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An *ab initio* Model Calculation of the π and σ Electronic Structure of the Ethylene Molecule

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The *ab initio* SCF–MO–LCAO calculation of the ethylene molecule considering explicitly all valence electrons and using a minimum basis set of Slater orbitals as well as the Mulliken approximation of integrals is presented. Further, a CI calculation including all mono-excited and some di-excited configurations has been carried out. The implications of this study with respect to the validity of the $\pi - \sigma$ separability conditions are discussed.

Es wird eine *ab initio* SCF–MO–LCAO Berechnung des Äthylenmoleküls vorgelegt, in der alle Valenzelektronen in Betracht gezogen sind. Als Funktionenansatz wurde ein aus Slater-Atomeigenfunktionen bestehendes System benützt, die Atomintegrale wurden nach der Mullikenschen Näherung berechnet. Weiter wurde eine CI-Rechnung mit Berücksichtigung aller einfach angeregten und einiger doppelt angeregten Zustände angeschlossen und die Folgerungen in Bezug auf die $\pi - \sigma$-Separation diskutiert.

Dans cette communication on présente les résultats d'un calcul *ab initio* par la méthode SCF–MO–LCAO, dans lequel on tient compte explicitement de tous les éléctrons de valence en utilisant une base minimum des orbitales de Slater et l'approximation des intégrals par Mulliken. On a aussi performé le calcul par la méthode de l'interaction des configurations avec toutes les configurations monoexcitées et quelques diexcitées. On discute les implications de cette étude en relation avec la validité des conditions de la $\pi - \sigma$ séparabilité.

Introduction

The approximations currently used in quantum-chemical calculations were introduced in most cases on the basis of physical or chemical intuition rather than on the basis of rigorous arguments. One of the approximations of this kind used extensively in the theory of π-electronic systems is so called $\pi - \sigma$ separability theorem. This theorem states that the electronic wave function of an unsaturated molecule with conjugated double bonds may be written as an antisymmetrized product of two functions, one describing the explicitly considered π-electronic part and the other one describing a rigid non-polarizable σ-core which is not subject to change during the electronic excitations. In spite of the fact that this approximation was accepted intuitively during the early days of quantum chemistry of π-electronic systems in the 1930's it took more than 20 years before the rigorous formulation of the $\pi - \sigma$ separability conditions had been given by LYKOS and PARR [*12*]. Unfortunately, no unambiguous proof of the validity of the $\pi - \sigma$ separability conditions was presented as yet. On the other hand, the theory based on the validity of this approximation was applied to the great variety of π-electronic systems with an apparent success enabling an interpretation and a prediction of a number of physical and physico-chemical properties. The validity of the $\pi - \sigma$ separability conditions is then even more questionable for non-conventional non-planar systems.

Any attempt to determine the validity of the $\pi - \sigma$ separability conditions requires simultaneous consideration of π and σ electronic states. Therefore, the calculations of this type were always limited to small molecular systems only. The ethylene molecule was most often considered for its relative simplicity. Nevertheless, contradictory results were obtained by different authors as far as $\pi - \sigma$ separability concerns. The MO–LCAO–CI calculations of

Moser [14] as well as the semiempirical treatment of I'Haya [11] seem to indicate that the $\pi - \sigma$ separation is valid to a very good approximation. On the other hand Altmann [1] using the VB method claims an importance of the $\pi - \sigma$ interaction in ethylene molecule, mainly in the excited states. Recently very detailed SCF–MO calculations by Moskowitz and Harrison [15] using an extensive Gaussian basis set support the conclusions of Moser [14] and I'Haya [11]. Besides the ethylene molecule the acetylene molecule was studied by Ross [26]. Further, a sophisticated treatment of the $\pi - \sigma$ interaction was given by Parks and Parr [19] for the formaldehyde molecule. These authors have applied the double – selfconsistency procedure, suggested by Lykos and Parr [12] in order to find optimal electronic wave functions for both π and σ parts in different electronic states. Within the six-electron model considered by the authors they came to the conclusion that the electronic rearrangement has much greater effect on the σ-electronic wave function itself than on the calculated energies.

The $\pi - \sigma$ interaction in non-planar systems was studied by the authors for the system of two interacting ethylene molecules [23] as well as for the system consisting of ethylene molecule and a point charge [22]. These studies have shown that within the one-electron approximation used, the $\pi - \sigma$ interaction does not influence significantly the predictions of spectral properties if both interacting parts are kept at physically reasonable distances. Nevertheless, for intermolecular separations between two ethylene molecules smaller than 3 Å the unimportance of the $\pi - \sigma$ interaction on the transition energies results due to the compensation of the $\pi - \sigma$ interaction energy shifts of the two electronic states between which the transition occurs.

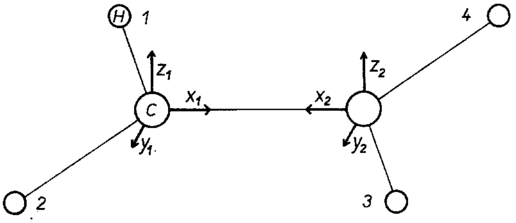

Fig. 1. Coordinate system

The purpose of this article is to study the $\pi - \sigma$ interaction in the planar model of the ethylene molecule (Fig. 1) using the CI–SCF–MO method with a Slater-type basis set, considering explicitly all twelve valence electrons.

Being aware of several limitations of our study, whether it is the use of a minimum basis set or the Mulliken approximation used for the evaluation of integrals, we consider it as a model calculation for a simple π-electronic system rather than as the study of the electronic structure of the ethylene molecule. Nevertheless, we believe that a study of this type may supply us with some physically interesting aspects as far as the $\pi - \sigma$ separation is concerned; the more so since there exists the possibility of comparison of our results with former studies of the ethylene molecule [cf. 3, 15, 21].

Model and Basis Functions Used

The same geometry was used as in paper [21] (e.g. the bond lengths C–C 2.53 a.u., C–H 2.00 a.u. and HCH angle 120°) which enabled us to use a number of integrals from this paper. In our calculations all twelve valence electrons were considered explicitly. A minimum basis set of Slater type orbitals was used. The effective nuclear charges were taken in accordance with the Slater rules: 1.0 for the $1s$ orbitals of the hydrogen, 3.25 for $(2s)$, $(2p_x)$, $(2p_y)$ and $(2p_z)$ orbitals of the carbon atoms.

The core consisting of two carbon nuclei each with two $1s$ electrons and, in addition, of four hydrogen nuclei was approximated in two different ways. The hydrogen nuclei were considered as point charges of $+1e$ in both cases. The carbon nuclei each carrying two $1s$ electrons were approximated in the first case as the point charges $+4e$. In the second case the carbon skeletons were approximated as a superposition of the point charge $+6e$ and the charge distribution of two Slater-type $1s$ orbitals with the effective nuclear charge 5.7.

Let us now introduce the notation of hybrid orbitals which will be actually used to represent Hartree-Fock operator (cf. Fig. 1 and [*21*]):

π_1 (π_2)	$2p_z$ atomic orbital localized on the carbon nucleus 1 (2);
σ_1 (σ_2)	sp^2 hybrid atomic orbital localized on the carbon nucleus 1 (2) and directed toward the carbon nucleus 2 (1);
${}^1\sigma_1$, ${}^2\sigma_1$, ${}^3\sigma_2$, ${}^4\sigma_2$	remaining sp^2 hybrid atomic orbitals localized on carbon nuclei specified by the lower indices and directed toward hydrogen nuclei specified by the upper indices;
χ_1, χ_2, χ_3, χ_4	hydrogen $1s$-atomic orbitals localized on the respective hydrogen nuclei.

The Dirac notation is used for the matrix elements.

SCF-Calculation

The nuclear attraction and two-electronic repulsion integrals were calculated using systematically the Mulliken approximation applied to hybrid atomic orbitals. In this way more accurate results are obtained as shown by Brion [*4*]. A comparison of accurate values of some two-centric integrals and of the approximate values obtained with Mulliken approximation applied to both original and hybrid atomic orbitals is given in Tab. 1.

Table 1. *A comparison of exact values of some two-electron exchange* (E), *hybrid* (H) *and one-electron two-center nuclear attraction* (N) *integrals with values obtained using Mulliken approximation applied both to the hybridized and non-hybridized atomic orbitals*

Integral[a]	Exact value	Mulliken approximation applied to		Type of the integral
		Slater AO	hybrid AO	
$(\pi_1 \pi_2 \mid \pi_1 \pi_1)$	0.1307[b]	0.1325	0.1325	H
$(\pi_1 \pi_2 \mid \pi_1 \pi_2)$	0.0387[b]	0.0358	0.0358	E
$(\pi_1 \pi_2 \mid \sigma_2 \sigma_2)$	0.1490[b]	—	0.1400	H
$(\sigma_1 \sigma_2 \mid \pi_1 \pi_1)$	0.4046[b]	—	0.3988	H
$(\sigma_1 \sigma_2 \mid \sigma_1 \sigma_1)$	0.5512[b]	—	0.5290	H
$(\sigma_1 \sigma_2 \mid \sigma_1 \sigma_2)$	0.4493[b]	—	0.4075	E
$({}^1\sigma_1 {}^1\sigma_1 \mid \chi_1 {}^1\sigma_1)$	0.5007	0.3777	0.4672	H
$(\chi_1 \chi_1 \mid \chi_1 {}^1\sigma_1)$	0.4473	0.3888	0.4304	H
$(\chi_1 {}^1\sigma_1 \mid \chi_1 {}^1\sigma_1)$	0.3541	0.2789	0.3253	E
$\langle \sigma_1 \mid 1/r_{C_1} \mid \sigma_2 \rangle$	0.5199	0.4758	0.5258	N
$\langle \pi_1 \mid 1/r_{C_1} \mid \pi_2 \rangle$	0.1432	0.1587	0.1587	N
$\langle \chi_1 \mid 1/r_{H_1} \mid {}^1\sigma_1 \rangle$	0.6458	0.5540	0.6213	N
$\langle \chi_1 \mid 1/r_{C_1} \mid {}^1\sigma_1 \rangle$	0.4461	0.4657	0.4657	N

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[a] The symbols used in the designation of the integrals are defined in the text.

[b] Obtained from paper [*14*], the other exact values from paper [*21*].

The matrix elements of the Hartree-Fock operator [*13*, *25*] in the representation of symmetry orbitals may be written in the following form using the above introduced approximations:

$$(\boldsymbol{F}^{\gamma})_{s,\,t} = \langle \gamma,\, s \mid \hat{h} \mid \gamma,\, t \rangle + Sp\,[({}^{\gamma}\boldsymbol{L}^{s,\,t})\,\boldsymbol{R}]\,, \tag{2}$$

where the factorization of the problem due to the symmetry is shown explicitly. The following notation was used in (2): $\hat{h}$ designates the core part of the HF operator, $\mid \gamma,\, s\rangle$ designates a normalized symmetry orbital, where γ represents a respective irreducible representation and s distinguishes the symmetry orbitals of the same symmetry species. The symmetry orbitals are further expressed as a linear combination of hybrid atomic orbitals

$$\mid \gamma,\, s\rangle = \sum_{\varrho} d_{\varrho}^{\gamma,\, s} \mid \varphi_{\varrho}\rangle\,. \tag{3}$$

In addition, the matrix elements of the matrix ${}^{\gamma}\boldsymbol{L}^{s,\,t}$ are given by the following formula:

$$\begin{aligned}({}^{\gamma}\boldsymbol{L}^{s,\,t})_{\mu,\,\nu} = \tfrac{1}{4} \sum_{\tau,\,\varrho} d_{\varrho}^{\gamma,\,s}\, d_{\tau}^{\gamma,\,t} \times \\ \times \{2\,\langle \varrho \mid \tau\rangle \langle \mu \mid \nu\rangle \cdot [(\varrho\varrho \mid \mu\mu) + (\varrho\varrho \mid \nu\nu) + (\tau\tau \mid \mu\mu) + (\tau\tau \mid \nu\nu)] - \\ - \langle \varrho \mid \nu\rangle \langle \mu \mid \tau\rangle\, [(\varrho\varrho \mid \mu\mu) + (\varrho\varrho \mid \tau\tau) + (\nu\nu \mid \mu\mu) + (\nu\nu \mid \tau\tau)]\}\end{aligned} \tag{4}$$

where

$$\langle \varrho \mid \tau\rangle = \langle \varphi_{\varrho} \mid \varphi_{\tau}\rangle$$

and

$$(\varrho\mu \mid \tau\nu) = \langle \varphi_{\varrho}(1)\, \varphi_{\tau}(2) \left| \frac{1}{r_{12}} \right| \varphi_{\mu}(1)\, \varphi_{\nu}(2)\rangle\,.$$

Furthermore, the matrix $\boldsymbol{R}$ is given by the relation

$$\boldsymbol{R} = \boldsymbol{T}\boldsymbol{T}^{\dagger} \tag{5}$$

where matrix $\boldsymbol{T}$ is a $n \cdot (n/2)$ matrix whose columns are formed by the LCAO coefficients of the $(n/2)$ ground state molecular orbitals expressed in the basis of hybrid atomic orbitals. $\boldsymbol{T}^{\dagger}$ designates a hermitian conjugate of $\boldsymbol{T}$. The first term on the right hand side of Eq. (2) may be expressed through the matrix elements over the hybrid orbitals $\langle \varphi_{\varrho} \mid \hat{h} \mid \varphi_{\tau}\rangle$ using Eq. (3). These matrix elements are then given by the following relation if the Mulliken approximation is used:

$$\langle \varphi_{\varrho} \mid \hat{h} \mid \varphi_{\tau}\rangle = \langle \varphi_{\varrho} \mid -\tfrac{1}{2}\Delta \mid \varphi_{\tau}\rangle + \tfrac{1}{2}\langle \varrho \mid \tau\rangle \sum_{\varkappa} \{\langle \varphi_{\varrho} \mid \hat{v}_{\varkappa} \mid \varphi_{\varrho}\rangle + \langle \varphi_{\tau} \mid \hat{v}_{\varkappa} \mid \varphi_{\tau}\rangle\}\,, \tag{6}$$

where the operator $\hat{v}_{\varkappa}$ represents the electrostatic potential energy due to the center $\varkappa$.

The SCF molecular orbitals were found using a conventional iterative procedure which was programmed for an Ural 2 computer. As the starting approximation the molecular orbitals obtained with extended Hückel method were used [*21*]. Twelve iterations were required in order to obtain the orbital energies to seven significant figures. Due to the approximations used the values of one and two-particle integrals were calculated by the Lagrange interpolation from SAHNI and COOLEY's tables [*27*] with the accuracy of four decimal places (in a.u.). The resulting SCF orbital energies and corresponding molecular orbitals are given in Tab. 2.

Table 2. SCF *orbital energies and corresponding molecular orbitals*

(The upper numbers correspond to the approximation of the core respecting the charge distribution of 1s electrons while the lower numbers correspond to the approximation of the core by the point charges as specified in the text)

No. of the MO	Symmetry	SCF orbital energy (a.u.)	Molecular orbitals							
			c_π	$\pi_1\pi_2$	c_{σ_i}	$\sigma_1\sigma_2$	c_{χ_i}	$\chi_1\chi_2\chi_3\chi_4$	$c_{j\sigma_i}$	${}^1\sigma_1\,{}^2\sigma_1\,{}^3\sigma_2\,{}^4\sigma_2$
1	a_{1g}	−1.5388 −1.5312	0		0.3911 0.3904	+ +	−0.0813 −0.0799	+ + + +	0.3836 0.3828	+ + + +
2	b_{3u}	−1.1000 −1.0936	0		0.3667 0.3651	+ −	0.0471 0.0496	+ + − −	0.4964 0.4942	+ + − −
3	b_{2u}	−0.6997 −0.6958	0		0		0.3230 0.3254	+ − − +	0.2253 0.2233	+ − − +
4	a_{1g}	−0.5394 −0.5348	0		−0.4213 −0.4218	+ +	0.3129 0.3163	+ + + +	0.0918 0.0875	+ + + +
5	b_{1g}	−0.4572 −0.4548	0		0		0.4578 0.4595	+ − + −	0.1968 0.1949	+ − + −
6	b_{1u}	−0.2833 −0.2780	0.6273 0.6273	+ +	0		0		0	
7	b_{3u}	0.4011 0.4025	0		−0.7155 −0.7141	+ −	0.7189 0.7192	+ + − −	−0.6614 −0.6633	+ + − −
8	b_{2g}	0.5860 0.5914	0.8279 0.8279	+ −	0		0		0	
9	a_{1g}	0.6150 0.6183	0		0.0281 0.0298	+ +	0.6301 0.6286	+ + + +	−0.7155 −0.7165	+ + + +
10	b_{2u}	0.8421 0.8453	0		0		−0.6904 −0.6892	+ − − +	0.5653 0.5661	+ − − +
11	b_{1g}	1.4316 1.4370	0		0		0.6870 0.6858	+ − + −	−0.7603 −0.7608	+ − + −
12	b_{3u}	1.5599 1.5672	0		1.4148 1.4159	+ −	0.2622 0.2609	+ + − −	−0.1328 −0.1320	+ + − −

CI-Calculation

The SCF molecular orbitals were used as the basis for a configuration interaction treatment. Since there is a very small difference between the SCF results for the two different approximations of the core potential considered, the CI calculations were performed only for the second case in which the $1s$ carbon orbitals were considered explicitly in the core potential (upper numbers in Tab. 2).

For singlet states all mono-excited and most significant di-excited configurations were considered, while only a rough estimate of the importance of the triexcited states was made. Only mono-excited states were considered for the triplet state.

The designation used for the configuration wave functions is clear from the following. Let us write the ground state single Slater determinant wave function in the following form

$$|\,0\rangle = |\,1\bar{1}\,\ldots\,i\bar{i}\,\ldots\,j\bar{j}\,\ldots\,n\bar{n}\,|\,. \tag{7}$$

Then the general mono and di-excited states may be written:

$$|\,{}^{k}_{i}\rangle = (1/\sqrt{2})\,\{|\,1\bar{1}\ldots i\bar{k}\,\ldots\,j\bar{j}\,\ldots\,n\bar{n}\,|+|\,1\bar{1}\,\ldots\,k\bar{i}\,\ldots\,j\bar{j}\,\ldots\,n\bar{n}\,|\}\,, \tag{8}$$

$$\begin{aligned}|{}^{k\,l}_{i\,j}\rangle_1 = (1/\sqrt{4\cdot 2^{\delta ij}\,2^{\delta kl}})\,\{|\,\ldots\,\bar{i}j\,\ldots\,k\bar{l}\,\ldots\,|+|\,\ldots i\bar{j}\,\ldots\,\bar{k}l\,\ldots\,|\,-\\ -\,|\,\ldots\,\bar{i}j\,\ldots\,kl\,\ldots\,|-|\,\ldots\,i\bar{j}\,\ldots\,k\bar{l}\,\ldots\,|\}\end{aligned} \tag{9}$$

$$\begin{aligned}|{}^{k\,l}_{i\,j}\rangle_2 = (1/\sqrt{12})\,\{|\,\ldots\,\bar{i}j\,\ldots\,k\bar{l}\,\ldots\,|+|\,\ldots\,i\bar{j}\,\ldots\,\bar{k}l\,\ldots\,|\,+\\ +\,|\,\ldots\,\bar{i}j\,\ldots\,\bar{k}l\,\ldots\,|+|\,\ldots\,i\bar{j}\,\ldots\,k\bar{l}\,\ldots\,|\,-\\ -\,2\,|\,\ldots\,\bar{i}j\,\ldots\,kl\,\ldots\,|-2\,|\,\ldots\,ij\,\ldots\bar{k}\bar{l}\,\ldots\,|\}\,.\end{aligned} \tag{10}$$

The second di-excited configuration function is considered only if $k \neq l$ and $i \neq j$. The matrix elements of the Hamiltonian in the basis of configuration function (7) – (10) were derived and their correctness was checked by a comparison with closed formulae for these elements given by ČIŽEK [5]. The required two-particle integrals over the molecular orbitals were computed using the programme written for the Ural 2 computer.

Due to the Brillouin theorem, no energy depression of the ground state is obtained with mono-excited states. The inclusion of di-excited states would give the secular problem of the order 125. In order to establish the effect of increasing number of configurations, we have included successively 20, 32 and 48 configuration functions. These configuration functions always included all mono-excited ones of the species A_{1g} and those di-excited ones of the same species which gave the largest 2nd order perturbation contribution to the energy depression of the ground state. The interaction of the ground state wave function with the di-excited state $|\,{}^{8\,8}_{6\,6}\rangle$ only gives a ground state energy depression of 0.0227 a.u.

The first electronic dipole allowed transition is ${}^1B_{3u} \leftarrow {}^1A_{1g}$. From 105 possible mono and di-excited configuration functions the secular problems of the orders 8, 20, 32 and 51 were constructed. In this case the 2nd order perturbation contributions are equal to zero for any di-excited state since in the Mulliken approximation all matrix elements between mono-excited state $|\,{}^{8}_{6}\rangle$ and any di-excited state disappear. Furthermore, the configuration function of the B_{3u} species having lowest energy is not the function $|\,{}^{8}_{6}\,\rangle$ but the function $|\,{}^{7}_{4}\,\rangle$ corresponding to a

$\sigma - \sigma$ excitation. Therefore, the lowest energy di-excited configurations were considered in addition to all mono-excited ones.

Further, the energies of the lowest triplet state $^3B_{3u}$ and of the first singlet state $^1B_{2g}$ were calculated including all mono-excited states.

The results of these calculations are given in Tab. 3 and 4.

Table 3. *Electronic energy of the ground state and of the most important excited states obtained with different extent of* CI

(The energies are given in a.u. *relative to the energy of the ground state configuration* $| 0\rangle$*)*

a) Ground state ($^1A_{1g}$)

Number of the configuration functions considered	Ground state energy	2nd order perturbation theory estimate of the ground state energy	2nd order perturbation theory estimate of the energy depression due to the remaining di-excited configurations
48	−0.0670	−0.0802	−0.0092
32	−0.0576	−0.0695	−0.0199
20	−0.0461	−0.0563	−0.0330

b) Excited states

Symmetry	Number of the configuration functions considered	Energy of the first two states of the given species	
$^1B_{3u}$	51	0.5751	0.6682
	32	0.5772	0.6695
	20	0.5785	0.6702
	8	0.5929[a]	0.6811[a]
$^3B_{3u}$	8	0.3795[a]	0.5635[a]
$^1B_{2g}$	4	0.3284[a]	0.7042[a]

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[a] Only the mono-excited configurations considered.

Discussion

Let us first compare our results with similar calculations existing in the literature. The comparison of orbital energies is depicted in Fig. 2. It is immediately apparent that we obtained the same sequence of orbital energies of occupied molecular orbitals as Moskowitz and Harrison [*15*] did with the SCF–MO treatment using Gaussian orbitals. The same sequence of occupied orbital energies was also obtained with the extended Hückel method by Hoffmann [*10, 21*]. On the other hand, the SCF occupied orbital energies obtained by Berthod [*3*] show less satisfactory correlation in spite of the fact that they show better agreement as far as the order of magnitude concerns.

The very large depression of the first two orbital energies (and of course the high energy of the corresponding virtual orbitals) is due to the use of the basis function set and of the Mulliken approximation applied to the hybrid orbitals. Indeed, we get for the valence state ionization potentials ε_φ of the atomic orbitals $|\varphi\rangle$ the following values: $\varepsilon_\chi = 13.6$ eV, $\varepsilon_\pi = 5.8$ eV and $\varepsilon_\sigma = 16.3$ eV. It is now

Table 4. CI *wave functions of the ground state and of the first two excited states of the B_{3u} symmetry species*

(only the coefficients of the 15 most important configuration functions are given)

Symmetry	$^1A_{1g}$		$^1B_{3u}$		$^1B_{3u}$	
No. of config. functs. considered	48		51		51	
Energy (a.u.)	−0.0670		0.5751		0.6682	
	coefficient	config. function	coefficient	config. function	coefficient	config. function
most important configurations	0.9835	$\vert 0\rangle$	0.7927	$\left\vert\begin{matrix}7\\ 4\end{matrix}\right\rangle$	0.7772	$\left\vert\begin{matrix}8\\ 6\end{matrix}\right\rangle$
	−0.1160	$\left\vert\begin{matrix}8 & 8\\ 6 & 6\end{matrix}\right\rangle$	−0.5808	$\left\vert\begin{matrix}8\\ 6\end{matrix}\right\rangle$	0.5801	$\left\vert\begin{matrix}7\\ 4\end{matrix}\right\rangle$
	−0.0388	$\left\vert\begin{matrix}7 & 7\\ 5 & 5\end{matrix}\right\rangle$	−0.0725	$\left\vert\begin{matrix}7\\ 1\end{matrix}\right\rangle$	−0.1536	$\left\vert\begin{matrix}9\\ 2\end{matrix}\right\rangle$
	0.0370	$\left\vert\begin{matrix}9 & 8\\ 6 & 2\end{matrix}\right\rangle_2$	0.0664	$\left\vert\begin{matrix}12\\ 4\end{matrix}\right\rangle$	0.1016	$\left\vert\begin{matrix}11\\ 3\end{matrix}\right\rangle$
	−0.0355	$\left\vert\begin{matrix}11 & 8\\ 6 & 3\end{matrix}\right\rangle_2$	−0.0620	$\left\vert\begin{matrix}7 & 9\\ 4 & 4\end{matrix}\right\rangle$	0.0738	$\left\vert\begin{matrix}7\\ 1\end{matrix}\right\rangle$
	0.0329	$\left\vert\begin{matrix}8 & 7\\ 6 & 1\end{matrix}\right\rangle_2$	−0.0604	$\left\vert\begin{matrix}8 & 9\\ 6 & 4\end{matrix}\right\rangle_2$	0.0724	$\left\vert\begin{matrix}10\\ 5\end{matrix}\right\rangle$
	−0.0317	$\left\vert\begin{matrix}10 & 7\\ 5 & 4\end{matrix}\right\rangle_1$	−0.0556	$\left\vert\begin{matrix}7 & 7\\ 5 & 3\end{matrix}\right\rangle$	−0.0477	$\left\vert\begin{matrix}12\\ 4\end{matrix}\right\rangle$
	0.0300	$\left\vert\begin{matrix}10 & 9\\ 4 & 3\end{matrix}\right\rangle_1$	0.0493	$\left\vert\begin{matrix}7 & 8\\ 6 & 2\end{matrix}\right\rangle_2$	−0.0469	$\left\vert\begin{matrix}7 & 9\\ 4 & 4\end{matrix}\right\rangle$
	0.0286	$\left\vert\begin{matrix}9 & 7\\ 5 & 3\end{matrix}\right\rangle_1$	−0.0440	$\left\vert\begin{matrix}10\\ 5\end{matrix}\right\rangle$	−0.0433	$\left\vert\begin{matrix}7 & 7\\ 5 & 3\end{matrix}\right\rangle$
	0.0267	$\left\vert\begin{matrix}12 & 8\\ 6 & 4\end{matrix}\right\rangle_2$	0.0385	$\left\vert\begin{matrix}9\\ 2\end{matrix}\right\rangle$	−0.0414	$\left\vert\begin{matrix}8 & 9\\ 6 & 4\end{matrix}\right\rangle_2$
	−0.0256	$\left\vert\begin{matrix}8 & 7\\ 6 & 4\end{matrix}\right\rangle_2$	−0.0360	$\left\vert\begin{matrix}11\\ 3\end{matrix}\right\rangle$	0.0410	$\left\vert\begin{matrix}7 & 8\\ 6 & 2\end{matrix}\right\rangle_2$
	−0.0251	$\left\vert\begin{matrix}12 & 8\\ 6 & 1\end{matrix}\right\rangle_2$	−0.0349	$\left\vert\begin{matrix}8 & 9\\ 6 & 4\end{matrix}\right\rangle_1$	0.0374	$\left\vert\begin{matrix}12\\ 1\end{matrix}\right\rangle$
	−0.0250	$\left\vert\begin{matrix}7 & 7\\ 4 & 4\end{matrix}\right\rangle$	−0.0345	$\left\vert\begin{matrix}12\\ 1\end{matrix}\right\rangle$	0.0313	$\left\vert\begin{matrix}7 & 9\\ 5 & 5\end{matrix}\right\rangle$
	−0.0243	$\left\vert\begin{matrix}9 & 9\\ 4 & 4\end{matrix}\right\rangle$	0.0343	$\left\vert\begin{matrix}7 & 9\\ 5 & 5\end{matrix}\right\rangle$	0.0244	$\left\vert\begin{matrix}8 & 9\\ 6 & 4\end{matrix}\right\rangle_1$
	0.0226	$\left\vert\begin{matrix}9 & 7\\ 4 & 2\end{matrix}\right\rangle_1$	−0.0285	$\left\vert\begin{matrix}7 & 8\\ 6 & 2\end{matrix}\right\rangle_1$	−0.0237	$\left\vert\begin{matrix}7 & 8\\ 6 & 2\end{matrix}\right\rangle_1$

evident from the values of ε_π and ε_σ that the valence state ionization potential for $2s$ carbon atomic orbital will be much lower than the usually accepted value 20.78 eV [*20*]. This depression of the $2s$ valence state ionization potential demonstrates itself in the depression of orbital energies of the first two molecular orbitals. Furthermore, this explains why the first two molecular orbitals have very much $2s$-character as can be seen from the molecular orbitals given in Tab. 5 after transformation to the ordinary atomic orbital basis. Moreover, this also destroys the possibility of localization of the σ-orbitals and the corresponding formation of the sp^2 hybrid orbitals (cf. [*21*]) what can be seen from the gross populations given in Tab. 5.

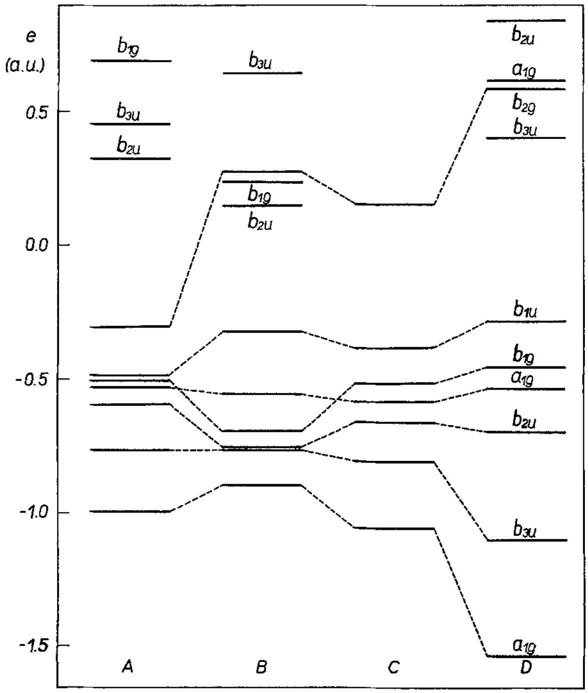

Fig. 2. The orbital energy scheme of occupied and low lying virtual orbitals: A-extended Hückel method [*21*] with Hoffmann parametrisation [*10*]; B-according to BERTHOD [*3*]; C-according to MOSKOWITZ and HARRISON [*15*]; D-this paper

Table 5. *Total gross atomic populations and total gross populations in hybrid and Slater atomic orbitals of the most important electronic states*

Orbital (atom)	${}^1A_{1g}$[a]	${}^1B_{3u}$(lowest)[b]	${}^1B_{3u}$(next lowest)[b]	${}^1B_{2g}$[c]
$N(\chi_i) \equiv N(\mathrm{H})$	0.844	0.914	0.873	1.062
$N(2s)$	1.922	1.974	1.944	1.981
$N(2p_x)$	0.650	0.458	0.571	0.655
$N(2p_y)$	0.740	0.740	0.740	0.740
$N(2p_z) \equiv N(\pi_i)$	1.000	1.000	1.000	0.500
$N(\sigma_i)$	0.935	0.848	0.899	1.014
$N({}^j\sigma_i)$	1.189	1.162	1.178	1.181
$N(\mathrm{C})$	4.312	4.172	4.255	3.876

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[a] Approximated by the ground state configuration function $|\,0\rangle$.

[b] Approximated by the proper linear combination of the $\left|\begin{smallmatrix}7\\4\end{smallmatrix}\right\rangle$ and $\left|\begin{smallmatrix}8\\6\end{smallmatrix}\right\rangle$ configuration functions, see Tab. 6.

[c] Approximated by the configuration function $\left|\begin{smallmatrix}7\\6\end{smallmatrix}\right\rangle$.

$\pi - \sigma$ *Separability*

Let us now consider the implications of our study as far as the $\pi - \sigma$ separability concerns. The general formulation of the $\pi - \sigma$ separability conditions was first established by LYKOS and PARR [*12*]. These conditions require the following form of the total n-electronic wave function

$$\Psi_{\text{tot}}(1 \ldots n) = \hat{\mathscr{P}}_{\Sigma\Pi}\left[\sum(1, \ldots, n_\sigma)\ \Pi(n_\sigma + 1, \ldots, n_\sigma + n_\pi)\right], \qquad (11)$$

where $\sum$ and Π are antisymmetrized and normalized functions of the n_σ σ-electrons and of the n_π π-electrons, respectively. n_σ and n_π are fixed integers, and $n = n_\sigma + n_\pi$. In addition $\hat{\mathscr{P}}_{\Sigma\Pi}$ is a partial antisymmetrizer ensuring the antisymmetry of the total wave function.

If the total wave function is expressed in the configuration space of Slater determinants constructed from the given basis set of one-particle functions it must be possible to divide the set of one-particle functions into two disjunct subsets each of which spans independently the $\sum$ and Π functions entering the total wave function Ψ_{tot}. The π-electron approximation is then defined as the approximation in which the total wave function for an arbitrary state satisfies the $\pi - \sigma$ separability conditions just mentioned with the same function $\sum$ for all states.

In the language of the CI treatment the $\pi - \sigma$ separability conditions require, that configurations corresponding to the $\sigma \rightarrow \pi$ or $\pi \rightarrow \sigma$ excitations which would change the fixed numbers n_σ and n_π of the σ and π electrons, respectively, do not enter the resulting total wave functions. Let us make it clear that our treatment cannot give any answer to this requirement which is in our case satisfied automatically due to the use of the Mulliken approximation.

On the other hand, our CI treatment allows us to check the invariability of the σ-core in different electronic states. In order to see eventual polarization of the σ-core we have carried out the Mulliken population analysis [*16*]. It is apparent from Tab. 4 that the ground state wave function is well approximated by the configurations $|\,0\rangle$ and $|\,{}^{8\,8}_{6\,6}\rangle$ while the lowest excited state of the ${}^1B_{3u}$ species is well approximated by the configurations $|\,{}^{7}_{4}\rangle$ and $|\,{}^{8}_{6}\rangle$. In this approximation the ground state energy becomes -0.0227 a.u. and the energy of the lowest ${}^1B_{3u}$ state yields 0.6144 a.u. The comparison of these values with those given in Tab. 4 for the more extensive CI treatment shows that this approximation is well justified. Further, because of the molecular orbitals ψ_6 and ψ_8 have the same partial gross populations it is sufficient to determine the gross populations of the ground state single determinant configuration $|\,0\rangle$. On the other hand, the consideration of the linear combination of determinantal functions in populational analysis of the excited states ${}^1B_{3u}$ was unvoidable. The results are given in Tab. 5.

It is immediately apparent that we are getting the right polarity for the CH bond (C^-H^+). Furthermore, our data are in very good agreement with the analogous ground state data of MOSKOWITZ and HARRISON [*15*].

The populations for the lowest excited singlet state of the B_{3u} species clearly show the considerable change in the gross populations as compared with those of the ground state. In general, the electronic charge is transferred from the central C–C bond to the C–H bonds upon the excitation to the lowest ${}^1B_{3u}$ state. This is in good agreement with the experimentally observed lengthening of the central bond upon the transition to the respective ${}^1B_{3u}$ state [*30*], in spite of the fact that the calculation was performed for a planar conformation only and corresponds, therefore, to a vertical excitation. On the other hand, the corresponding lowest triplet state ${}^3B_{3u}$ has the same gross populations as the ground state configuration $|\,0\rangle$ within the CI considering mono-excited states. Therefore, these results clearly show a significant polarization of the σ-core upon the electronic excitation to the ${}^1B_{3u}$ states. Moreover, the resulting wave functions of the first two ${}^1B_{3u}$ states do not satisfy the basic assumption of the $\pi - \sigma$ separability theorem since they cannot be expressed in the product form (11). In this respect the recent calculation by Orloff and Sinanoğlu [*17*] should be mentioned, which also indicates the importance of the $\pi - \sigma$ interaction in $\pi^* \leftarrow \pi$ electronic transitions.

Let us further examine the lowest excited state of the ${}^1B_{2g}$ species. The corresponding transition ${}^1B_{2g} \leftarrow {}^1A_{1g}$, which is of the $\sigma^* \leftarrow \pi$ type, is dipole forbidden. It was recently shown by Robin, Hart and Kuebler [*24*] on the basis of the SCF calculations using the expanded Gaussian type orbitals that the frequency corresponding to the $\mathrm{CH}^* \leftarrow \pi$ transition lies in the near ultraviolet region. Therefore, they have suggested the assignement of the weak "mystery band" of mono-olefins, which is usually found in the 2300 – 2000 Å region, to the $\mathrm{CH}^* \leftarrow \pi$ transition. This mystery band was formerly assigned by Berry [*2*] to the $\pi^* \leftarrow \mathrm{CH}$ transition. Furthermore, it was shown by Hart and Robin [*9*] that even the $\mathrm{CH}^* \leftarrow \mathrm{CH}$ and the $\pi^* \leftarrow \mathrm{CH}$ transitions might be eventual candidates for the assignement of the bands in the UV region of the ethylene spectrum. It is apparent already from the orbital energy scheme (Fig. 2) that our calculations support the assignement made by Robin, Hart and Kuebler [*24*]. The excitation energy to the lowest ${}^1B_{2g}$ state is much lower than the excitation energy to the ${}^1B_{3u}$ state (see Tab. 3). In addition the population analysis was carried out for the mono-excited configuration $|\,{}^7_6\rangle$ having by far the largest coefficient in the CI wave function of the lowest ${}^1B_{2g}$ state. The gross populations given in Tab. 5 clearly show the shift of the electronic charge mainly to the hydrogen atoms, thus reversing the polarity of the CH bond found in the ground state.

Configuration Interaction

Let us now discuss the effect of the extent of CI. It may be stated in general that the CI treatment using the virtual SCF–MO's especially those obtained with the minimum basis set which are localized practically in the same region of space as the occupied SCF–MO's, will not be very effective in improving the wave function and energy as far as the correlation is concerned.

Further, very poor results obtained for the excitation energies cannot be corrected in this way either. The reasons for this are well known from the papers on semiempirical theories (cf. [*18*, *7*]). Furthermore, our results corroborate the well known fact of a very slow convergency of this method (compare for ex. [*8*, *9*]). Tab. 3 and 4 show that the di-excited configurations with the exception of the configuration function $|\,{}^{8\,8}_{6\,6}\rangle$ give very small ground state energy depressions, so that the estimates using the 2nd order perturbation theory are very good.

The effect of the di-excited configurations on the excited ${}^1B_{3u}$ state is even smaller. On the other hand one can expect the tri-excited configuration to be more effective in this case. A rough estimate of the influence of the tri-excited configurations corroborates this expectation. Because of the mono-excited states $\left|\begin{smallmatrix}7\\4\end{smallmatrix}\right\rangle$ and $\left|\begin{smallmatrix}8\\6\end{smallmatrix}\right\rangle$ are the most important ones in the two lowest ${}^1B_{2u}$ states, we have tried the effect of the following tri-excited configurations $\left|\begin{smallmatrix}7\\4\end{smallmatrix}\binom{8}{6}^2\right\rangle$, $\left|\begin{smallmatrix}8\\6\end{smallmatrix}\binom{7}{4}^2\right\rangle$ and $\left|\begin{smallmatrix}8\\6\end{smallmatrix}\binom{7}{5}^2\right\rangle$. Their effect, which is certainly much more significant than that of the di-excited configurations, is apparent from Tab. 6.

Nevertheless, these results leave no doubt that the CI of the type mentioned above cannot account for the drawbacks of the minimum basis set used in the SCF calculation as far as the excited state energies are concerned (16.1 eV for the ${}^1B_{3u} \leftarrow {}^1A_{1g}$ transition and 10.3 eV for the ${}^3B_{3u} \leftarrow {}^1A_{1g}$ transition with CI including mono-excited states; the experimental values are 7.6 eV [*29*] and 4.6 eV [*6*] respectively). If di-excited configurations are included, the energy of excitation to the ${}^1B_{3u}$ state is even increased to 17.5 eV since the depression of the ground state energy is greater than that of the ${}^1B_{3u}$ state when di-excited configurations are considered.

On the other hand, a more reasonable value is obtained for the ionisation potential using the Koopman's theorem (7.71 eV — the experimental value is 10.52 eV [*28*]).

Table 6. *The effect of some tri-excited configurations on the first two ${}^1B_{3u}$ states*

No. of configurations		2		5	
Energy (a.u.)		0.6144	0.7284	0.6025	0.7110
Configuration and corresp. coefficients	$\left\|\begin{smallmatrix}8\\6\end{smallmatrix}\right\rangle$	−0.5401	0.8416	−0.4391	0.8959
	$\left\|\begin{smallmatrix}7\\4\end{smallmatrix}\right\rangle$	0.8416	0.5401	0.8920	0.4277
	$\left\|\begin{smallmatrix}7\\4\end{smallmatrix}\binom{8}{6}^2\right\rangle$	—	—	−0.1044	−0.1108
	$\left\|\begin{smallmatrix}8\\6\end{smallmatrix}\binom{7}{4}^2\right\rangle$	—	—	−0.0202	−0.0351
	$\left\|\begin{smallmatrix}8\\6\end{smallmatrix}\binom{7}{5}^2\right\rangle$	—	—	0.0141	−0.0289

It is also worth mentioning that a very small difference occurs in results using the two different approximations of the core. Clearly, the explicit consideration of the 1*s* electrons of the carbon atoms does not have any practical significance.

In conclusion, we would like to stress again that this study should be considered as a model calculation of the $\pi - \sigma$ interaction rather then an attempt to study the electronic structure of the ethylene molecule. Unfortunately, the ethylene molecule is not the best model for the study of the $\pi - \sigma$ interaction effects since it is well known that the molecular geometry is drastically changed upon the excitation to the first allowed singlet state. Unfortunately, the same situation is encountered even with other simple molecules studied in this respect, namely the acetylene and formaldehyde molecules, in both of which serious geometry rearrangements take place upon the excitation.

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