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Use of Perturbation Methods for the Study of Configuration Interaction Effects

IV. Localized SCF Orbitals and Second-Order Energy Correction

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Localized SCF orbitals are obtained by using the self-energy criteria in the framework of semi-empirical methods (Pariser-Parr, Pople-Segal). The delocalisation problem is discussed. These localized orbitals (both occupied and virtual) are used for the calculation of the second-order correlation energy. Qualitative and quantitative features are discussed. The use of localized orbitals allows a deep reduction of the significant terms in the correlation energy.

Es werden lokalisierte Orbitale mittels des Selbstenergie-Kriteriums im Rahmen semiempirischer Methoden (Pariser-Parr, Pople-Segal) konstruiert und das Delokalisierungsproblem diskutiert. Mit diesen lokalisierten Orbitalen (besetzt und virtuell) wird die Korrelationsenergie zweiter Ordnung berechnet, was zu einer erheblichen Reduktion wichtiger Terme führt. Die Ergebnisse werden diskutiert.

Dans le cadre des méthodes semi-empiriques (Pariser-Parr, Pople-Segal) on obtient des orbitales localisées S.C.F. en utilisant essentiellement le critère de localisation d'Edmiston et Ruedenberg. Le problème de la délocalisation est discuté. Ces orbitales localisées (occupées et virtuelles) sont utilisées pour le calcul de l'énergie de corrélation au second-ordre de la théorie des perturbations. Les modifications qualitatives et quantitatives apportées par l'emploi des orbitales localisées sont discutées. Elles permettent de réduire massivement le nombre de termes nécessaires à l'évaluation de l'énergie de corrélation.

1. Introduction

It seems to be no need for emphasizing the importance of localized atomic and molecular orbitals (or geminals). This problem has been the subject of a great number of publications from the pioneering work of Lennard-Jones and Coll. [1] to the recent revival of the subject by Edmiston and Ruedenberg [2]. A good review is given by Gilbert [3]. Nevertheless many important aspects of the problem have been insufficiently studied as far as practical numerical applications remain limited [4–8]. The main benefit from the use of localized orbitals appears in the field of perturbation theory. This is quite evident in the study of chemical substitution and in the problem of orbital transfer. But, localized orbitals seem to be of outstanding importance in the use of perturbation theory to overcome the independant particle approximation in the many electron problem of quantum chemistry. Sinanoglu [9] and Nesbet [10] have stressed this importance of localized orbitals in the correlation problem.

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Localized orbitals which are obtained by transforming SCF canonical molecular orbitals are to a high degree of accuracy localized on atoms or bonds of the molecule [2–8, 17]. Thus, using localized bond orbitals, with suitable hybridization and polarities, allows to construct a one determinant wave function which approximates fairly well the SCF solution [11]. Taking full advantage of this fact leads, following the original work of Mac Weeny and Ohno on the water molecule [12], to develop a configuration interaction treatment based on localized bond orbitals (both occupied and virtual). This is what we have done systematically using perturbation theory in a method called PCILO (Perturbative Configuration Interaction using Localized Orbitals) [13–16].

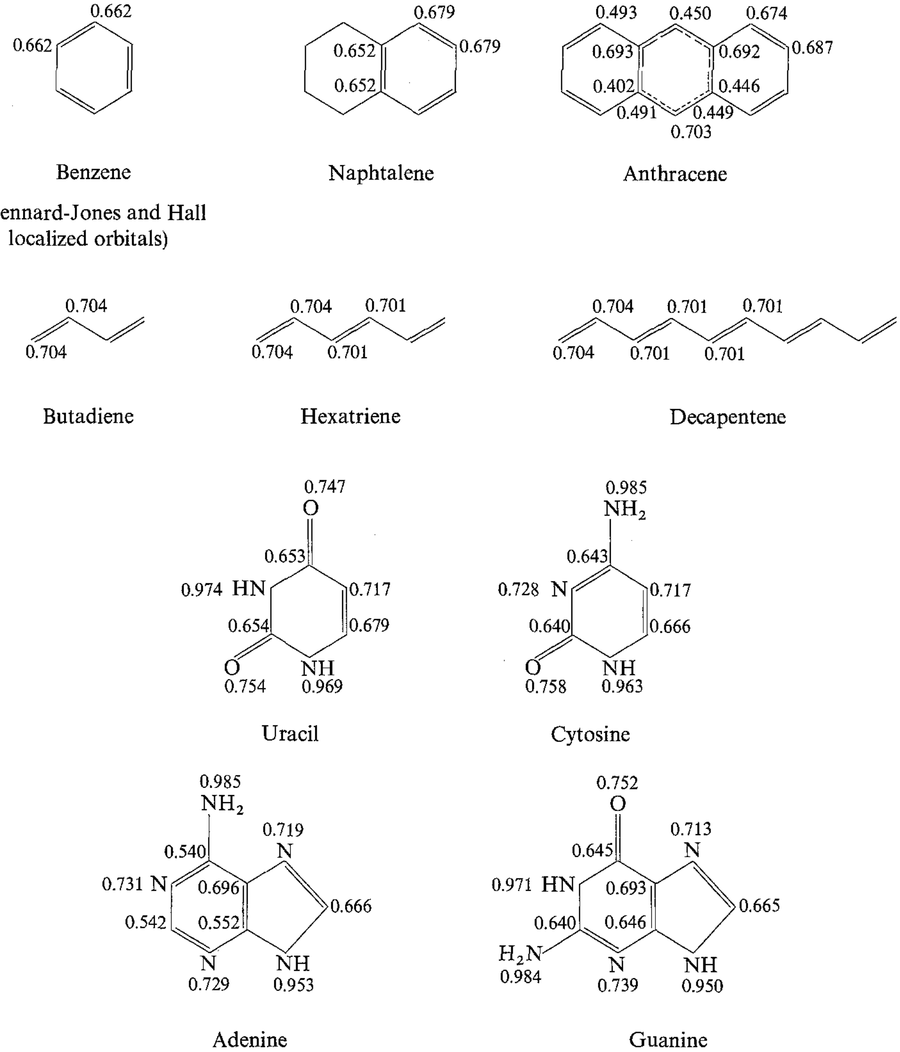
In this paper we want only describe the results one obtains using *localized* SCF *orbitals* instead of canonical to calculate second-order correction to the SCF energy. This work, done in the beginning in the framework of Pariser-Parr method for π electrons [17–19] is now extended to $\sigma-\pi$ electrons using the CDNO approximations of Pople and Segal.

2. Localized SCF Orbitals

Among the different criteria of localization Ruedenberg [20] distinguishes two kinds of criteria: intrinsic and extrinsic. Intrinsic criteria are independant of any topochemical partition of the molecule, whereas extrinsic criteria necessitate an a priori recognition of chemical bonds, lone pairs ... In an ab initio calculation instrinsic criteria are usually very cumbersome in their application. But in a semi-empirical method using a ZDO hypothesis, these criteria can be applied without involving lengthy calculations. So that in the semi-empirical framework we prefer intrinsic criteria because they do not make any *a priori* assumption on the existence of the bonds and reveal the explicit existence of these bonds in the wave function. We have worked with the Edmiston and Ruedenberg's self-energy criteria and Boy's criteria on the centroïds [21]. These two criteria lead practically to the same results in all the systems studied. One must remark that, due to the peculiar assumptions on coulombic integrals in the CDNO method (no distinction between σ and π electrons in bicentric coulombic integrals) one can equally obtain banana-type multiple bonds with the self-energy criteria (and one obtains always such bonds for double-bonds in Boys method). In order to avoid banana-bonds we have systematically localized independently σ and π orbitals. In Figs. 1 and 2 we report some numerical results for occupied orbitals. For each localized orbital we give only the two main coefficients on the atomic orbitals of the bond where this orbital is mainly localized. For lone pairs we just give the value of the main coefficient on the atom bearing this lone pair.

All results are presented in a basis of hybrid atomic orbitals: $2p\pi$ orbitals in Pariser-Parr method, canonical hybridization in CNDO method. For acetonitrile, due to hyperconjugation, the π orbitals of the $C\equiv N$ bond are not very well localized with the self-energy criteria. In order to get a better result one has to use an extrinsic criteria (e.g. maximisation of the bond populations).

In Table 1 one gives as example results obtained with the three localization criteria for the ethylene molecule. The three processes converge remarkably toward nearly the same result.



Benzene

(Lennard-Jones and Hall
localized orbitals)

Naphtalene

Anthracene

Butadiene

Hexatriene

Decapentene

Uracil

Cytosine

Adenine

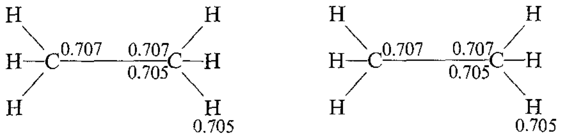
Guanine

Fig. 1. Localized π electrons SCF orbitals (Self-energy criteria)

Let us consider the chemical bond i (or lone pair), defined by two (resp. one) hybrid orbitals X_{i_1} and X_{i_2}. Then, the molecular orbital φ_i mainly defined on this chemical bond has two (one) main coefficients C_{i_1} and C_{i_2} on the atomic orbitals X_{i_1} and X_{i_2}. One may define a population on the chemical bond i in φ_i. In the ZDO approximation, this population will be

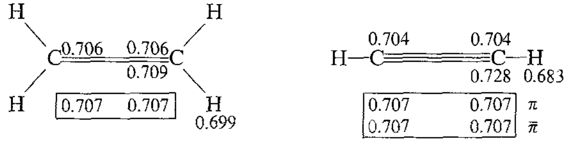
$$\varrho_i = C_{i_1}^2 + C_{i_2}^2 .$$

If the MO's were fully localized the quantities ϱ_i would be equal to 1. For the SCF localized orbitals, these quantities are slightly lower than 1. This gives a sort of index of localization: the quantity $1 - \varrho_i$ represents the probability for an "electron" of the bond i to be on the other chemical bonds. It may be called the delocalization



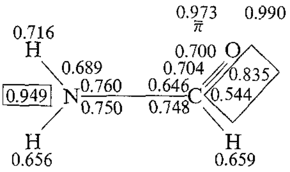
Ethane (staggered)

Ethane (eclipsed)

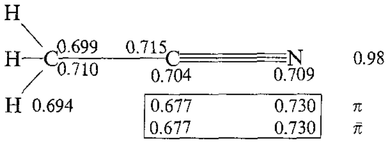


Ethylene

Acetylene



Formamide (Hybridization *sp* on the oxygen atom)



Acetonitrile (Population criteria)

Fig. 2. SCF localized orbitals (CNDO method, self-energy criteria) (Data for orbitals with dominant π character are given inside rectangles)

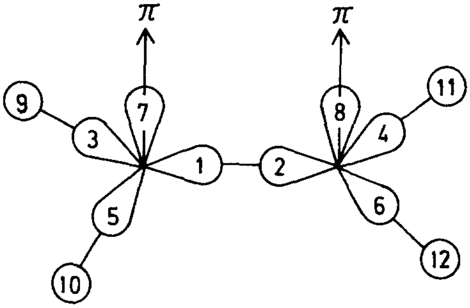
of the "electrons" of the bond i. These values of ϱ_i are given on Figs. 3 and 4 for all different bonds and lone pairs.

Under the name of each compound we have reported the total percentage of localization: $\Sigma\varrho_i/N$ where N is the total number of electron. This number can be considered as total index of localization.

The delocalization of the σ systems is surprisingly small. If one starts from fully localized bond orbitals, the SCF variational procedure only delocalizes less than 1% of the electrons from the σ bond to the other ones. The π bonds in the linear polyenes are less localized: but only 2% of the electrons leave their bond. The σ lone pairs are more delocalized $\varrho_i \simeq 0.95$, and the π lone pairs and π bonds in cyclic conjugated double bonds (aromatic conjugation) are much more delocalized. ($\varrho_i \simeq 0.80 - 0.90$).

Table 1. *Localized* SCF *orbitals for the ethylene molecule. Comparison of different localization criteria*

	C–C (σ bond)			C–H (bond 3–9)		
	Ruedenberg	Boys	Population	Ruedenberg	Boys	Population
1	0.706	0.706	0.706	−0.029	−0.021	−0.015
2	0.706	0.706	0.706	0.000	0.009	0.015
3	0.029	0.020	0.014	0.709	0.709	0.710
4	0.029	0.020	0.014	0.034	0.034	0.034
5	0.029	0.020	0.014	0.024	0.025	0.025
6	0.029	0.020	0.014	−0.050	−0.050	−0.050
7	0.000	0.000	0.000	0.000	0.000	0.000
8	0.000	0.000	0.000	0.000	0.000	0.000
9	0.000	0.009	0.015	0.699	0.699	0.698
10	0.000	0.009	0.015	−0.021	−0.021	−0.021
11	0.000	0.009	0.015	−0.031	−0.031	−0.031
12	0.000	0.009	0.015	0.049	0.049	0.049



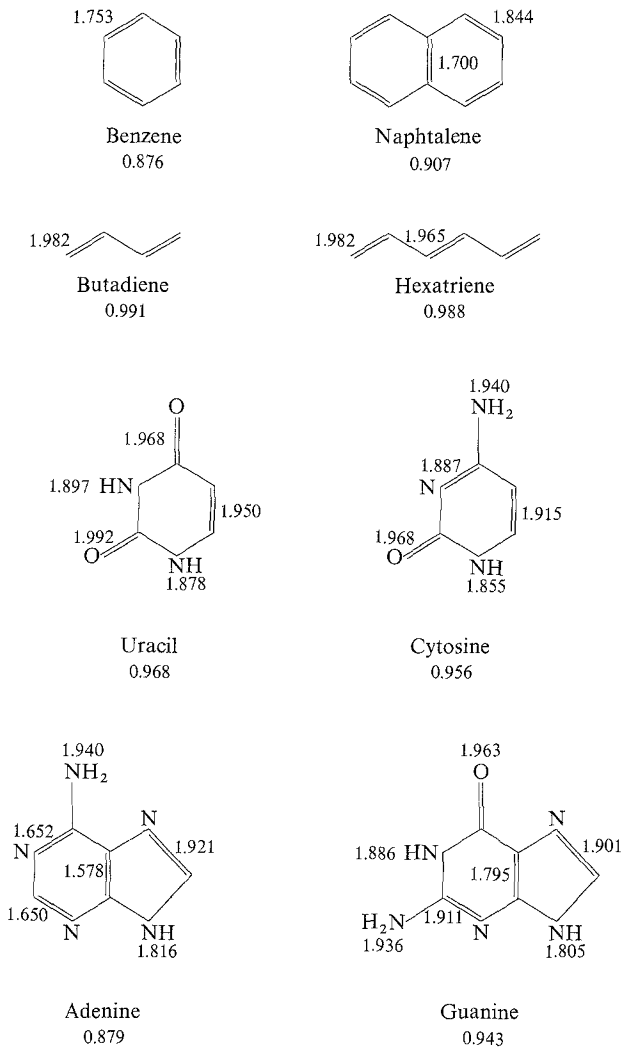
The different types of chemical bonds may be classified according to their increasing delocalization:

- σ bond $1-\varrho_i \leqq 1\%$,
- π bonds with linear conjugation $1-\varrho_i \leqq 2\%$,
- σ lone pairs $1-\varrho_i \simeq 2-5\%$,
- π lone pairs, π bonds with cyclic conjugation $1-\varrho_i \simeq 10-20\%$.

As seen from the example of acetonitrile, the hyperconjugation delocalizes the electron from a π bond by the same amount (1%) than the conjugation with an other π bond.

The classical opposition between the π delocalized and the σ localized molecular orbitals appears therefore rather unjustified. This is even a deep misunderstanding as far as people consider localization as an attribute of the physical electron and it is currently said or written that "π electrons in conjugated systems are delocalized".

The distinction between π and σ molecular orbitals and the use of π delocalized orbitals are very useful for a simple approximate interpretation of the electronic spectroscopy of conjugated compounds in the framework of independent

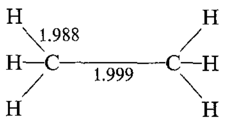


Benzene 0.876
Naphtalene 0.907
Butadiene 0.991
Hexatriene 0.988
Uracil 0.968
Cytosine 0.956
Adenine 0.879
Guanine 0.943

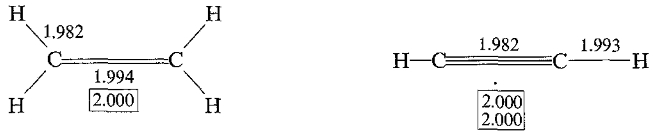
Fig. 3. Localisation indexes of bonds and lone pairs (ϱ_i)

particle models. But many quantum chemists tried to "legitimate" this useful model by some difference in the physical state of the involved electrons. And during many years most of the quantum chemists rationalized the technical impossibility to calculate with all valence electrons by building erroneous considerations about "the fundamental specificity of the π systems".

It was known from the work of Lennard Jones and Hall in 1950 that delocalized and localized orbitals where equivalent as far as one describes the ground state of a molecule in the one determinant approximation. But it was felt – without any calculation – that π orbitals would be much more difficult to localize than ϱ orbitals. Our work shows that from the point of view of localizability (and only from that point of view) the main distinction is between π orbitals in aromatic

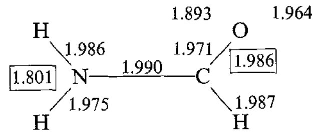


Ethane
0.995

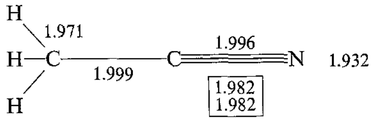


Ethylene
0.993

Acetylene
0.997



Formamide
0.975



Acetonitrile
0.988

Fig. 4. Localization indexes of bonds and lone pairs (ϱ_i)

conjugated systems and all the other orbitals (π and σ). And even in aromatic compounds π orbitals are much more localizable than the "π electron mythology" would have suggested by a simple consideration of delocalized orbitals.

3. Second Order Correlation Energy Using SCF Localized Orbitals

The result of a complete configuration interaction calculation is invariant toward any peculiar choice of basis in the Hartree-Fock SCF subspace and its complementary subspace spanned by the virtual orbitals. This invariance does not exist in a limited configuration interaction or in a perturbative treatment limited to a given order. In fact, *for a given partition of the total hamiltonian*, the perturbative treatment is invariant toward the choice of a basis in the subspace complementary to the zeroth-order state (this is evident from the operator form of perturbation theory). But, for a *given basis* in that subspace, it is necessary to define an adapted partition of the hamiltonian because the actual calculation of the perturbation series requires the knowledge of the reduced resolvent of the unperturbed operator, which can only be easily constructed in a basis of eigenvectors of H_0. So that changing basis leads to change the unperturbed hamiltonian and does not keep invariant the different contributions in the perturbation series (except the zeroth-order one).

In a given basis of states, the most general expression for the Rayleigh-Schrödinger series for the energy, limited to the second-order is

$$E = \langle 0|H|0\rangle + \sum_{I\neq 0} \frac{|\langle 0|H|I\rangle|^2}{E_0 - E_I}. \tag{1}$$

Such an expansion explicits only the diagonal form of the unperturbed hamiltonian, requiring only the knowledge of eigenvalues associated with the eigenstates $|I\rangle$. We have seen in a precedent paper [18] the respective merits of two different partitioning of the total hamiltonian, corresponding to the unperturbed operators in their spectral form:

$$\text{(M.P.)}\ H_0 = \sum_I \langle I|H_{\mathrm{SCF}}|I\rangle \quad |I\rangle\langle I|, \tag{2}$$

$$\text{(E.N.)}\ H_0 = \sum_I \langle I|H|I\rangle \quad |I\rangle\langle I|. \tag{3}$$

They give rise to two series called by us: Möller-Plesset (M.P.) and Epstein-Nesbet (E.N.).

If we use a basis of determinants built from independently localized occupied and virtual orbitals, it can always be considered as an eigenstate basis of a correctly defined $H^{\mathrm{loc}}_{\mathrm{SCF}}$ operator (obtained by adding a localization potential to the canonical H_{SCF} operator (3)), so that everything remains formally unchanged in the formulas (1) to (3). In the Möller-Plesset series, the difference $E_0 - E_I$ remains expressed as the difference between individual orbital energies. In practice, it is not necessary to define explicitly, in a operator form, $H^{\mathrm{loc}}_{\mathrm{SCF}}$; we just need the values of the orbital energies corresponding to this operator and they can be defined as

$$\varepsilon_i = \langle \varphi_i | h_{\mathrm{SCF}} | \varphi_i \rangle$$

where h_{SCF} is the monoelectronic SCF operator $\left(H_{\mathrm{SCF}} = \sum_m h_{\mathrm{SCF}}(m) + C\right)$ and φ_i are the localized orbitals. h_{SCF} is invariant in the localization transformation. Notice that even the Brillouin theorem remains valid with SCF localized orbitals so that only diexcited states are involved in the summation for the second-order correction.

But going from canonical to localized SCF orbitals changes deeply the pattern of the contributions to the second-order correction. What happens is easily seen by thinking in terms of fully localized bond orbitals (orbitals with their tails artificially cut off) in a ZDO (zero differential overlap) approximation, as it is done in the PCILO method [13, 16]. In this simplified picture the only contributions to second order correction are due to intra-orbital correlation (diexcited states $\left(\frac{i^*\bar{i}^*}{i\bar{i}}\right)$) and inter-orbital correlation due to diexcited states $\left(\frac{i^*j^*}{ij}\right)$. These contributions are due to the diexcited states which involve no electron transfer during excitation (that is a $k \to l^*$ excitation). In a general method using localized orbitals (not necessarily totaly localized) these contributions, arising from interaction between bond transition dipole (ii^*) must be large while contributions with electron transfer implying transfer distributions (ij^*) would be small if the localisation is important. *Although their number is proportional to* n^2*, the excitations without electrons transfer should give a dominant contribution over contributions arising from the* n^3 *diexcitations with one electron transfer* $\left(\frac{i^*k^*}{ij}\right)$ *and the* n^4 *contributions with two electron transfers* $\left(\frac{j^*l^*}{ik}\right)$.

Let us introduce at that point another partition of the different contributions to second-order correlation energy, which is valid in the both pictures: delocalized and localized orbitals. The second order correction can be broken in terms due to diexcited states involving: a) four different orbitals (Q), b) three different orbitals (T) and c) two different orbitals (D)[1]. In the PCILO framework Q reduces to the contribution of diexcited states $\left(\frac{i^*j^*}{ij}\right)$, T is always zero and D reduces to the contribution of diexcited states $\left(\frac{i^*\bar{i}^*}{i\bar{i}}\right)$.

This picture is only slightly modified when localized orbitals with tails are used.

In Sinanoglu's notations [9] the second order correlation energy would be the sum of the different pair correlation energies

$$E^{(2)} = \sum_i \sum_j \varepsilon_{ij}$$

It's easy to show that for alternant hydrocarbons:

$$\sum\sum_{i \neq j} \varepsilon_{ij} = Q + \tfrac{1}{2} T$$

$$\sum_i \varepsilon_{ii} \quad = D + \tfrac{1}{2} T .$$

4. Numerical Results

The second-order energy correction to the SCF energy (second-order correlation energy) has been calculated for some compounds in the framework of semi-empirical methods using the localized orbitals of § 2. Table 2 gives the results

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[1] In other words, diexcited states with four unpaired electrons (Q), two unpaired electrons (T) or closed shell (D). Such an analysis has also been made in a recently published paper: Bonnacorsi (R), Petrongolo (C), Scrocco (E), Tomasi (J).: Theoret. chim. Acta (Berl.) **15**, 332 (1969), in which ab initio SCF orbitals are localized according to Boys criteria for occupied orbitals. Virtual orbitals are localized in order to reduce to zero that part of T which corresponds to open shell configurations in the virtual orbitals. But these transformed virtual orbitals are not all well localized.

Table 2. *Second order correlation energy in Pariser-Parr method (eV)*
(M. P. Möller-Plesset, E. N. Epstein-Nesbet)

	Canonical orbitals					Localized orbitals				
	M.P.	E.N.				M.P.	E.N.			
		Q	T	D	Total		Q[a]	T	D[b]	Total[c]
Polyenes										
$n=4$	1.020	0.958	0.000	1.084	2.042	1.008	0,038	0.006	2.496	2.540
6	1.526	1.429	0.260	0.982	2.671	1.502	0.082	0.011	3.666	3.759
10	2.540	2.594	0.353	0.845	3.792	2.490	0.172	0.023	6.004	6.199
Polyacenes										
Benzene	1.455	1.485	0.000	1.556	3.041	1.504	1.262 (0.70)	0.112	2.158 (0.91)	3.532 (0.81)
Naphtalene	2.622	3.155	0.142	1.358	4.655	2.458	1.321 (0.69)	0.100	4.600 (0.98)	6.020 (0.90)
Anthracene	3.629	4.339	0.258	1.345	5.943	3.335	2.034 (0.60)	0.241	5.455 (0.96)	7.730 (0.84)
Heterocycles										
Uracile	2.236	1.447	0.961	1.787	4.195	2.131	0.145 (0.65)	0.083	5.436 (0.99)	5.664 (0.97)
Cytosine	1.993	1.699	0.642	1.235	3.576	1.867	0.310 (0.67)	0.092	4.204 (0.99)	4.606 (0.95)
Adenine	2.298	2.119	0.554	1.387	4.060	2.136	1.022 (0.62)	0.301	3.270 (0.94)	4.593 (0.80)
Guanine	2.644	2.494	0.753	1.295	4.542	2.482	0.599 (0.65)	0.131	5.285 (0.98)	6.015 (0.93)

[a] Numbers between parentheses are fraction of the Q term due to $\left(\frac{i^*j^*}{ij}\right)$ diexcited states.

[b] Numbers between parentheses are fraction of the D term due to $\left(\frac{i^*\bar{i}^*}{i\bar{i}}\right)$ diexcited states.

[c] Numbers between parentheses are fraction of the total energy due to the two types of diexcited states mentionned above.

obtained for π electrons in the Pariser-Parr method, using theoretical values of Slater exponents (e.g. carbon $Z=3.25$) to calculate coulombic integrals. Table 3 gives the results in the CNDO scheme for all valence electrons.

One can see in these tables that:

1) As with canonical orbitals, the E.N. second-order correlation energy is larger than the M.P. one when calculated with localized orbitals.

2) Using SCF localized orbitals instead of canonical leads to a small decrease in M.P. second-order energy.

3) On the contrary, the use of localized orbitals instead of canonicals, leads to a significative increase of the Epstein-Nesbet second-order energy correction for π electrons. This increase is larger, the largest the localizability and the geometrical dimension of the system.

Such an increase does not occur for the compounds studied in the CNDO scheme. This is due to the fact that in these relatively small systems, localizing the σ orbitals leads to an increase in transition energies which is not counterbalanced by the corresponding increase of interaction matrix elements. This would not be the case in larger systems, e.g. long paraffinic chains, where we have verified that the Epstein-Nesbet second-order correlation energy increases by considering localized orbitals.

Table 3. *Second order correlation energy in* CNDO *method (eV)* (M.P. Möller-Plesset, E.N. Epstein-Nesbet)

	Canonical orbitals					Localized orbitals				
	M.P.	E.N.				M.P.	E.N.			
		Q	T	D	Total		Q^a	T	D^b	Total^c
Ethane (eclipsed)	1.401	1.373	0.223	0.431	2.028	1.359	0.320 (0.70)	0.012	1.731 (1.00)	2.063 (0.95)
Ethane (staggered)	1.404	1.367	0.231	0.434	2.032	1.358	0.314 (0.68)	0.014	1.730 (1.00)	2.060 (0.94)
Ethylene	1.722	1.824	0.098	0.716	2.638	1.673	1.113 (0.86)	0.016	1.438 (1.00)	2.569 (0.93)
Acetylene	2.047	2.444	0.060	0.727	3.231	2.009	2.154 (0.98)	0.005	1.018 (1.00)	3.176 (0.99)
Formamide	2.877	2.998	0.851	0.514	4.363	2.811	2.436 (0.59)	0.038	1.647 (0.97)	4.122 (0.74)
Acetonitrile	3.268	3.828	0.378	0.570	4.776	3.108	3.156 (0.91)	0.033	1.670 (1.00)	4.859 (0.93)

[a, b, c] Cf. Table 2.

4) With localized orbitals the major part of second order correlation energy is given by the contribution of the diexcited states $\left(\frac{i^*\bar{i}^*}{i\bar{i}}\right)$ and $\left(\frac{i^*j^*}{ij}\right)$. The fraction of this contribution is given between parentheses in Table 1 and 2. One can see that *these two kinds of diexcited states without electron transfer contribute in general to a minimum of* 80% *of the correlation energy*. The stronger the localization, the largest this contribution is (cf. the series benzene, naphtalene, anthracene).

5) Much more, the main contribution is given by the intra-bond correlation energy, that is by the diexcited states $\left(\frac{i^*\bar{i}^*}{i\bar{i}}\right)$ which constitute nearly all the contribution to the term D and by the diexcited states $\left(\frac{i^*j^*}{ij}\right)$ where i and j belongs to the *same* chemical bond. In compounds where there is only one bond orbital by chemical bond one observe a transfer of contributions from the Q (and eventually T) term to the D term, this transfer representing the *emergence of intra-bond correlation as the main contribution to second-order correlation energy*. Nevertheless the inter-bond correlation energy remains non negligeable.

5. Discussion

The use of localized orbitals in perturbation theory allows to pick up the main contributions to correlation energy. Our work is just a numerical illustration of this general principle on the second-order correlation energy. Another point of interest is the convergence of the perturbation expansion. It is generally thought that a transformation to localized orbitals may be important for the rapid convergence of the perturbation expansion [24]. For example, for the π electrons of butadiene orbitals localized according to all criteria are identical so that they also maximize the second-order energy correction. In fact, it seems that the use of localized orbitals leads to some overestimation of the intra-bond correlation energy, giving often a second order energy lower than the exact one [22, 14]. Butadiene has been extensively studied and it has been shown by our work and the works of Staemmler and Kutzelnigg using the APSG method [23] and Kapuy using the Extended Separate Pair Theory [22] that the use of localized orbitals instead of delocalized gives a second-order energy nearer to the exact one. But this result is by no mean general and the main benefit one has from using localized orbitals is to improve the "convergence" of the configuration interaction development in the sense that the number of important configurations is strongly reduced. As to the perturbation series used to calculate the configuration interaction it's convergency cannot be assessed in general.

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