

Extension of the PCILO-Method to the Localized Free Radicals

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The formulas for the energy calculations up to the 3rd order are given for free radicals where the unpaired electron is well-localized on an atomic orbital. One compares with the CNDO variational results. The method is applied to the conformational study of the vinyl radical. The 2nd order spin-densities of the β protons are approximately 6/10 of the CNDO-SCF results and are determined by a direct delocalization through space.

Die Ausdrücke für die Berechnung der Energien bis zur 3. Ordnung werden für den Fall freier Radikale, bei denen das ungepaarte Elektron in einem Atom-Orbital sitzt, angegeben, auf das Vinyl-Radikal angewendet und die Resultate mit denen des CNDO-Verfahrens verglichen. Die Spindichten 2. Ordnung am β -Proton werden durch direkte räumliche Lokalisierung bestimmt und sind ungefähr 6/10 der CNDO-Ergebnisse.

On donne les formules permettant de calculer jusqu'au 3^{ème} ordre l'énergie de radicaux où l'électron libre est bien localisé sur une Orbitale-Atomique. On compare aux résultats CNDO variationnels. La méthode est appliquée à l'étude de la conformation du radical vinyle. Les densités de spin des protons en β , calculées au 2^{ème} ordre, valent 6/10 des résultats CNDO-SCF et apparaissent déterminées par une délocalisation directe à travers l'espace.

Introduction

In preceding papers [1–3], a method based on the use of bond orbitals and perturbation theory has been developed for the calculation of the ground state energy of a closed shell molecule. This method, hereafter called PCILO (Perturbative Configuration Interaction using Localized Orbitals), gives lower energies than the SCF procedure in a much shorter time: it has been widely employed to study the conformation of large molecules [4–6]. The analysis of the various contributions allows an interpretation of energy differences in terms of zeroth-order repulsion, delocalization, polarization and correlation effects.

Similar conformational problems appears for radicals, and seem to be important for the interpretation of E.S.R. hyperfine splittings. (See for instance [7–9]). Therefore an extension of the PCILO method for radical systems seems worthwhile.

However, one must keep in mind that the PCILO method requires that one may build a good approximation of the ground state wave function with only *one* determinant constructed from *localized* molecular orbitals. Consequently we cannot treat in that simple scheme the radicals in which the unpaired electron is delocalized, such as in the radical ions of conjugated system or in the radicals

of the allylic type. These problems will be treated later by an "excitonic" version of the present algorithm, where the ground state wave function is a linear combination of several determinants. The present treatment deals for instance with the saturated radicals and all the cases where the unpaired electron may be localized mainly on one atomic orbital (the benzyl radical represents a limit for the validity of the method).

1. Method

We just summarize the PCILO method.

One chooses a set of reasonable bonding and antibonding orbitals localized on the chemical bonds. The bonding orbitals are used to build a fully localized determinant. The basis of excited states is built using the antibonding orbitals. One calculates the lower eigenvalues of the CI matrix in this basis by a Rayleigh Schrödinger expansion.

To construct the ground state wave function of a free radical with $2n + 1$ electrons the simplest hypothesis that may be made is to suppose that the $(2n)$ electrons of the system are shared by pairs, each member of which has opposed spin, on molecular orbitals φ_i . The last electron is alone with a spin function α (or β) on the last molecular orbital. The zeroth order ground state wave function is given by:

$$\Phi_0 = \frac{1}{\sqrt{n}} |\varphi_1 \bar{\varphi}_1 \dots \varphi_i \bar{\varphi}_i \dots \varphi_n \bar{\varphi}_n \varphi_\mu|.$$

In the PCILO method, the molecular orbital occupied by the unpaired electron is just the atomic hybrid orbital μ (and not a linear combination of two hybrids); So in this case the antibonding orbital does not exist.

A. Zeroth Order Energy

The energy of the ground state determinant Φ_0 , is given by

$$E_0 = \sum_{i=1}^n 2I_i + I_\mu + \sum_{i \neq j}^n (2J_{ij} + J_{ii}) + \sum_{i=1}^n 2J_{i\mu}. \quad (1)$$

The exchange integrals disappear, due to the complete localization of the MO and to the CNDO hypothesis. One may introduce mono-electronic energies, for the molecular orbitals, calculated as mean values of the Hartree-Fock Hamiltonian for this set of MO: $\varepsilon_i = \langle \varphi_i | h | \varphi_i \rangle$

$$h_{(\alpha)} = h_m + \sum_{j=1}^n 2J_j - K_j + J_\mu - K_\mu$$

$$h_{(\beta)} = h_m + \sum_{j=1}^n 2J_j - K_j + J_\mu \quad (2)$$

where h_m is the (kinetic + nuclear attraction) operator. The nullity of the exchange integrals between MO's on different bonds implies that the orbital energies are the same for the α spin and β spin Molecular Orbitals of the same space part,

except for the Molecular Orbital μ :

$$\text{for } i \neq \mu \left\{ \begin{array}{l} \varepsilon_i = \varepsilon_i = I_i + \sum_{j=1}^n 2J_{ij} - J_{ii} + J_{i\mu} \\ \varepsilon_{i^*} = \varepsilon_{i^*} = I_{i^*} + \sum_{j=1}^n 2J_{i^*j} - K_{ii^*} + J_{i^*\mu} \end{array} \right. \quad (3)$$

where $I_i = \langle \varphi_i | h_m | \varphi_i \rangle$.

For $i = \mu$, one gets two different energies for μ and $\bar{\mu}$.

$$\begin{aligned} \varepsilon_\mu &= I_\mu + \sum_{j=1}^n 2J_{j\mu} \\ \varepsilon_{\bar{\mu}} &= I_\mu + \sum_{j=1}^n 2J_{j\mu} + J_{\mu\mu} = \varepsilon_\mu + J_{\mu\mu}. \end{aligned} \quad (4)$$

Using these definitions, the energy of the ground state determinant may be written

$$E_0 = \sum_{i=1}^n (e_i + I_i) + \frac{e_\mu + I_\mu}{2}. \quad (5)$$

B. Second Order Correction

The first order correction is zero by definition of our perturbation series [10]. For all orders of perturbation, the energy denominators

$$\langle 0 | H | 0 \rangle - \langle I | H | I \rangle$$

will be calculated by the following formula:

If $|I\rangle$ is a k -excited determinant obtained from $|\Phi_0\rangle$ by creating k particle-hole pairs:

$$|I\rangle = \left(\prod_{p=1}^{2k} b_{i(p)}^+ \right) |0\rangle$$

where $b_{i(p)}^+$ is a creation operator of particle or hole in a given spin orbital i ,

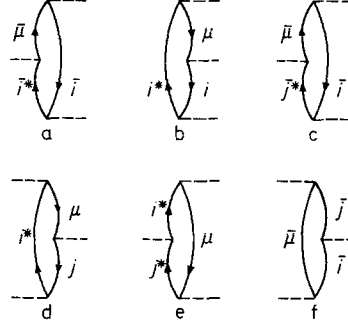
$$\begin{aligned} &\langle 0 | H | 0 \rangle - \langle I | H | I \rangle \\ &= \sum_{p=1}^{2k} \varepsilon_{i(p)} (-1)^{(l-n)} - \frac{1}{2} \sum_{\substack{p \\ =1}}^{2k} \sum_{\substack{q \\ =1}}^{2k} (J_{i(p)k(q)} - K_{i(p)k(q)}) X (-1)^{(n_i+n_k)} \end{aligned} \quad (6)$$

where n_i is the occupation number of the spin-orbital i in the ground state determinant. This formula is valid, without any approximation, $|\Phi_0\rangle$ being closed shell or openshell, if the ε_i are defined as the mean values of the Hartree Fock mono-electronic hamiltonian for $|\Phi_0\rangle$. This formula is demonstrated by Kruglyak *et al.* [11].

If one considers a determinant $|I\rangle$ obtained from $|\Phi_0\rangle$ by the action of b_p^+ creation operators which do not involve the μ spin-orbital, one may associate to $|I\rangle$ another determinant $|I'\rangle$ obtained by the action of the operators b_p^+ ,

The only changes with respect to the closed shell systems concern the cases where I or (and) J imply the unpaired electron. One may then use the formulas given in Ref. [3]¹.

The μ or $\bar{\mu}$ orbitals only appear in the polarization-delocalization and delocalization-delocalization corrections. They correspond to the following diagrams



$$\text{a) } |I\rangle = \left(\frac{\bar{j}^*}{\bar{i}} \right) J = \left(\frac{\bar{\mu}}{i} \right) \text{ polarization-delocalization}$$

$$2 \sum_{i=1}^n v_{i i^*} v_{i \mu} h_{\mu i^*}$$

$$\text{b) } |I\rangle = \left(\frac{i^*}{i} \right) J = \left(\frac{i^*}{\mu} \right) \text{ polarization-delocalization}$$

$$-2 \sum_{i=1}^n v_{i i^*} v_{\mu i^*} h_{i \mu}$$

$$\text{c) } |I\rangle = \left(\frac{\bar{j}^*}{\bar{i}} \right) J = \left(\frac{\bar{\mu}}{\bar{i}} \right) \text{ delocalization-delocalization}$$

$$2 \sum_{\substack{i \neq j \\ =1}}^n v_{i j^*} v_{i \mu} h_{\mu j^*}$$

$$\text{d) } |I\rangle = \left(\frac{i^*}{j} \right) |J\rangle = \left(\frac{i^*}{\mu} \right) \text{ delocalization-delocalization}$$

$$-2 \sum_{\substack{i \neq j \\ =1}}^n v_{j i^*} v_{\mu i^*} h_{\mu j}$$

¹ There are two typographical errors in that paper: The delocalization-delocalization correction 1b) should be read $4 \sum_i \sum_{j < k} (\dots)$ the interaction between two bonds diexcitations 3a) should be read $2 \sum_l \sum_{j < k} (\dots)$.

$$e) |I\rangle = \left(\frac{j^*}{\mu}\right) |J\rangle = \left(\frac{i^*}{\mu}\right) \text{ delocalization-delocalization}$$

$$\sum_{i \neq j}^n v_{\mu j^*} v_{\mu i^*} h_{i^* j^*}$$

$$f) |I\rangle = \left(\frac{\bar{\mu}}{i}\right) |J\rangle = \left(\frac{\bar{\mu}}{j}\right) \text{ delocalization-delocalization}$$

$$\sum_{i=1}^n \sum_{\substack{j=1 \\ \neq i}}^n -v_{i\mu} v_{j\mu} h_{ij}$$

This method allows, by a double perturbation treatment a rapid and interpretable calculation of the spin densities. The corresponding development up to the third order, will be given soon [12]. However, the second order spin density on a bond $i \neq \mu$ is given by

$$\begin{aligned} \rho = & - \left(2v_{i\mu} \frac{h_{\mu i^*}}{\Delta E_{i i^*}} + 2v_{\mu i^*} \frac{h_{i\mu}}{\Delta E_{i i^*}} \right) \langle i | \frac{1}{M_s} S_z \delta | i^* \rangle \\ & + v_{\mu i^*}^2 \langle i^* | \frac{1}{M_s} S_z \delta | i^* \rangle + v_{i\mu}^2 \langle i | \frac{1}{M_s} S_z \delta | i \rangle. \end{aligned} \quad (10)$$

If the bond polarity of the molecular orbital i is zero, and if one may write

$$\Delta E_{i i^*} = 2\Delta E_{i \bar{\mu}} = 2\Delta E_{\mu i^*}$$

(which appears to be reasonable from the numerical results), the spin density on a proton may be approximated by

$$\rho_H = \frac{1}{2} \langle 1s_\mu | S_z \delta | 1s_\mu \rangle (v_{i\mu} - v_{\mu i^*})^2. \quad (11)$$

The monocentric exchange integrals which appear in the INDO approximation [17] could be included in the perturbation operator, to give the spin-polarization.

2. Results

A. Comparisons with CNDO Calculations

We have made some radical energy calculations with both the CNDO and PCILO method. As it has been noted for closed shell systems [2]; a) the interaction with monoexcited configurations brings the energy practically to the SCF level; b) the second order energy is very low compared to the SCF level; c) the third order energy correction is positive; so that the second order energy being certainly lower than exact solution of configurations interaction, the third order energy seems thus a better approximation of the "true" energy.

Table 1 summarizes CNDO II and PCILO results obtained for one conformation of the radical of malic acid $\text{COOH-CH-CHOH-COOH}^2$ and for the methyl radical and ethyl radical.

The following examples also imply comparisons with variational calculations which supports the same conclusions. But as they involve conformational problems, we have treated them in a more detailed way.

² A complete conformation study of this radical has been done elsewhere [13] by this method.

Table 1. Energy terms of the perturbation development and CNDO II energy (all terms are in eV)

Energy terms	Methyl radical	Malic [13] acid radical	Ethyl radical
Zereth order	-247.82	-3356.20	-483.08
Zereth order + Monoexcited configuration interaction	-248.20	-3376.36	-485.05
Second order	-248.95	-3386.45	-486.62
Third order	-248.83	-3379.70	-486.79
CNDO II method	-248.07	-3376.86	-485.14

B. The Vinyl Radical (Fig. 1)

To explain the experimental data [7], it must be required that a) This radical exists in two forms which are interconverting. An estimate of 2 Kcal/mole has been made for the inversion barrier [7].

b) The actual structure is somewhere between two limits: the first one is obtained when the radical is linear, so the C-H bond uses a sp hybrid from the carbon and the electron resides in a pure p orbital. The second one is obtained when the CH bond uses a sp^2 hybrid from the carbon and the unpaired electron resides in a second sp^2 hybrid. It seems that the actual structure is closer to the later.

An SCF-Gaussian calculation in a basis set [14] indicates that the most stable conformation corresponds to a \widehat{CCH} angle of 138° , which is in agreement with a semi-empiric determination based on the relation between spin density and experimental coupling constants in valence bond method: $130 < \widehat{CCH} < 150$ [15].

A simplified all valence electron calculation [16] gives a stable linear form and a good agreement with the experimental spin densities for $\widehat{CCH} \simeq 150^\circ$.

With the CNDO II approximations (Table 2, column 2), the minimum occurs for $\widehat{CCH} \simeq 160^\circ$ but the inversion barrier is much too small (0.13 Kcal/mole). The INDO approximations give almost the same result [17].

In the PCIO-calculation the hybrid atomic orbital containing the unpaired electron is determined by orthogonality to the two C→C and C→H hybrids realizing the maximum overlap in the C-C and CH bonds. Therefore, one studies only the dependence of the energy (Table 2) and spin density (Table 3) with respect to the $\widehat{C-C-H}$ angle γ .

If we consider the zeroth order determinant energy (Table 2, column 3), the minimum occurs for $\gamma = 180^\circ$, due to the repulsion between H and the CH_2 group.

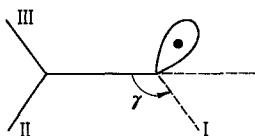


Fig. 1.

Table 2. Conformational study of the vinyl radical. 0, 2nd, 3rd order energies and polarization, delocalization, inter bond correlation, delocalization-delocalization corrections as a function of the γ bond angle value (the values are given in Kcal/mole)

γ	CNDO II	Zero energy	Zero order energy and monoexcitations corrections	2nd order energy	3rd order energy	2nd order polarization correction	2nd order delocalization correction	2nd order (a) diexcited inter bond correction	3rd order delocalization correction
-120	-10077.29	-10006.03	-10070.46	-10118.38	-10114.43	-2.40	-62.03	-19.86	-7.65
-130	-10084.00	-10013.29	-10077.27	-10124.38	-10121.26	-2.80	-61.19	-19.70	-8.18
-140	-10088.14	-10018.15	-10081.51	-10129.10	-10125.10	-3.22	-60.13	-19.62	-8.14
-150	-10090.15	-10021.26	-10083.77	-10131.32	-10127.17	-3.62	-58.89	-19.58	-7.84
-160	-10090.78	-10023.06	-10084.85	-10132.21	-10127.67	-3.97	-57.66	-19.57	-7.42
-170	-10090.72	-10023.99	-10084.33	-10132.44	-10127.56	-4.21	-56.73	-19.57	-7.06
-180	-10090.65	-10024.27	-10084.96	-10132.96	-10127.45	-4.29	-56.39	-19.57	-6.92

 Table 3. Hydrogen hyperfine coupling constants (in Gauss) as a function of the γ angle. The relation $a_H = Qq$ where q is the spin density on the 1s Atomic Orbital and Q is taken equal to 539.86 G [18]. The numbers between parentheses are calculated according to the approximate Eq. (11)

γ values	CNDO-SCF		PCILO (from 2nd order spin densities)	
	α	β_2	α	β_2
120	39.4	69.6	24.1 (22.2)	38.2 (27.6)
130	32.2	72.6	19.4 (17.8)	41.7 (30.5)
140	24.6	75.8	14.2 (13.3)	44.5 (32.4)
150	16.2	78.4	9.1 (8.4)	46.8 (33.8)
160	8.2	79.3	4.4 (4.2)	47.9 (34.3)
170	2.0	77.9	1.2 (1.1)	47.7 (34.3)
190	0	73.2	0	46.1 (33.0)
Exper.	+13.4	+65.0		

After the second order correction, the minimum is found again for $\gamma = 180^\circ$ but the energy difference between the two conformations characterized by $\gamma = 180^\circ$ and $\gamma = 150^\circ$ is now 1,2 Kcal/mole (instead of 3.0 Kcal/mole at the zeroth order). From Table 2, we can observe, for the γ angle values ranging from 120° to 180° , an 1.89 Kcal/mole increase of the polarization correction and a 5.64 Kcal/mole diminution of the delocalization correction (in absolute value).

After the third order correction the minimum occurs for $\gamma = 160^\circ$. This minimum position change is due to the delocalization-delocalization correction, the inversion barrier being low (0.22 Kcal/mole).

Although, there is a small interbond correlation effects on the energy differences (Table 2, column 9), the conformation appears to be governed mainly by the zeroth order energy and the delocalization effects at the 2nd and 3rd orders, which explains the similarity of the PCILO and SCF results.

The formulas (Eqs. 10–11) for the spin density calculations allow the determination of the hyperfine constant in gauss (using the value for Q given by Pople [18]): see Table 3. The 2nd order spin densities follow the same evolution than the SCF–CNDO spin densities when the geometry changes. They represent only 0.6 of the variational spin densities. This means that the main part of the SCF–CNDO spin densities comes from a direct delocalization through space from the localized unpaired electron to the concerned bonds. But the third order contributions, which involves processes going by steps through the intermediate bonds, are not negligible.

C. The Ethyl Radical (Fig. 2a)

The experimental intensities and spacings of lines of the ESR spectra of the ethyl radical arise from a radical with one group of two and a second group of three equivalent protons. This symmetry can be understood if the three β protons

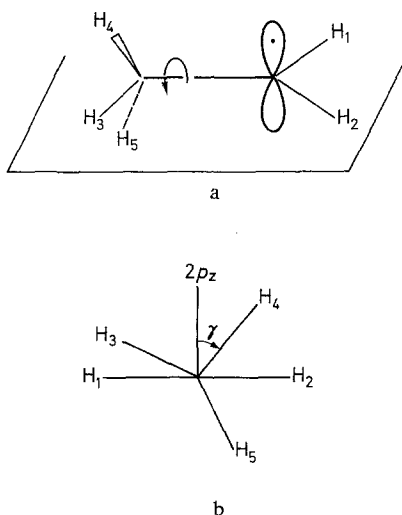


Fig. 2. Ethyl radical

are made equivalent by rapid internal rotation, indicating a very low rotational barrier.

Both CNDO II-SCF and PCILO method indicate that, with the regular geometry that we used (angles of 120° and 109°), the rotation barrier is smaller than 0.005 eV. One may demonstrate easily that the sum of the spin densities on the protons of the methyl group is constant under the rotation. This is due to the fact that v_{iu} and v_{ui^*} between the $2p_z$ atomic orbital and the CH molecular orbitals vary like $\cos \gamma$ (Fig. 2b), and the sum of the spin densities is proportional to $\cos^2 \gamma + \cos(\gamma + 2\pi/3)^2 + \cos(\gamma + 4\pi/3)^2$ which is constant.

For $\gamma = 90^\circ$, one has two proton coupling constants of 38.6 G for the CNDO/2 SCF calculation, and 24.1 (15.4 for Eq. (11)) in the 2nd order PCILO result.

For $\gamma = 60^\circ$, one has two proton coupling constants of 12.8 G and one of 51.7 G, while the PCILO 2nd order results give 6.1 (5.2) and 28.7 (20.6) Gauss. The mean value of the three splitting constants is practically constant under the rotation of the methyl group.

At the second order the spin density calculation does not require any summation. At the third order it would require a single summation of the MO's, and would remain therefore still more rapid than the energy calculation. The PCILO method should be very convenient for the study of large radicals³.

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³ For an example see Ref. [13]. For the malic acid radical, 110 different conformations are studied in 7 mn on a 360.75 computer.