Theoret. chim. Acta (Berl.) 15, 100—110 (1969)

Localized Bond Orbitals and the Correlation Problem

III. Energy up to the Third-Order in the Zero-Differential Overlap Approximation. Application to σ-Electron Systems

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Received January 16, 1969

Formulas are given allowing the calculation of electronic molecular energy up to the third-order in a perturbation theory using fully localized bond orbitals with zero differential overlap between them. The method is applied to small molecules using the CNDO approximations of Pople and Segal.

Es werden Formeln angegeben, die die Berechnung der Energie von Molekülen bis zur 3. Ordnung in einer Störungstheorie erlauben. Der Rechnung liegen dabei völlig lokalisierte Bindungsorbitale und die ZDO Näherung zugrunde. Die Methode wird auf kleine Moleküle angewandt, wobei die CNDO-Approximationen von Pople und Segal benutzt werden.

Rappel des formules permettant le calcul de l'énergie électronique d'un système moléculaire au troisième ordre de la théorie des perturbations à l'aide d'une base d'orbitales de liaison totalement localisées et à recouvrement différentiel nul. Application à de petites molécules dans le cadre des approximations de la méthode CNDO de Pople et Segal.

1. Introduction

In preceeding papers [1, 2] we have developped a method based on the use of bond orbitals and perturbation theory for the calculation of the ground state energy of a molecule. For future reference we call this method: PCILO, that means: Perturbative configuration interaction using localized orbitals. The usefullness and power of this method has been illustrated on π-electron systems in the semi-empirical approach [2]. In this paper we want to gather the general formulas for the energy up to the third-order in the zero-differential overlap approximation. These are the working formulas used in the computer program, and may be useful for anyone interested in the application of our method, especially for large systems (20 to 100 electrons). The use of these formulas will be illustrated on σ-electron systems in the Pople-Segal CNDO framework.

Bond orbitals appearing in the formulas do not belong to a specific type. We just require that they satisfy a zero differential overlap property. That means that bonding bond orbitals are defined on separate domains. This strong condition can be released on each physical bond[1] where we can just require orthogonality

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[1] In this paper we introduce three different bond terminologies: a physical bond is the region of space between two neighbour atoms where electrons are concentrated, a chemical bond is a pair of electrons assuming a physical bonding between two atoms, we speak of σ- or π-electron chemical bonds. A chemical bond will be often simply called a bond, a bond-orbital is a function essentially defined between two atoms connected by chemical bonds. In our formulation bond-orbitals are often simply called bonds.

between bonding orbitals. We shall not present formula for this case. To each bonding bond orbital corresponds an orthogonal antibonding bond orbital.

In a basis of atomic hybrids, bond orbitals are built as linear combinations of distinct hybrids two by two. Orthogonality of bond orbitals can be achieved by orthogonalisation of hybrids or, in an approximative way, by choosing hybrids according to maximum overlap criteria [3—5]. Zero-differential overlap between bond orbitals is achieved either by ZDO assumption for hybrids, as in the semi-empirical methods, or by truncation [6, 7].

To each bond orbital i we associate a virtual bond orbital i^*[*]; according to our hypothesis the only non zero-molecular bielectronic integrals are of the type

$$(i'j'|i''j'') \quad \text{where} \quad \begin{array}{l} i', i'' = i \quad \text{or} \quad i^*, \\ j', j'' = j \quad \text{or} \quad j^*. \end{array} \tag{1}$$

The perturbation development can be formulated either in a basis of configurations built on the bond orbitals or in the corresponding basis of singlet spin eigenfunctions. Up to the third order in energy we need only mono- and di-excited configurations. As a rule we represent an excited configuration by replacing in the ground state determinant the empty spin-orbital by the occupied excited one, at the same place.

$$\left(\frac{j^*}{i}\right) = \frac{1}{\sqrt{2n!}} |\ldots j^* \bar{i} \ldots|,$$

$$\left(\frac{j^* \bar{l}^*}{i \bar{k}}\right) = \frac{1}{\sqrt{2n!}} |\ldots j^* \bar{i} \ldots k \bar{l}^* \ldots|.$$

This is the convention used for example by Pople [6]. It has the advantage of allowing the spin eigenfunctions to be written in a symmetric way:

$$^1\Psi_i^{j^*} = \frac{1}{\sqrt{2}} \left\{ \left(\frac{j^*}{i}\right) + \left(\frac{\bar{j}^*}{\bar{i}}\right) \right\} \tag{2}$$

$$^1\Psi_{ik}^{j^* l^*} = \frac{1}{2} \left\{ \left(\frac{j^* l^*}{ik}\right) + \left(\frac{\bar{j}^* l^*}{\bar{i}k}\right) + \left(\frac{j^* \bar{l}^*}{i\bar{k}}\right) + \left(\frac{\bar{j}^* \bar{l}^*}{\bar{i}\bar{k}}\right) \right\} \tag{3}$$

and

$$^1\Psi_{ik}^{j^* l^{*\prime}} = \frac{1}{2\sqrt{3}} \left\{ \left(\frac{j^* l^*}{ik}\right) + \left(\frac{\bar{j}^* \bar{l}^*}{\bar{i}\bar{k}}\right) - \left(\frac{\bar{j}^* l^*}{\bar{i}k}\right) - \left(\frac{j^* \bar{l}^*}{i\bar{k}}\right) - 2\left(\frac{\bar{l}^* j^*}{\bar{i}k}\right) - 2\left(\frac{l^* \bar{j}^*}{i\bar{k}}\right) \right\} \tag{4}$$

The four configurations occuring in $^1\Psi_{ik}^{j^* l^*}$ have the same matrix element with the ground state configuration: $(ik|j^* l^*)$, the exchange integral $(ik|l^* j^*)$ being zero if the first one is different from zero. Then, the configurations $\left(\frac{l^* \bar{j}^*}{i\bar{k}}\right)$ and

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[*] In minimal basis sets no virtual orbital corresponds to the lone pairs. However one may use the general formalism developped hereafter without any caution if one considers the lone pair as a bonding orbital defined with a conventional atomic orbital removed to infinity, but completely polarized on the actual lone pair. Then the corresponding antibonding molecular orbital has a zero coefficient on the lone pair and its use in the configuration interaction has absolutely no effect, except to simplify the programming.

$\left(\frac{\bar{l}^* j^*}{\bar{i} k}\right)$ have a zero interaction with the ground state, this interaction being equal to $(ik|l^* j^*)$. It follows that the second diexcited spin eigenfunction ${}^1\Psi_{ik}^{j^* l^*}$ does not interact with the ground state and therefore does not play any role in the energy expression up to the third order, formulated in a spin eigenfunctions basis.

Though these simplification are significant,the formulation of the perturbation series is more involved in a spin eigenfunctions basis than in a configuration basis. This is also true for programming an electronic computer. This is the reason why we use a configuration basis (as in our preceding works [14]). It has the traditional desagreement of enlarging (formally) the basis, but we don't care of it in a perturbation treatment. The n^{th} order perturbed wave function differs of a spin-eigenfunction by $(n+1)^{\text{th}}$ order terms only. In fact, the two formulations are formally quite the same, apart two terms of third order which are indicated in the right places. The only significant modification is the replacement of transition energy between configurations by transition energies between states.

2. Second Order Energy

The zeroth order energy is the energy of the Slater determinant built with the bonding bond orbitals. It is not in general the sum of terms which could be considered as bond energies. The first order energy correction is zero merely by definition of our perturbation series. The first non zero correction is the second-order one:

$$E^{(2)} = \sum_{I \neq 0} \frac{|\langle 0|H|I\rangle|^2}{E_0 - E_I} \tag{5}$$

where I labels the different excited configurations and 0 the ground state zeroth order configuration. E_I is the energy of the determinant $|I\rangle$, that is

$$E_I = \langle I|H|I\rangle .$$

Configurations can be of only the mono-or diexcited types.

1. *$|I\rangle$ is a mono-excited configuration.*

a) *Monoexcitation in a bond:* $|I\rangle = \left(\frac{i^*}{i}\right)$ (polarization energy)

$$\sum_i 2 v_{ii}^2 (E_0 - E_I) \tag{6}$$

with

$$v_{ii} = \frac{\langle i|h|i^*\rangle + \sum_{j \neq i} 2(ij|i^* j) + (ii|i^* i)}{E_0 - E_I} . \tag{7}$$

b) *Monoexcitations between two bonds* (delocalization energy)

$$\sum_i \sum_{j \neq i} 2 v_{ij}^2 (E_0 - E_I) \tag{8}$$

with

$$v_{ij} = \frac{\langle i|h|j^*\rangle}{E_0 - E_I} . \tag{9}$$

For a given bond i the total effect of the interactions of $|0\rangle$ with $\left(\frac{j^*}{i}\right)$ and $\left(\frac{i^*}{j}\right)$ corresponds to a net charge transfer to or from the bond i.

Let us remark here that in our method we don't really associate a virtual orbital i^* to a lone pair localized orbital i. This has for evident consequence that there is only charge transfer *from* the lone pair. A well known empirical result in usual minimal basis LCAO delocalized MO methods, where atomic orbitals corresponding to lone pairs bear a charge always less than 2. Using localized orbitals allows to prove immediately this property which otherwise follows from the spinless first order density matrix property not to have occupancy numbers greater than 2 [7].

2. $|I\rangle$ *is a diexcited configuration.*

Due to ZDO hypothesis between bond orbitals only two kinds of diexcited configuration have a non zero effect:

a) *Diexcitation in one bond:* $|I\rangle = \left(\frac{i^*\bar{i}^*}{i\bar{i}}\right)$ (intra bond correlation energy [9]

$$\sum_i d_{ii}^2 (E_0 - E_I) \tag{10}$$

with

$$d_{ii} = \frac{(ii|i^*i^*)}{E_0 - E_I}. \tag{11}$$

b) *Monoexcitations in two bonds:* $|I\rangle = \left(\frac{i^*j^*}{ij}\right)$ (interbond correlation energy [9])

$$\sum_{i<j}\sum 4 d_{ij}^2 (E_0 - E_I) \tag{12}$$

with

$$d_{ij} = \frac{(ij|i^*j^*)}{E_0 - E_I}. \tag{13}$$

Viewed as if they represent the result of physical processes the fundamental four configurations interacting with ground state in the second-order energy can be referred as: polarization, delocalization, bond-diexcitation, two-bonds diexcitation.

3. Third Order Energy

From our definition of the perturbation operator V it follows that

$$E^{(1)} = 0,$$

$$\langle I|V|I\rangle = 0,$$

and

$$E^{(3)} = 2 \sum_{\substack{I<J \\ \neq 0}}\sum \frac{\langle 0|H|I\rangle \langle I|H|J\rangle \langle J|H|0\rangle}{(E_0 - E_I)(E_0 - E_J)}. \tag{14}$$

The different types of interactions arise from the interaction of the four fundamental types of configurations which have played a role in the second order energy.

1. *$|I\rangle$ and $|J\rangle$ are monoexcited configurations.*

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

$$\sum_i \sum_{j \neq i} 4 v_{ii} (ij|i^* j^*)\, v_{jj}\,. \tag{15}$$

When working in a basis of configurations one must also take in account interaction between $\left(\frac{i^*}{i}\right)$ and $\left(\frac{\bar{i}^*}{\bar{i}}\right)$ which gives the matrix element $(ii|i^* i^*)$ and leads to a total contribution

$$\sum_i (ii|i^* i^*)\, v_{ii}^2\,. \tag{16}$$

b) $|I\rangle = \left(\frac{j^*}{i}\right) |J\rangle = \left(\frac{l^*}{k}\right)$ *delocalization*

$$4 \sum_i \sum_j \sum_l \langle j^*|h|l^*\rangle\, v_{ij} v_{il} - \langle j|h|l\rangle\, v_{ji} v_{li} (j, l \neq i)\,. \tag{17}$$

c) $|I\rangle = \left(\frac{i^*}{i}\right) |J\rangle = \left(\frac{j^*}{k}\right)$ *polarisation and delocalization*

$$2 \sum_i \sum_{j \neq i} 2(\langle i^*|h|j^*\rangle\, v_{ii} v_{ij} - \langle i|h|j\rangle\, v_{ii} v_{ji})\,. \tag{18}$$

2. *$|I\rangle$ is a monoexcited and $|J\rangle$ a diexcited configuration.*

a) $|I\rangle = \left(\frac{i^*}{i}\right) |J\rangle = \left(\frac{i^* \bar{i}^*}{i \bar{i}}\right)$ *polarization and bond-diexcitation*

$$2 \sum_i 2 v_{ii} (v_{ii} (E_0 - E_I) - (ii|i^* i) + (ii^*|i^* i^*))\, d_{ii}\,. \tag{19}$$

b) $|I\rangle = \left(\frac{i^*}{i}\right) |J\rangle = \left(\frac{l^* j^*}{lj}\right)$ *polarization and two bonds diexcitation*

$$2 \sum_i \sum_{j \neq i} 4 v_{ii} (v_{jj} (E_0 - E_K) - (ji|j^* i) + (ji^*|j^* i^*))\, d_{ij} \tag{20}$$

with

$$E_K = E\left(\frac{j^*}{j}\right).$$

c) $|I\rangle = \left(\frac{j^*}{i}\right) |J\rangle = \left(\frac{i^* j^*}{ij}\right)$ *delocalization and two bonds diexcitation*

$$-2 \sum_i \sum_{j \neq i} 2 v_{ij} \langle j|h|i^*\rangle\, d_{ij}\,. \tag{21}$$

3. *$|I\rangle$ and $|J\rangle$ are diexcited configurations.*

a) $|I\rangle = \left(\frac{i^* j^*}{ij}\right) |J\rangle = \left(\frac{k^* j^*}{kj}\right)$ *two bonds diexcitations*

$$2 \sum_i \sum_j \sum_k 8 d_{ij} (jk|j^* k^*)\, d_{ik} (j, k \neq i)\,. \tag{22}$$

When working in a basis of configurations one must also take in account interaction between $\left(\frac{i^* j^*}{ij}\right)$ and $\left(\frac{\bar{i}^* j^*}{\bar{i} j}\right)$ which gives the matrix element $(ii|i^* i^*)$ and leads to a total contribution

$$\sum_{i}\sum_{j\neq i} 4d_{ij}^2\,(jj|j^*j^*)\,. \tag{23}$$

b) $|I\rangle=\left(\frac{i^*i^*}{ii}\right)|J\rangle=\left(\frac{i^*j^*}{ij}\right)$ *bond diexcitation and two bonds diexcitation*

$$2\sum_{i}\sum_{j\neq i} 4d_{ii}(ij|i^*j^*)\,d_{ij}\,. \tag{24}$$

4. Typical Results for σ—π Electrons Systems

Let us illustrate the method in the framework of the widely used CNDO approximation of Pople and Segal [8]. The basis of the pure *s* and *p* orbitals is transformed into a basis of hybrids directed along the bonds. These hybrids are not specifically adjusted to take into account the particular geometry or to maximize the overlap; they are simple canonical sp, sp^2 or sp^3 hybrids according to the most trivial chemical picture. Bond orbitals were built as combinations of these hybrids two by two with coefficients taking in account bond polarity as it appears in population analysis of the corresponding SCF wavefunction. The influence of hybridization and polarity on the final result will be systematically investigated in the next paper of this series (part 4) [9].

The results are given for some representative molecules and are listed in Table 1[2]. One can make the following remarks:

a) polarization energy (m_1) has been reduced by introducing convenient polarities of the bond orbitals.

b) delocalization energy (m_2) is the dominant contribution from monoexcited configurations to the second order energy. In formamide and in ketene half of this contribution comes from the π-system delocalization.

c) In pure σ-systems the interaction with monoexcited configurations only, brings the energy practically to the SCF level. In this case the determinant which could be built from the monoexcited configurations is nearly the same as the SCF determinant. This is due to the fact that the SCF orbitals of pure σ-systems are highly localizable according to standard localization criteria: Edmiston-Ruedenberg [11], Boys [12] or Magnasco-Perico [13]. Localizability always exceeds 95%. π-orbitals are as a rule less localizable, even in the small systems studied here. We have seen that for π electrons, interaction with monoexcited configurations only at the second order is not in general sufficient to approach the SCF energy (Paper II, Table 4).

d) Two bonds diexcitations include diexcitations on two bond orbitals located on the same physical bond in the case of multiple bonds. These two bonds diexcitations give important contributions to the second-order energy. This is the case for ethylene where $(\sigma\pi/\sigma^*\pi^*)$ gives 95% of the interbond correlation energy (d_2). The same occurs in acetylene where the fundamental role is played by the configurations: $(\sigma\pi/\sigma^*\pi^*)$, $(\sigma\bar{\pi}/\sigma^*\bar{\pi}^*)$ and $(\pi\bar{\pi}/\pi^*\bar{\pi}^*)$. The presence of triple bonds has

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[2] The results reproduced in Table 1 have been obtained in a basis of spin-eigenfunctions for monoexcited states and one bond diexcited states, and in a basis of configurations for two-bond diexcited states. This, somewhat hybrid, calculation does not introduce any significant differences with pure treatment in one kind of basis only.

Table 1. *Energy terms of the perturbation development in small molecules*[a]

Energy terms	Acetylene	Ethylene	Ethane (stag.)	Ethane (eclipsed)	Formal- dehide	Formamide	Aceto- nitrile	Ketene
Zeroth order[b]	**+0.560**	**+1.605**	**+1.449**	**+1.363**	**+1.630**	**+5.480**	**+3.043**	**+6.521**
m_1[c]	−0.025	−0.030	−0.033	−0.032	−0.155	−0.556	−0.077	−0.308
m_2[d]	−0.485	−1.428	−1.282	−1.199	−1.241	−5.466	−2.755	−6.615
Zeroth order + monoexcited[b]	**+0.050**	**+0.147**	**+0.134**	**+0.132**	**+0.234**	**−0.542**	**+0.211**	**−0.402**
d_1[e]	−1.027	−1.482	−1.782	−1.782	−1.459	−1.988	−1.798	−1.734
d_2[f]	−2.137	−0.971	−0.217	−0.228	−1.309	−1.598	−3.126	−1.922
After second order[b]	**−3.116**	**−2.308**	**−1.866**	**−1.880**	**−2.536**	**−4.128**	**−4.716**	**−4.059**
$m_1 - d_1$[g]	0.006	0.006	0.005	0.005	−0.007	−0.068	0.006	−0.040
$m_1 - m_1$[g]	−0.002	0.000	0.000	0.001	0.000	−0.006	0.001	0.000
$m_1 - m_2$[g]	0.035	0.071	0.056	0.054	0.103	0.726	0.110	0.424
$m_1 - d_2$[g]	0.001	0.002	0.003	0.003	−0.016	−0.185	−0.011	−0.157
$m_2 - d_2$[g]	−0.002	−0.015	−0.008	−0.017	0.000	−0.006	−0.043	−0.042
$d_1 - d_2$[g]	0.673	0.350	0.066	0.069	0.613	0.803	1.180	0.746
$m_2 - m_2$[g]	−0.058	−0.148	−0.138	−0.126	−0.337	−0.287	−0.222	−0.217
$d_2 - d_2$[g]	0.843	0.150	0.025	0.029	0.218	0.322	1.548	0.315
Third order correction	1.501	0.416	0.009	0.019	0.574	1.293	2.564	1.006
After third order[b]	**−1.615**	**−1.892**	**−1.857**	**−1.861**	**−1.962**	**−2.835**	**−2.152**	**−3.053**
Energy of correl. (SCF)	**−3.2317**	**−2.6384**	**−2.0325**	**−2.0285**	**−3.4256**	**−4.4233**	**−4.7765**	**−4.9649**
Energy of correl. (localized SCF)[h]	**−3.1765**	**−2.5687**	**−2.0597**	**−2.0632**	**−3.2042**	**−4.1221**	**−4.6841**	**−4.8104**

[a] All energy terms in eV.

[b] Expressed with respect to the SCF energy.

[c] Polarization term in monoexcitations (i^*/i).

[d] Charge transfer term in monoexcitations (j^*/i).

[e] Diexcitations, intra-bond correlation (i^*i^*/ii).

[f] Diexcitations, inter-bond correlation (i^*j^*/ij).

[g] Interaction of the terms mentioned under c, d, e and f.

[h] Ruedenberg localization.

for effect that the interbond correlation energy (d_2) can be greater than the intra-bond correlation energy (d_1). But in general the intra-bond correlation energy is the dominant term at the second order (see ethane for example).

e) The total second order energy compares fairly well with the energy we obtain by a second-order perturbation applied to the SCF solution, using either delocalized canonical or localized orbitals [10] (see last two lines of Table 1).

f) The main contributions to the third order energy correction arise from the interaction of: one and two-bonds diexcitations ($d_1 - d_2$), two bonds diexcitations between themselves ($d_2 - d_2$) and delocalization monoexcited configurations between themselves ($m_2 - m_2$). The first two contributions being positive and the second-one negative. When multiple bonds (especially triple) are present, an important term arises from the interaction of two bonds diexcitations between themselves; this comes evidently from two-bond diexcitations on the same physical bond. This behaviour of multiple bonds has some specific effect on the convergence of the perturbation series (cf. next paragraph g).

This situation has generally for consequence that the third order correction is either very small or non negligible and positive. The second-order energy being certainly in general lower than the exact solution of configuration interaction [2], the third order energy is thus a better approximation of the true energy.

Table 2. *Order of magnitude of the computing times*

Increasing accuracy	SCF + CI perturbation	Our method
↓		Fully localized determinant: N^2
	SCF N^3	
	Second order N^5	Second order N^2
	Third order N^6	Third order N^3

The fourth-order correction would be in principle obtainable along the formulation outlined in Part II of this series [2]. This computation is totaly feasible from computational time point of view as it appears from Table 2. The necessity of including fourth order correction comes from the fact that it can be greater than the third order correction, which does not mean that the perturbation series diverges. Work is done in this direction and will appear in the next future.

g) It's worthwhile to analyze the relative orders of magnitude of the various molecular integrals playing a role in the contribution of diexcited states. Two types of integrals are involved: $(ii|i^*i^*)$, $(ij|i^*j^*)$. Their expressions are

$$(ii|i^*i^*) = C_{i2}^2 C_{i2}^2 (g_{i1i1} + g_{i2i2} - 2g_{i1i2}),$$
$$(ij|i^*j^*) = C_{i1} C_{i2} C_{j1} C_{j2} (g_{i1j1} + g_{i2j2} - g_{i1j2} - g_{i2j1}).$$

The first integral is proportional to the difference between a monocentric coulombic integral and a bicentric one on the bond. The second one represents a dipole-dipole interaction. If i and j are defined on two different physical bonds (that's on two different spatial areas) this interaction is rather small: even for adjacent bonds it is about one fourth of $(ii|i^*i^*)$. On the contrary if i and j are on the *same* physical bond (different chemical bonds in a multiple bond) $(ij|i^*j^*)$ is of the same order of magnitude as $(ii|i^*i^*)$; in CNDO approximations for homopolar bonds they are even equal. This explains the importance of the inter-bond term in the second-order correction for multiple bonds.

Diexcited configurations interacting between themselves in the third order, one obtains different orders of magnitude for contributions arising in these different situations.

The general term occurring in the summations for these contributions (formulas 22) is of the form:

$$\frac{(ij|i^*j^*)\,(jk|j^*k^*)\,(ik|i^*k^*)}{\Delta E^2}\,.$$

When multiple bonds are lacking, the greater terms are of the type

$$\frac{(ii|i^*i^*)\,(ik|i^*k^*)^2}{\Delta E^2}\,.$$

For a double bond, the mixed diexcited configurations $\left(\frac{\sigma^*\pi^*}{\sigma\pi}\right)$ may interact with the $\left(\frac{\sigma^*\bar{\sigma}^*}{\sigma\bar{\sigma}}\right)$ and $\left(\frac{\pi^*\bar{\pi}^*}{\pi\bar{\pi}}\right)$ intra-bond configurations giving a strong matrix element $(\sigma\pi|\sigma^*\pi^*)$ of the same order of magnitude as $(ii|i^*i^*)$. This gives to the greater contributions a magnitude approximatively equal to

$$\frac{(ii|i^*i^*)^3}{\Delta E^2}\,.$$

Whence the significant positive third order correction appearing in molecules with double bonds.

When triple bonds are present much more interactions of this types are possible leading to a still greater positive correction in the third order.

This positive third-order correction gives an oscillatory behaviour to the Epstein-Nesbet perturbation series, which is strongly characteristic of triple bonds. In a Moller-Plesset [1] perturbation series, where the diagonal terms of the perturbation matrix are non zero important negative terms, the contributions

$$\frac{\langle 0|V|I^2\rangle\,\langle I|V|I\rangle}{\Delta E^2}$$

compensate largely the preceeding positive contributions. This has for effect to eliminate the oscillatory behaviour and explains the satisfactory results obtained by Grimaldi on $N\equiv N$ with M.P. perturbation [15] and the behaviour of E.N. perturbation [16]. It is likely that one would not have the same conclusion on saturated molecules.

5. Conclusion

The main defect of the method is the use of the CNDO hypothesis. It should be noticed, however, that it does not require the neglect of the differential overlap in the bonds, where it seems almost absurd, but only between the bonds. We have verified that the overlap between bond orbitals is never larger than 0.2 (even between adjacent bonds) and the ZDO approximation becomes as legitimate as in the π-systems. The method thus offers a way to rationalize the CNDO hypothesis: the characteristic parameters of the bonds, which no longer pertain to the atomic orbitals but to the bond distributions, could be adjusted on ab initio calculations without simplification of the integrals in the bonds.

In any event, if one accepts the CNDO hypothesis for calculating energies of large systems, the method appears very convenient, it gives better energy than the classical SCF procedure in a much shorter time (17 seconds to calculate the second and third order corrections on formamide, as opposed to the 30 minutes required to calculate via the SCF process followed by a second order correlation calculation on the IBM 1130). Table 2 gives the order of magnitude (in powers of the number N of electrons) of the time necessary for achieving the different steps of the classical SCF way (plus correlation) and of our method.

The results for conformational analysis are as reasonable as in the canonical CNDO SCF process. The rotational barrier (in ethane) arises from a difference (for the staggered and eclipsed conformations) mainly of the delocalization monoexcitations (cf. Table 3)[3].

Table 3. *Origin of the rotational barrier in ethane*

	Ethane (staggered) eV	Ethane (eclipsed) eV	Barrier	
			eV	kcal/mole
Nuclear repulsion	+ 719.681	+ 719.887		
Electronic energy SCF	−1231.550	−1231.651	0.105	2.42
Zeroth order	−1230.101	−1230.288	0.019	0.44
Second order (monoexcitations only)	−1231.416	−1231.519	0.103	2.37
Second order	−1233.416	−1233.531	0.091	2.10
Third order	−1233.407	−1233.512	0.101	2.33

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[3] It is interesting to compare this analysis of the rotational barrier with Sovers *et al.* results [17]. These authors build a determinant with the 1s lone pairs and seven bonding bond orbitals, choosen from the classical hybridization scheme, and orthogonalized by a $S^{-1/2}$ procedure. This wave function could be considered as the zeroth order of a perturbation procedure in an *ab initio* scheme. It is interesting to notice that in their case the zeroth order wave function gives already the rotational barrier, while in our problem, it comes mainly from the delocalization excitations. Gilbert (private communication) has noticed that in *ab initio* calculations, starting from $S^{-1/2}$ orthogonalized bond orbitals, one gets a very small mixing of the bonding orbitals with the anti-bonding orbitals on the other bonds: the delocalization configurations $i \to j^*$ have a much more important role in the CNDO scheme than in analogous *ab initio* calculations. This might be due to the fact that the $S^{-1/2}$ orthogonalization in the *ab initio* calculation already gives a reasonable delocalization in the zeroth order wave function, while this delocalization is only obtained from the first order correction in the CNDO scheme.

A different version of the program could select the terms which undergo changes with a change in conformation, to calculate directly these conformational differences between these selected terms rather than as differences between two very large numbers. Further applications on larger molecules will be presented at a later time.

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