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Commentationes

The Double-Bond in Ethylene

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A full configuration interaction treatment has been carried out for the four electrons of the double bond of ethylene using a minimal STO basis set. The excent to which $\sigma - \pi$ separability provides a good approximation for the eigenfunctions of the low-lying states and for transitions between them has been examined. Alternative formulations using various more localised orbitals as the basis are derived for a number of the states. These have been examined and discussed.

Eine vollständige Konfigurationswechselwirkung wurde für die vier Elektronen der Doppelbindung von Äthylen durchgeführt, wobei eine minimale STO-Basis benutzt wurde. Das Maß, in dem die $\sigma - \pi$-Separierbarkeit eine gute Näherung für Eigenfunktionen der niedrigliegenden Zustände und für Übergänge zwischen ihnen darstellt, wurde untersucht. Alternativformulierungen, die verschiedene, lokalisierte Orbitale als Basis benutzen, werden für eine Anzahl von Zuständen angegeben und diskutiert.

Interaction de configuration complète pour les quatre électrons de la double liaison de l'éthylène dans une base STO minimale. La séparabilité $\sigma - \pi$ est examinée pour les plus bas états et les transitions entre ces états. D'autres formulations utilisant des orbitales plus localisées sont obtenues pour certains états. Ces formulations sont discutées.

Introduction

The object of this investigation was in part to examine, by carrying out a configuration interaction calculation, whether it was a good approximation to treat the wave functions for the various states of the double bond in ethylene as a product of a σ-function and a π-function. The greatest interest lay in the functions for the lower states. Consideration was given to the extent to which the more low-lying excitations can be regarded as involving a change in the π-function only, the σ-function remaining unchanged. An examination was also made of alternative ways of representing the wave function of the ground state. This problem of $\sigma - \pi$ separability has been studied by Lykos and Parr [1], by Löwdin [2], by Nesbet [3] and by Ruedenberg [4] among others. A configuration interaction treatment of ethylene, very similar to the present one, was carried out by Moser [5]. Our results differ slightly from his and the analysis of the results has been extended.

Calculation and Results

A full configuration interaction treatment of the ethylene molecule was carried out using a minimal Slater type orbital basis set for the four electrons of the carbon-carbon bond. The orbital exponent ξ was taken to be 1.625 and the carbon-carbon internuclear distance was set at 1.335 Å.

Table 1. *Definition of spatial & spin functions*

C.⊢— 1.335 Å —⊣C.
a b

σ_a, σ_b: sp^2 hybridized Slater type orbitals centered at a&b with positive regions between a&b.

π_a, π_b: p orbitals perpendicular to sp^2 plane.

$\sigma = (\sigma_a + \sigma_b)/(2 + 2\langle\sigma_a|\sigma_b\rangle)^{1/2}$; $\sigma^* = (\sigma_a - \sigma_b)/(2 - 2\langle\sigma_a|\sigma_b\rangle)^{1/2}$
$\pi = (\pi_a + \pi_b)/(2 + 2\langle\pi_a|\pi_b\rangle)^{1/2}$; $\pi^* = (\pi_a - \pi_b)/(2 - 2\langle\pi_a|\pi_b\rangle)^{1/2}$
$P_a = (\sigma_a + \pi_a)/\sqrt{2}$; $M_a = (\sigma_a - \pi_a)/\sqrt{2}$
$P_b = (\sigma_b + \pi_b)/\sqrt{2}$; $M_b = (\sigma_b - \pi_b)/\sqrt{2}$
$X_a = (\sigma_a + \pi_b)/\sqrt{2}$; $W_a = (\sigma_a - \pi_b)/\sqrt{2}$
$X_b = (\sigma_b + \pi_a)/\sqrt{2}$; $W_b = (\sigma_b - \pi_a)/\sqrt{2}$
$S_0 = \alpha\beta\alpha\beta$
$S_1 = (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)/2$
$S_2 = [(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha) - 2(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha)]/2\sqrt{3}$
$S_3 = \alpha\beta(\alpha\beta - \beta\alpha)/\sqrt{2}$
$S_4 = \alpha\beta(\alpha\beta + \beta\alpha)/\sqrt{2}$
$S_5 = (\alpha\beta - \beta\alpha)(\alpha\beta + \beta\alpha)/2$

The one electron integrals were evaluated in the Goeppert Mayer-Sklar [6] approximation. The two electron, one centre integrals were evaluated from formulae given by Roothaan [7] and the two centre integrals were taken from Kopineck's tables [8].

Four transformations among the one electron orbitals were used to present the results of the configuration interaction. These are defined in Table 1 and numerical results for the four lowest $1A_{1g}$ states, the $^3B_{1u}$ and the $^1B_{1u}$ states are presented in Tables 2a, b, c.

Two variations of the NPSO model [9] were investigated in order to find a single determinant function which, when projected according to spatial and spin symmetry requirements, would represent the C. I. function for the ground state of the ethylene molecule.

Two sets of one electron orbitals were formed by mixing pair-wise and cyclicly the ordered sets of atomic orbitals $[\sigma_a\sigma_b\pi_b\pi_a]$ = NPSO and $[\sigma_a\sigma_b\pi_a\pi_b]$ = XNPSO.

The spin function was given the form $\sin(\varepsilon) S_1 + \cos(\varepsilon) S_2$ (see Table 1) and ε was varied from 0 to π in units of $\pi/16$. For each value of ε the set of mixing parameters which gave maximum value of the overlap integral $\langle$NPSO|C. I.$\rangle$ or $\langle$XNPSO|C. I.$\rangle$ was determined. Comparison of configurations contained in the C. I. function showed that there were large discrepancies in coefficients for values of overlap up to 0.99. In both cases the fit corresponded to a value of $\varepsilon = \pi/2$, corresponding to pure S_1.

Table 3 gives the explicit form of the best approximation functions and comparison with the C. I. function.

Discussion

$\sigma - \pi$ Separability

The most important term in the C. I. function for the ground state is $\sigma\sigma\pi\pi$, but $\sigma\sigma^*\pi\pi^*$ also makes a considerable contribution (see Table 2a). The overlap integral of a combination of these two terms with the C. I. function would be about 0.99. Together they may be represented alternatively by

$$\sigma\sigma[c_1(\pi_a\pi_b+\pi_b\pi_a)+c_2(\pi_a\pi_a+\pi_b\pi_b)] \tag{1}$$

In this form the σ-molecular orbitals are used and the π-part is separated into covalent and ionic terms. The covalent terms have greater weight than the ionic ones ($c_2 \sim 0.41\, c_1$). If the σ-function were separated in a similar way the ionic terms would have about 61% of the weight of the covalent terms.

For the next ${}^1A_{1g}$ state, the simplest reasonable approximation is again that the function can be represented by a combination of covalent and ionic terms:

$$\sigma\sigma[c_1'(\pi_a\pi_b+\pi_b\pi_a)-c_2'(\pi_a\pi_a+\pi_b\pi_b)] \tag{2}$$

But, in this case the π-ionic terms have greater weight and $c_1' \sim 0.74\, c_2'$. The overlap integral with the C. I. function would be about 0.95. For this state the terms involving $\sigma\pi\sigma^*\pi^*$ are of some importance: and their size limits the $\sigma-\pi$ separability of the whole function.

The lowest triplet state is the ${}^3B_{1u}$ state. The overlap of the single $\sigma\sigma\pi\pi^*$ term with the C. I. function is greater than 0.99.

The next state is the lowest member of class ${}^1B_{1u}$. The overlap of the $\sigma\sigma\pi\pi^*$ term with the C. I. function is 0.98. So, to that degree, the excitation from the ground state can be regarded as simply a change in the π-part of the function without any change in the σ-function. However, the term $\pi\pi\sigma\sigma^*$ contributes 3% and $\pi^*\pi^*\sigma\sigma^*$ 1% to $\langle\Psi^2\rangle$. Any increase in accuracy above using $\sigma\sigma\pi\pi^*$ on its own would therefore require a sacrifice of $\sigma-\pi$ separability.

The next state energetically is the second member of the ${}^3B_{1u}$ class. The overlap of the $\pi\pi\sigma\sigma^*$ term with the C. I. function would be 0.985. Compared with the ground state it involves a change in both the σ and π-parts of the function. The lowest ${}^3B_{2g}$ state involves very considerable $\sigma-\pi$ mixing.

To summarise: For the ground state and the lowest ${}^3B_{1u}$ state it is correct, to the extent of achieving an overlap with the C. I. function greater than 0.99, to treat the functions as separable and the excitation as involving a change in the π-part only. For the next state (${}^1B_{1u}$) the accuracy of this description is reduced a little. The function for the next state (second ${}^3B_{1u}$) is separable into a product of a σ-part and a π-part (achieving an overlap with the C. I. function of 0.985). However, excitation from any of the lower states requires a change of both the σ- and π-parts of the function. For the second ${}^1A_{1g}$ state, the function is separable to about the same accuracy and excitation from the ground state, or from the lowest ${}^1B_{1u}$ and ${}^3B_{1u}$ states, can be treated quite accurately as purely π-excitations.

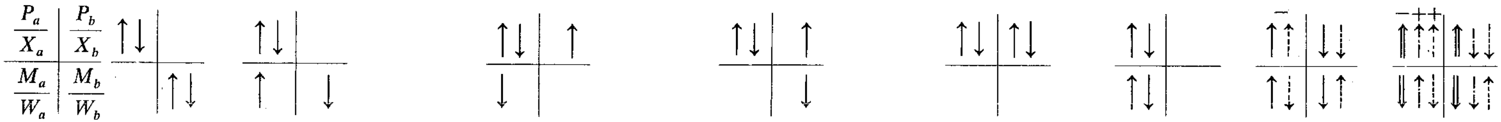
The functions for the states of the ${}^3B_{2g}$, ${}^1B_{2g}$, ${}^3B_{3u}$, ${}^1B_{3u}$ and ${}^3A_{1g}$ do not show good $\sigma-\pi$ separability but all those of the ${}^3B_{1u}$ class do. Separability for the intermediate states of class ${}^1A_{1g}$ is poor.

Alternative Representations

In Table 2 the results for four alternative representations are listed for the lower states of the ${}^1A_{1g}$ class and the states of the ${}^1B_{1u}$ and ${}^3B_{1u}$ classes. The representations are based on (i) M. O. s; (ii) V. B. type functions using σ- and π-type orbitals; (iii) V. B. functions using four localised hybrids of the type $(\sigma_a+\pi_a)$;

Table 2. *Exact representations of the C. I. functions for low-lying states of the ethylene double bond. a)* $^1A_{1g}$*; b)* $^3B_{1u}$*; c)* $^1B_{1u}$[a]

M. O.	$\sigma\sigma\pi\pi S_0$	$\sigma\sigma\pi^*\pi^* S_0$	$\sigma^*\sigma^*\pi\pi S_0$	$\sigma\sigma\sigma^*\sigma^* S_0$	$\pi\pi\pi^*\pi^* S_0$	$\sigma^*\sigma^*\pi^*\pi^* S_0$	$\sigma\sigma^*\pi\pi^* S_1$	$\sigma\sigma^*\pi\pi^* S_2$
$^1A_{1g}$ Energy in e.V.								
−165.32	0.9641	−0.2498	−0.0367	−0.0109	−0.0064	0.0151	0.0722	−0.034
−149.81	0.2347	0.9482	0.0097	−0.0452	−0.0836	−0.0277	0.1760	0.0703
−130.69	0.0308	−0.0156	−0.0156	0.7034	0.0711	−0.0254	−0.0274	0.7049
−129.82	0.0194	0.1056	−0.1049	0.6875	−0.0568	−0.0104	−0.1666	−0.6883
V. B.	$\sigma_a\sigma_a\pi_b\pi_b S_0$ + $\sigma_b\sigma_b\pi_a\pi_a S_0$	$\sigma_a\sigma_a\pi_a\pi_b S_3$ + $\sigma_b\sigma_b\pi_a\pi_b S_3$	$\pi_a\pi_a\sigma_a\sigma_b S_3$ + $\pi_b\pi_b\sigma_a\sigma_b S_3$	$\sigma_a\sigma_a\sigma_b\sigma_b S_0$	$\pi_a\pi_a\pi_b\pi_b S_0$	$\sigma_a\sigma_a\pi_a\pi_a S_0$ + $\sigma_b\sigma_b\pi_b\pi_b S_0$	$\sigma_a\sigma_b\pi_a\pi_b S_1$	$\sigma_a\sigma_b\pi_a\pi_b S_2$
$^1A_{1g}$								
−165.32	0.1105	0.1629	0.1055	−0.0231	−0.0067	0.0025	0.4110	0.0509
−149.81	0.3131	−0.1548	0.3298	−0.0956	−0.0885	0.0496	−0.3852	−0.1053
−130.69	−0.0618	0.0359	0.0601	1.4889	0.0753	−0.0207	−0.0246	−1.0552
−129.82	−0.1923	−0.1171	0.1584	1.4547	−0.0602	0.0571	0.0946	1.0297



One centre equivalent orbitals	$P_aP_aM_bM_bS_0$ + $P_bP_bM_aM_aS_0$	$(P_aP_a+P_bP_b)M_aM_bS_3$ + $(M_aM_a+M_bM_b)P_aP_bS_3$	$(P_aP_a+M_bM_b)P_bM_aS_3$ + $(P_bP_b+M_aM_a)P_aM_bS_3$	$(P_aP_a+M_aM_a)P_bM_bS_3$ + $(P_bP_b+M_bM_b)P_aM_aS_3$	$P_aP_aP_bP_bS_0$ + $M_aM_aM_bM_bS_0$	$P_aP_aM_aM_aS_0$ + $P_bP_bM_bM_bS_0$	$P_aP_bM_aM_bS_1$	$P_aP_bM_aM_bS_2$
$^1A_{1g}$								
−165.32	0.1285	0.1342	−0.0287	−0.0058	−0.0329	0.0025	0.3930	0.0818
−149.81	0.0598	0.0857	0.2441	−0.0025	0.1612	0.0496	−0.1320	−0.5440
−130.69	0.8110	0.0481	0.0122	0.4998	−0.0906	−0.0207	−0.8970	0.4564
−129.82	−0.1700	0.0208	0.1379	0.5356	0.6780	0.0571	0.0724	1.0690
Two centre equivalent	$X_aX_aW_bW_bS_0$ + $X_bX_bW_aW_aS_0$	$(X_aX_a+X_bX_b)W_aW_bS_3$ + $(W_aW_a+W_bW_b)X_aX_bS_3$	$(X_aX_a+W_bW_b)X_bW_aS_3$ + $(X_bX_b+W_aW_a)X_aW_bS_3$	$(X_aX_a+W_aW_a)X_bW_bS_3$ + $(X_bX_b+W_bW_b)X_aW_aS_3$	$X_aX_aX_bX_bS_0$ + $W_aW_aW_bW_bS_0$	$X_aX_aW_aW_aS_0$ + $X_bX_bW_bW_bS_0$	$X_aX_bW_aW_bS_1$	$X_aX_bW_aW_bS_2$
$^1A_{1g}$								
−165.32	0.1186	0.1342	−0.0287	−0.0058	−0.1310	0.1105	0.2950	0.1496
−149.81	−0.1631	0.0857	0.2441	−0.0025	0.1206	0.3131	−0.1726	−0.2648
−130.69	−0.0724	0.0481	0.0122	0.4998	0.8436	−0.0618	0.0372	0.9485
−129.82	0.8470	0.0208	0.1379	0.5356	−0.0896	−0.1923	−0.6954	0.3377

Table 2. (b)

M. O.	$\sigma\sigma\pi\pi^* S_4$	$\pi\pi\sigma\sigma^* S_4$	$\sigma^*\sigma^*\pi\pi^* S_4$	$\pi^*\pi^*\sigma\sigma^* S_4$
$3B_{1u}$				
−161.41	0.9953	0.0893	−0.0430	−0.0226
−150.36	−0.0867	0.9850	−0.0072	−0.1489
−121.58	0.0111	0.1506	0.0315	0.9880
− 97.71	0.0419	0.0060	0.9986	−0.0332
V. B.	$\sigma_a\sigma_b\pi_a\pi_b S_5$	$(\sigma_a\sigma_a+\sigma_b\sigma_b)\pi_a\pi_b S_4$	$(\pi_a\pi_a+\pi_b\pi_b)\,\sigma_a\sigma_b S_4$	$\pi_a\pi_b\sigma_a\sigma_b S_5$
$^3B_{1u}$				
−161.41	0.5338	0.2158	0.0279	0.1002
−150.36	−0.0170	−0.0393	0.4377	1.0200
−121.58	−0.0790	0.0625	1.0294	−1.2052
− 97.71	−2.6366	1.8892	−0.0281	0.0498

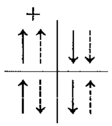
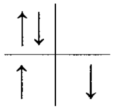
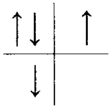
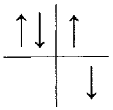
$\frac{P_a}{X_a}$ $\frac{P_b}{X_b}$ $\frac{M_a}{W_a}$ $\frac{M_b}{W_b}$				
One centre equivalent orbitals	$P_aP_bM_aM_bS_5$ $+$ $M_aM_bP_aP_bS_5$	$(P_aP_a+P_bP_b)\,M_aM_bS_4$ $+$ $(M_aM_a+M_bM_b)\,P_aP_bS_4$	$(P_aP_a+M_bM_b)\,P_bM_aS_4$ $-$ $(P_bP_b+M_aM_a)\,P_aM_bS_4$	$(P_aP_a-M_aM_a)\,P_bM_bS_4$ $-$ $(P_bP_b-M_bM_b)\,P_aM_aS_4$
$^3B_{1u}$				
−161.41	0.3170	0.1219	0.0940	0.1533
−150.36	0.5016	0.1991	−0.2386	−0.3667
−121.58	−0.6422	0.5460	−0.4835	0.3982
− 97.71	−1.2934	0.9306	0.9587	−0.9498
Two centre equivalent orbitals	$X_aX_bW_aW_bS_5$ $+$ $W_aW_bX_aX_bS_5$	$(X_aX_a+X_bX_b)\,W_aW_bS_4$ $+$ $(W_aW_a+W_bW_b)\,X_aX_bS_4$	$(X_aX_a+W_bW_b)\,X_bW_aS_4$ $-$ $(X_bX_b+W_aW_a)\,X_aW_bS_4$	$(X_aX_a-W_aW_a)\,X_bW_bS_4$ $-$ $(X_bX_b-W_bW_b)\,X_aW_aS_4$
$^3B_{1u}$				
−161.41	0.2168	0.0940	0.1219	0.2241
−150.36	−0.5188	−0.2386	0.1991	0.3545
−121.58	0.5632	−0.4835	0.5460	−0.4541
− 97.71	−1.3432	0.9587	0.9306	−0.9146

Table 2. (c)

M. O.	$\sigma\sigma\pi\pi^* S_3$	$\pi\pi\sigma\sigma^* S_3$	$\sigma^*\sigma^*\pi\pi^* S_3$	$\pi^*\pi^*\sigma\sigma^* S_3$
$^1B_{1u}$				
−153.85	0.9818	−0.1594	−0.0228	−0.1009
−132.28	0.1235	0.9490	−0.0818	−0.2782
−116.02	0.1310	0.2410	−0.2031	0.9399
− 87.78	0.0606	0.1261	0.9755	0.1700
V. B.	$\sigma_a\sigma_a\pi_b\pi_b S_0$ $-$ $\sigma_b\sigma_b\pi_a\pi_a S_0$	$(\sigma_a\sigma_a - \sigma_b\sigma_b)\,\pi_a\pi_b S_3$	$(\pi_a\pi_a - \pi_b\pi_b)\,\sigma_a\sigma_b S_3$	$\sigma_a\sigma_a\pi_a\pi_a S_0$ $-$ $\sigma_b\sigma_b\pi_b\pi_b S_0$
$^1B_{1u}$				
−153.85	−0.3109	0.0023	0.3354	0.0424
−132.28	0.2901	0.8232	0.1905	0.1248
−116.02	0.9755	−0.7532	0.4209	0.4909
− 87.78	−1.1404	−0.0877	−1.8153	1.4779

$\begin{array}{c\|c} \frac{P_a}{X_a} & \frac{P_b}{X_b} \\ \hline \frac{M_a}{W_a} & \frac{M_b}{W_b} \end{array}$ [b]	$\begin{array}{c\|c} \uparrow\downarrow & \uparrow \\ \hline & \downarrow \end{array}$	$\begin{array}{c\|c} \uparrow\downarrow & \\ \hline \uparrow & \downarrow \end{array}$	$\begin{array}{c\|c} \uparrow\downarrow & \uparrow \\ \hline \downarrow & \end{array}$	$\begin{array}{c\|c} \uparrow\downarrow & \\ \hline \uparrow\downarrow & \end{array}$
One centre equivalent orbitals	$(P_aP_a + M_aM_a)\, P_bM_bS_3$ $-$ $(P_bP_b + M_bM_b)\, P_aM_aS_3$	$(P_aP_a - P_bP_b)\, M_aM_bS_3$ $+$ $(M_aM_a - M_bM_b)\, P_aP_bS_3$	$(P_aP_a - M_bM_b)\, P_bM_aS_3$ $-$ $(P_bP_b - M_aM_a)\, P_aM_bS_3$	$P_aP_aM_aM_aS_0$ $-$ $P_bP_bM_bM_bS_0$
$^1B_{1u}$				
−153.85	0.2198	0.1688	0.1666	0.0424
−132.28	−0.2052	0.5068	−0.3164	0.1248
−116.02	−0.6897	−0.1662	0.5870	0.4909
− 87.78	0.8064	−0.9515	−0.8638	1.4779
Two centre equivalent orbitals	$(X_aX_a + W_aW_a)\, X_bW_bS_3$ $-$ $(X_bX_b + W_bW_b)\, X_aW_aS_3$	$(X_aX_a - X_bX_b)\, W_aW_bS_3$ $+$ $(W_aW_a - W_bW_b)\, X_aX_bS_3$	$(X_aX_a - W_bW_b)\, X_bW_aS_3$ $-$ $(X_bX_b - W_aW_a)\, X_aW_bS_3$	$X_aX_aW_aW_aS_0$ $-$ $X_bX_bW_bW_bS_0$
$^1B_{1u}$				
−153.85	0.0300	0.1666	0.1688	0.3109
−132.28	0.0882	−0.3164	0.5068	−0.2901
−116.02	0.3470	0.5870	−0.1662	−0.9755
87.78	1.0438	−0.8638	−0.9515	1.1404

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[a] Results for the other states of the $^1A_{1g}$ class and for all the other symmetry classes are contained in the Ph. D. Thesis of A. Amaral, Cambridge, 1968. The symbols used are defined in Table 1.

[b] In the diagrams the four equivalent orbitals $(\sigma_a + \pi_a)$ etc. are represented by the four quadrants of a plane. For those configurations involving S_1, S_2 and S_5 more than one combination of spins is summarised in the diagram. Products be formed arrows of the same type and combined according to the signs shown in the diagrams (cf. Table 1 for definitions of the spin functions).

(iv) V. B. functions using hybrids of the type $(\sigma_a + \pi_b)$. Only low-lying states will be discussed.

$^1A_{1g}$ *States.* The M. O. function of the ground state has been examined already. The σ-part is represented quite well by $\sigma\sigma$ alone, but the π-part requires $\pi\pi$ and $\pi^*\pi^*$. The first V. B. form shows the high importance of the terms involving four separate orbitals, and in particular of those for which electrons of opposite spin occupy the two σ-orbitals and two of opposite spin occupy the two π-orbitals. The combination which associates the two orbitals on the same atom with the same spin function is fractionally more important. This appears surprising but probably happens because this is the means by which this particular type of function includes electron correlation on the same atom. The terms which assign the electrons entirely in pairs, either in both σ, or both π-orbitals or on the same atom, are unimportant. The terms in the first three columns are of intermediate importance as would be expected. The $\sigma_a^2\pi_a\pi_b$ type of term is the most important of these.

The four equivalent orbitals used in representation (iii) are localised as shown in Fig. 1. To a considerable extent these orbitals divide the space between the carbon atoms into four separate regions and may be considered in this way. In Table 2 a diagramatic representation of the orbital occupation for the various configurations is included along with the algebraic form. This representation can also be discussed in terms of two Baeyer-type bonds (banana or bent bonds) rather than pure σ or π-type bonds. Since these orbitals are more localised from one another they provide a better means of describing the spatial distribution because cross terms (overlap terms) in Ψ^2 are less important. Again the double Heitler-London type terms (last column but one) are the most important. The sign of the term in the last column shows that the members which assign electrons of the same spin to the same atom are favoured relative to those which assign electrons of opposite spin. This feature has already been discussed. The terms

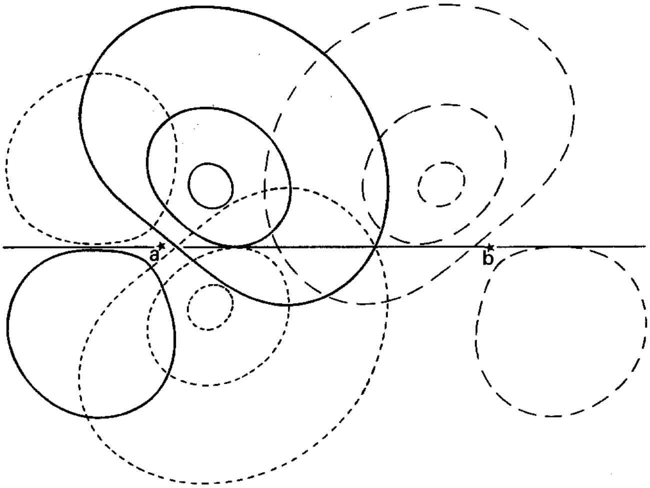

Fig. 1. Density contour plots for Baeyer-type V. B. functions. (——) $(\sigma_a + \pi_a)/\sqrt{2}$, (- - - -) $(\sigma_a - \pi_a)/\sqrt{2}$, (— — —) $(\sigma_b + \pi_b)/\sqrt{2}$

in the first two columns are of considerable importance. They are ionic terms and assign two electrons to each Baeyer-type bond. The first places zero formal charge on each atom; the second contains covalent terms for one bond and ionic for the other. The terms which assign all four electrons to the same atom are of negligeable importance. The terms which assign three electrons to one Baeyer-bond and one to the other have negative coefficients (i. e. they produce a reduction in the probability of such dispositions). This means that the electron pairs are even more strongly localised separately in the two Baeyer-bond regions than would be given by using the main terms alone. Likewise the terms which plane four electrons in one bond region (fifth column) have a negative coefficient.

The four equivalent orbitals of type (iv) $(\sigma_a + \pi_b)$ are not localised in separate regions of space in contrast to the $(\sigma_a + \pi_a)$ type orbitals. Each orbital has two regions of high density, one between the atoms and the other in one quadrant similar to type (iii). They are less successful than those of the type $(\sigma_a + \pi_a)$ as is shown by the fact that there are only two small coefficients for the ground state function whereas with the more localised functions there are four.

The M. O. formulation of the second $^1A_{1g}$ state has already been discussed. In the $\sigma - \pi$ V. B. form the terms that were very small for the ground state are still small. All the other terms have fairly large coefficients. The change in sign between the π-ionic and π-covalent terms can be seen; there is no change in sign between the σ-ionic and σ-covalent terms (cf. M. O. form). Compared with the ground state, the terms which assign all four electrons to separate orbitals have decreased in importance relative to the terms in the first three columns. The increased energy is therefore partly due to an increase in the one-electron terms in the energy, and partly to an increase in the mean inter-electron repulsion energy.

Using the four equivalent orbitals of type (iii), the largest terms are still those which assign the four electrons to four separate orbitals as might have been expected because it is fairly low-lying. However, the most important terms of this type are those which assign the same spin functions to the two component orbitals of the same Baeyer-bond. The terms which assign electrons of the same spin to the same atom are next in importance. The third pair of members of this set which assign electrons of opposite spin both to the two bonds and to the two atoms have much smaller coefficients. So the largest terms correspond to both bonds behaving as triplets, though the resultant state is a singlet. The other important terms are those in the third and the fifth columns. Both were unimportant in the ground state function.

$^3B_{1u}$ *States.* The M. O. formulation of the lowest $^3B_{1u}$ state shows that it is described quite accurately by the single term $\sigma\sigma\pi\pi^*$ though the term $\pi\pi\sigma\sigma^*$ has a coefficient which is about one tenth that of the leading term. The other coefficients are very small.

The spin functions, S_4 and S_5, which appear in the $\sigma - \pi$ V. B. formulation are arranged so that the first pair of spatial orbitals combine as a singlet and the second pair as a triplet. For the lowest $^3B_{1u}$ state the first two terms have large coefficients which shows that the σ-part of the function is primarily singlet and bonding while the π-part is primarily triplet in character. The magnitude of the coefficient in the last column shows that the inverse situation makes some contribution.

In the formulation (iii) the main terms are those which assign the four electrons to the four different orbitals which is consistent with the fact that it is the only other state besides the ground state which has an energy below -160 eV. However, the pair of orbitals forming one Baeyer-bond is associated with a singlet spin function while the pair forming the other has triplet character. The other three terms which assign one electron pair to a single orbital have coefficients which are about a third or a half of the largest coefficient so they do have considerable importance. It is interesting that all electron distributions of this kind have the same weight; there is no indication of particular bonding arrangements in the region between the atoms being favoured.

The second ${}^3B_{1u}$ state is quite well represented by $\pi\pi\sigma\sigma^*$ though the coefficients of the $\pi^*\pi^*\sigma\sigma^*$ terms are not negligeable. The reversal of sign shows that covalent π-terms are favoured. This can be seen from the $\sigma-\pi$ V. B. results. The coefficient of the $\pi_a\pi_b\sigma_a\sigma_b$ terms for which the π-orbitals combine as a singlet while the σ-orbitals combine as a triplet is the largest, though the corresponding π-ionic terms ($\pi_a\pi_a\sigma_a\sigma_b$) are fairly important. The terms which involve the σ-orbital combination being singlet and the π triplet are of very low importance indeed.

In the Baeyer-V. B. form the most important term is the one assigning one electron to each region though the pair of orbitals associated with one bond are combined to form a singlet and those with the other a triplet. The two terms which involve a combination of a three-electron Baeyer-bond with a one-electron one have considerable coefficients but there is a change of sign from the first two terms. For the ground state all the coefficients had the same sign.

As for the ${}^1A_{1g}$ states representation (iv) does not provide a useful way of analysing the molecular wave functions.

${}^1B_{1u}$ *States.* For the lowest state of symmetry class ${}^1B_{1u}$, $\sigma\sigma\pi\pi^*$ is the most important term in the M. O. formulation. The $\pi\pi\sigma\sigma^*$ and $\pi^*\pi^*\sigma\sigma^*$, though much less important, are hardly negligeable. In the $\sigma-\pi$ V. B. form, one pair of terms is clearly negligeable and another pair which assign all four electrons to the same atom is of low importance. The other two pairs of terms have equal weight but the coefficients have opposite signs. The first pair are ionic in the σ-orbitals and also in the π-orbitals though the electron pairs are on different atoms so that the formal charge on each atom is zero. The other functions are ionic in the π-orbitals but covalent in the σ-orbitals. So the π-terms are ionic only, while the σ-bond contains ionic and covalent terms. However, those σ-ionic terms which would place all four electrons on the same atom are relatively unimportant. There is therefore a limitation on the ionic terms.

In the Baeyer-V. B. formulation which uses four equivalent orbitals all the terms which assign two electrons to one region and the other two to two of the other regions are important, and about equally so. The configuration which assigns the electrons as two pairs on the same atom is less important. The spatial distribution is not therefore readily considered in terms of bonds but more satisfactorily by examining the way in which the whole space between the carbon atoms is occupied. The occupation of the four equivalent orbitals by four electrons is not allowed for singlet states of this symmetry so their energies are higher than those of the corresponding triplet states for which it is allowed (Hund's Rule).

Table 3. *Comparison of the configurations contained in the approximate* NPSO *functions with the ground state* C. I. *function for the ethylene double bond*

Configurations	$\sigma_a\sigma_a\pi_b\pi_b S_0$ + $\sigma_b\sigma_b\pi_a\pi_a S_0$	$\sigma_a\sigma_a\pi_a\pi_b S_3$ + $\sigma_b\sigma_b\pi_a\pi_b S_3$	$\pi_a\pi_a\sigma_a\sigma_b S_3$ + $\pi_b\pi_b\sigma_a\sigma_b S_3$	$\sigma_a\sigma_a\sigma_b\sigma_b S_0$	$\pi_a\pi_a\pi_b\pi_b S_0$	$\sigma_a\sigma_a\pi_a\pi_a S_0$ + $\sigma_b\sigma_b\pi_b\pi_b S_0$	$\sigma_a\sigma_b\pi_a\pi_b S_1$	$\sigma_a\sigma_b\pi_a\pi_b S_2$
C. I.	0.1105	0.1152	0.0746	−0.0231	−0.0068	0.0025	0.4110	0.0509
NPSO ⟨CI|NPSO⟩ = 0.99925	0.0987	0.1283	0.0849	0	0	0	0.3810	0.0239
XNPSO ⟨CI|XNPSO⟩ = 0.99903	0.1103	0.1241	0.0709	0	0	0	0.4010	0.0121

$\Psi(\text{NPSO}) = N(1+\sigma_{a\leftrightarrow b})(\varrho_+ + \varrho_-)\,[(\sigma_a + 0.7\sigma_b)(\sigma_b + \sqrt{0.2}\pi_b)(\pi_b + 0.5\pi_a)(\pi_a + \sqrt{0.2}\,\sigma_a)]\,S_1.$

$\Psi(\text{XNPSO}) = N(1+\sigma_{a\leftrightarrow b})(\varrho_+ + \varrho_-)\,[(\sigma_a + 0.6\,\sigma_b)(\sigma_b + \sqrt{0.2}\,\pi_a)(\pi_a + 0.3\,\pi_b)(\pi_b - \sqrt{0.2}\,\sigma_b)]\,S_1.$

$\sigma_{a\leftrightarrow b}$ is operator that interchanges σ_a with σ_b and π_a with π_b.

ϱ_+ takes positive square root.

ϱ_- takes negative square root.

N is normalization constant.

See Table 1 for definition of remaining symbols.

Summary

The general conclusion from the examination of the various representations is that the M. O. formulation provides overall the most effective basis for describing the various low-lying states in as simple a manner as possible. Some states are represented satisfactorily by one configuration only; some require two. In some cases the $\sigma - \pi$ V. B. formulation is useful as for instance in discussing the $^1B_{1u}$ state. The formulation based on four equivalent hybrids is very useful for examining the mutual distribution of the four electrons as a set though it does not provide as simple a representation of the various states as does the M. O. The different representations therefore clarify different aspects of the distribution. The M. O. formulation has advantages for considering the one-electron energy while the formulation using four separated equivalent orbitals may be useful for making an approximate estimate of inter-electron effects.

NPSOFunctions for the Ground State

Both the NPSO functions that have been tested provide a good approximation to the C. I. function for the ground state as is shown by the comparison of the coefficients made in Table 3. With the exception of the last column the XNPSO function is better than the NPSO function. It is not easy to analyse either of these functions because of the considerable overlap of the various NPSO orbitals. However, the four basis orbitals clearly achieve a very satisfactory balance between separation and overlap. The four equivalent orbitals of type (iii) are apparently too localised to provide a simple representation of the C. I. function when a single electron is placed in each orbital, which would be equivalent to the NPSO functions under discussion here.

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