\begin{aligned}
 &= \int \varphi_p (\widehat{T}(i) + \widehat{V}_A) \varphi_p d\tau + \int \varphi_p \sum_{B \neq A} \widehat{V}_B \varphi_p d\tau = \\
 &= W_p - \sum_{B \neq A} \int \varphi_p \frac{Z_B e^2}{r_B} \varphi_p d\tau = \\
 &= W_p - \sum_{B \neq A} Z_B e^2 \int \varphi_p \frac{1}{r_B} \varphi_p d\tau \tag{16}
 \end{aligned}$$

where  $W_p$  is the energy of the electron on orbital  $\varphi_p$  in the field of the core of isolated atom  $p$ .

Be  $Z_B$  the number of valence electrons on atom B, then the core of atom B will have a positive charge  $Z_B \cdot e$ . Approximating the interaction of this core with the orbital  $\varphi_r$  by repulsion Coulomb integral of the electron on orbital  $\varphi_p$  and of the  $Z_B$  valence electrons belonging to atom B, and separating this interaction into terms  $Z_{B\beta\gamma p\beta}$  according to orbitals on atom B:

$$-Z_B e^2 \int \varphi_p \frac{1}{r_B} \varphi_p d\tau = -Z_{B\gamma p B} = \sum_B Z_{B\beta\gamma p\beta} \tag{17}$$

Naturally, the number of all valence electrons on atom B equals to the total of electrons on the particular orbitals, i. e.

$$Z_B = \sum_{\beta} Z_{B\beta} \tag{18}$$

Approximating the nondiagonal elements between given orbitals of atoms A and B according to HELMHOLTZ and WOLFSBERG:

$$I_{pq} = \langle \varphi_p | H_0 | \varphi_q \rangle = \beta_{pq}^0 = \frac{1}{2} K(I_p + I_q) S_{pq}. \tag{19}$$

A relation is known to exist between the ionization energy and the one-electron, non perturbed eigenvalue of valence orbital  $p$  on atom A:

$$-I_p = W_p + \sum_{\alpha \neq p} Z_{A\alpha} \langle p\alpha | p\alpha \rangle = W_p + \sum_{\alpha \neq p} Z_{A\alpha} \gamma_{p\alpha} \quad \text{and } \alpha \in A. \tag{20}$$

Replacing Eqs (17) and (20) into (16), we obtain:

$$I_{pp} = -I_p - \sum_{\alpha \neq p} Z_{A\alpha} \gamma_{p\alpha} - \sum_{B \neq A} \sum_{\beta} Z_{B\beta} \gamma_{p\beta}. \tag{21}$$

Substituting (21) for diagonal matrix elements and introducing simplified notation for electronic repulsion integrals  $\gamma_{p\alpha} = \langle p\alpha | p\alpha \rangle$ ,  $\gamma_{p\beta} = \langle p\beta | p\beta \rangle$ ,  $\gamma_{pq} = \langle pq | pq \rangle$ , Eq. (13) becomes:

$$F_{pp} = -I_p + \frac{1}{2} q_{p\beta} \gamma_{pp} + \sum_{\alpha \neq p} (q_\alpha - Z_\alpha) \gamma_{p\alpha} + \sum_{B \neq A} \sum_{\beta} (q_\beta - Z_\beta) \gamma_{p\beta} \quad (22)$$

and the nondiagonal matrix element expressed in terms of Eqs (14) and (20):

$$F_{pq} = \beta_{pq}^0 - \frac{1}{2} P_{pq} \gamma_{pq} \quad (23)$$

if orbitals  $p$  and  $q$  belong to different atoms.

If orbitals  $p$  and  $q$  are on the same atom, Eq. (15) takes the form

$$F_{pq} = -1/2 P_{pq} \gamma_{pq} . \quad (24)$$

It can be proven that, after certain simplifications and introducing:

$$\begin{aligned} \sum_{\alpha \neq p} q_\alpha &= P_{AA} - q_p, & \gamma_{\alpha p} &= \gamma_{AA} = \gamma_{pp} \\ \sum_{\alpha \neq p} Z_\alpha &= Z_{AA} - 1, & \gamma_{\beta p} &= \gamma_{AB} = \gamma_{pq} \\ \sum_{\beta} q_\beta &= P_{BB} \end{aligned} \quad (25)$$

Eq. (22) can be written as:

$$\begin{aligned} F_{pp} &= -I_p + 1/2 q_p \gamma_{AA} + (P_{AA} - q_p - Z_{AA} + 1) \gamma_{AA} + \\ &+ \sum_{B \neq A} (P_{BB} - Z_B) \gamma_{AB} . \end{aligned} \quad (26)$$

Incorporating  $1/2 q_p \gamma_{AA}$  into terms in parentheses and taking Eq. (1) into account:

$$\begin{aligned} F_{pp} &= -\frac{1}{2} (I_p + A_p) + \left[ (P_{AA} - Z_A) - \frac{1}{2} (q_p - 1) \right] \gamma_{AA} + \\ &+ \sum_{B \neq A} (P_{BB} - Z_B) \gamma_{AB} \end{aligned} \quad (27)$$

Eq. (23) may be transformed similarly,

$$F_{pq} = \beta_{pq}^0 - 1/2 P_{pq} \gamma_{AB} , \quad (28)$$

Eqs (27) and (28) correspond to the formalism of the CNDO/2 method.

Solving the eigenvalue equation (9), the MO energies  $\epsilon_k^{SCF}$  are obtained, identifiable, on the basis of KOOPMANS' theorem, with the one-electron ionization energies.

In the knowledge of SCF-MO energies and coefficients of the particular MO, the total electron energy of a system ( $E_e$ ) is easy to give in the LCVO-MO approximation:

$$E_e = \sum_{k=1}^{n/2} (I_{kk}^{SCF} + \epsilon_k^{SCF}) \quad (29)$$

where

$$I_{kk}^{SCF} = \sum_{p=1}^n c_{k,p}^{*SCF} \left[ -I_p - \sum_{\alpha \neq p} Z_\alpha \gamma_{p\alpha} - \sum_{B \neq A} \sum_{\beta} Z_\beta \gamma_{p\beta} \right] c_{k,p}^{SCF} + \sum_{p \neq q} c_{k,p}^{*SCF} \beta_{pq}^0 c_{k,p}^{SCF}. \quad (30)$$

The respective electron energies of atoms A, B, C . . . are:

$$\begin{aligned} E_A &= \sum_p Z_p (-I_p - \sum_{\alpha \neq p} Z_\alpha \gamma_{\alpha p}) + \sum_{i < j} \gamma_{ij} = \\ &= \sum_p [-Z_p I_p + (Z_p - 1) \gamma_{pp}] - \sum_{p < \alpha} Z_p Z_\alpha \gamma_{p\alpha} \end{aligned} \quad (31)$$

where  $i, j$  are electron numerals;  $Z_p$  and  $Z_\alpha$  are numbers of electrons on orbitals  $p$  and  $\alpha$ , respectively;  $\gamma_{ij}$  is the Coulomb integral for interaction between electrons  $i$  and  $j$ .

The repulsion energy between nuclei may be written as:

$$E_M = \sum_{B \neq A} \frac{Z_A Z_B}{R_{AB}} \cdot 14.397 [eV]. \quad (32)$$

The total energy in ground state is given by the algebraic sum of Eqs (29) and (32),

$$E_T = E_e + E_M. \quad (33)$$

Subtracting the atomic electron energies, Eq. (31), from the total energy yields the dissociation (binding) energy:

$$E_D = E_e + E_M - E_A. \quad (34)$$

In the LCVO-MO approximation the MULLIKAN population analysis can be applied. For example, the partial charge  $\delta_A^e$  may be defined as:

$$\delta_A^e = Z_A - p_{AA} \quad (35)$$

where

$$P_{AA} = \sum_{\alpha} q_{\alpha} \quad (36)$$

the total population on atom A and  $q$  the population on orbital  $\alpha$  of atom A. Bond orders, hard or sophisticated to obtain from the CNDO/2 approximation, are easy to derive by the LCVO method such as:

$$P_{AB} = \sum_{r \in A} \sum_{s \in B} P_{rs} \quad (37)$$

where  $p_{AB}$  is the total bond order between atoms A and B,  $p_{rs}$  is the bond order between valence orbitals  $r$  and  $s$ .

The dipole moment  $\mu$  consists of two parts, namely atomic dipoles  $\mu_e$  and electron displacement  $\mu_{hyb}$ , i. e.

$$\mu = \mu_e + \mu_{hyb} \quad (38)$$

The electron displacement part:

$$\mu_e = 4.803 \sum_A \vec{R}_A \delta_A^e \quad (39)$$

where  $\vec{R}$  is a position vector with the nucleus as origin.  $\mu_{hyb}$  in Eq. (38) can further be divided into two parts, namely the atomic dipole parts of hybrid orbitals  $sp$  and  $pd$ :

$$\mu_{hyb} = \mu_{sp} + \mu_{pd} \quad (40)$$

If both atoms A and B form a bond by hybrid orbitals, then the hybrid atomic dipole  $sp$  tending from atom A to atom B is:

$$\mu_{sp}(A) = -q_0 \frac{2e\sqrt{a^2 + b^2 + c^2}}{1 + a^2 + b^2 + c^2} \bar{z}_{sp} \quad (41)$$

where  $a$ ,  $b$  and  $c$  are hybridization factors,  $q_0$  is the charge in orbital  $\varphi_p$  and

$$\bar{z}_{sp} = \int s \widehat{M}_z p d\tau = \int s \bar{z} p d\tau \quad (42)$$

The value of  $\bar{z}_{sp}$  can be evaluated for atoms with principal quantum numbers 2 and 3 as follows,

$$\bar{z}_{sp}(n=2) = \frac{5}{\sqrt{3}} \frac{(z_s z_p)^{5/2}}{[1/2(z_s + z_p)]^6} a_0 \quad (43)$$

$$\bar{z}_{sp}(n=3) = (2/3)^7 \frac{7}{\sqrt{3}} \frac{(z_s z_p)^{7/2}}{[1/3(z_s + z_p)]^8} a_0 \quad (44)$$



where  $z_s$  and  $z_p$  are the BURNS effective nuclear charges belonging to orbitals  $s$  and  $p$ , respectively;  $a_0 = 0,5292 \text{ \AA}$ .

Definition of the hybrid atomic dipole  $pd$ :

$$\mu_{pd}(A) = \mu_{pd}(x)\vec{i} + \mu_{pd}(y)\vec{j} + \mu_{pd}(z)\vec{k} \quad (45)$$

where  $\mu_{pd}(x)$ ,  $\mu_{pd}(y)$  and  $\mu_{pd}(z)$  are the dipole vector components along the three Cartesian co-ordinates; this dipole  $\mu_{pd}$  may similarly be evaluated as it was shown for  $\mu_{sp}$ .

It has already been mentioned that electronic excitation energies and oscillator strengths can be calculated by LCVO method. The one-electron excitation energies of singlet and triplet  $a \rightarrow b$  transition ( ${}^{1,3}E_{a \rightarrow b}^{SCF}$ ) can be derived in the known way [9] from the SCF-LCVO-MO method.

Considering the ZDO condition used in LCVO-MO approximation:

$$\begin{aligned} {}^{1,3}E_{a \rightarrow b}^{SCF} = & \varepsilon_b^{SCF} - \varepsilon_a^{SCF} - \sum_{p, q \neq 1}^n c_{a,p}^{*SCF} c_{b,q}^{*SCF} \cdot \\ & \cdot (c_{a,p}^{SCF} c_{b,q}^{SCF} + {}^{1,3}k c_{a,q}^{SCF} c_{b,p}^{SCF}) \gamma_{pq} \end{aligned} \quad (46)$$

where  ${}^1k = -2$ ,  ${}^3k = 0$ ,  $a$  and  $b$  designate the ground and the excited state, respectively.

Starting from the SCF-LCVO molecular orbitals obtained by LCVO method, the configurational interaction can be taken into account. The state function related to excited state ( ${}^{1,3}\Phi$ ) is obtained as the linear combination of eigenfunctions belonging to one-electron singlet and triplet excited configurations:

$${}^{1,3}\Phi(1, 2, \dots, n) = \sum_{a \rightarrow b} {}^{1,3}C_{a \rightarrow b} \Delta_{ab}(n) \quad (47)$$

where  $\Delta_{ab}(n)$  is a SLATER determinant.

For determining the  ${}^{1,3}C_{a \rightarrow b}$  constants a variational calculation has to be carried out in the known way. Finally the  ${}^1E$  (singlet) and  ${}^3E$  (triplet) one-electron transition energies modified by configurational interaction are obtained. In the knowledge of  ${}^{1,3}C_{a \rightarrow b}$  constants the transition dipole moments and oscillator strengths can also be calculated [10]. The LCVO method gives the orbital energies, ionization energies, total energy and bond energy, as it will be shown in a subsequent paper. Varying bond lengths and bond angles yields the potential curve and force constants, the dipole moment and singlet and triplet transitions energies for each set of bond lengths and bond angles.

With an appropriate variation of parameters the method is likely to give fair results for the physical quantities needed.

### Summary

1. A stricter alternative of CNDO/2 method, the so-called LCVO-MO method has been developed. The MO eigenfunctions are approximated by the linear combination of valence orbital (VO) base functions.

2. The ZDO condition zeroes all three-centre and four-centre integrals, only the one- and two-center integrals of type  $\gamma_{pq}$  are taken into account.

3. The resonance integrals are given by the HELMHOLZ-WOLFSBERG formula and the necessary overlap integrals are calculated from VO eigenvalues according to BURNS' rules.

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