Theoret. chim. Acta (Berl.) 31, 1—17 (1973)

Commentationes

A Comparative *ab initio* Study of Ethylene, Acetylene and Benzene

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Received April 3, 1973

Ground state properties have been calculated by use of a medium-sized Gaussian basis set and comparison with other bases has been made. Contraction to "double-zeta" of a comparatively small basis is found to be superior to a large set of primitive Gaussians contracted to minimal basis. Molecular optimization is not important for double-zeta bases. Inclusion of a balanced set of polarization functions is essential in all cases studied. Population analysis gives a certain insight in molecular properties but contour maps are found to be significantly superior. This is demonstrated on bonding properties of corresponding orbitals within the series. In case of benzene Slater's energy-band plot is shown to be useful for classifying bonding properties.

Key words: Ab initio calculation – Basis set – Hydrocarbons – Ionization potentials – Orbital mapping.

1. Introduction

The present paper is concerned with theoretical investigations of ground state properties of small unsaturated organic molecules by means of non-empirical, all-electron calculations. The main goal was to compare calculated properties of the series acetylene, ethylene, benzene, obtained under similar conditions. Several basis sets were used and the effect of various modifications of the basis was studied. The most extensive studies were performed on ethylene. Comprehensive calculations on acetylene were also made, whereas for obvious reasons, applications to benzene were much more restricted.

Section 2 describes the method. In Section 3 the results for ethylene are presented and discussed. Sections 4 and 5 are concerned with acetylene and benzene, respectively. Corresponding orbitals of the different molecules are discussed in Section 6, and Section 7 collects the main results.

2. Method

Basis sets of Gaussian type functions localized at the various atoms of the molecule were used. The main part of the study is concerned with calculations employing a basis of nine s-type and five p-type functions at each carbon atom, (C/9,5), contracted to "double zeta", i.e. two basis functions for each atomic shell, $\langle C/4,2\rangle$. For hydrogen, four s-type functions, (H/4), were contracted to $\langle H/2\rangle$. The effect of including polarization functions, one d-function on each carbon and one p-function on each hydrogen, was also investigated. Arguments for this type of basis set have been given previously by Roos and Siegbahn [1, 2].

Within this frame an optimal basis set for unsaturated hydrocarbons was determined using ethylene as a probe. A similar investigation has recently been published by Schulman *et al.* [3]. However their study differs from ours in several respects. Most important, their basis set is a minimal one without polarization functions collated to ours of the double-zeta type and including polarization. Furthermore the details of the optimizing procedure were different.

Table 1a. Orbital exponents and contraction coefficients of the Gaussian basis sets. When ethylene-optimized values (B') deviate from atom-optimized, B, both values are given

Exponent	Coefficient	Exponent	Coefficient
A: (C/11, 6) [4]		$B(B')$: (C/9, 5)	
s-type			
15469.4	0.000242	—	—
2316.47	0.001879	5182.95	0.000947
527.10	0.009743	778.756	0.007256
149.438	0.039167	178.073	0.036292
48.8562	0.123636	50.8779	0.130515
17.6209	0.288316	16.7876	0.320715
6.81082	0.421504	6.14362	0.439516
2.72760	0.254118	2.40398	0.212694
0.756743	1.0	B: 0.511903	1.0
0.300728	1.0	(B': 0.462000	1.0)
0.114093	1.0	0.156594	1.0
p-type			
32.6921	0.005869	18.8418	0.013271
7.47261	0.039121	4.15924	0.092479
2.23924	0.151011	B: 1.206710	0.293686
0.772812	0.351470	(B': 1.136000	0.293686)
0.274838	1.0	B: 0.385541	0.472915
		(B': 0.395000	0.472915)
$p\sigma$			
0.095838	1.0	0.121939	1.0
$p\pi$			
0.095838	1.0	B: 0.121939	1.0
		(B': 0.131600	1.0)
$d\sigma\sigma = d\sigma\sigma' = d\pi\pi$			
0.898	1.0	B: 1.000	1.0
		(B': 0.898	1.0)
$d\sigma\pi$			
0.700	1.0	B: 1.000	1.0
		(B': 0.700	1.0)

Table 1b. See Table 1a for explanation

Exponent	Coefficient	Exponent	Coefficient
A: (H/5, 1) [4]		*B*′: (H/4, 1)	
s-type			
33.865014	0.006068	16.7019	0.019060
5.094788	0.045316	2.51663	0.134240
1.158786	0.202846	0.567196	0.474490
0.325840	1.0	0.154146	1.0
0.102741	1.0		
$p\sigma$			
1.200	1.0	1.200	1.0
$p\pi$			
1.000	1.0	1.000	1.0

As starting-point we have chosen the best-atom basis (C/9,5) determined by van Duynenvelt [4] and the (H/4) basis of Huzinaga [5], retaining the linear coefficients determined for the atoms. The contraction used for carbon *s*-type functions was (5, 2, 1, 1) and for *p*-type functions (4, 1). Calculations showed the *p*-type contraction (3, 2) to be considerably inferior. For the *s*-type functions of hydrogen the contraction (3, 1) was used.

During optimization the innermost carbon functions were left unchanged. The exponents of the outer functions, two of *s*-type and three of *p*-type, were varied independently. The outermost *p*-function was chosen differently for σ-orbitals and for π-orbitals. In the case of hydrogen *s*-type functions a scale factor, common to all the exponents, was varied. The polarization functions of hydrogen, $p\sigma$ and $p\pi$, were scaled independently. In case of the *d*-type polarization functions of carbon the exponent of the $d\sigma\pi$-functions (e.g. dxz of C_2H_4, where x is perpendicular to the plane of the molecule) was varied separate from the other *d*-functions. The final exponents and contraction coefficients are listed in Table 1. It was found that the total energy varied rather slowly with the orbital exponents of the polarization functions. Therefore these exponents could not be determined with high accuracy. The energy was insensitive to small variations above the value 1.25 of the hydrogen *s*-function scale factor. In accord with previous work [2, 6] we have therefore retained the value 1.25 of this factor.

It is interesting to compare the result of the present optimization with that of Schulman *et al.* [3]. These authors found that an ethylene-optimized basis was obtained by contraction of all the best-atom 2*s* Gaussians by a common scale factor equal to 1.206. The $2p\sigma$-functions were also contracted, the factor being 1.213, while $2p\pi$ was expanded by a factor 0.932. The ratio between $2p\sigma : 2p\pi$ was 1.3. The present results show much smaller changes from best-atom to best-molecule values. The ratio $2p\sigma : 2p\pi$ was found to be 0.93, i.e. *smaller* than unity for the outermost orbital, the others being unity, cf. Table 1. This result indicates that the higher flexibility of a double-zeta compared to a minimal basis is sufficient to ensure almost optimal conditions, the optimization of the exponents being rather unimportant in the double-zeta case.

In order to study the level of accuracy obtainable by the optimized (C/9, 5) basis, the results for ethylene were compared with results obtained by both larger and smaller bases. The largest basis used in the present investigation was the best-atom (C/11, 6, 1) basis of van Duynenvelt [4], contracted with the partitionings (6, 2, 1, 1, 1) and (4, 1, 1) to ⟨C/5, 3, 1⟩, combined with his (H/5, 1) basis contracted (3, 1, 1) to ⟨H/3, 1⟩. This basis is reproduced in Table 1. In view of the experience obtained during optimization of the (C/9, 5) basis no attempt was made to optimize the exponents of this even larger basis. The results emerging from this basis are likely to be very close to the Hartree-Fock limit, cf. C_2H_2 below. Comparison has also been made with previously published results [6], obtained from the (C/7, 3) basis [1], contracted (4, 1, 1, 1), (2, 1) to ⟨C/4, 2⟩, combined with Huzinaga's [5] (H/4) basis with a scaling factor 1.25 and contracted (3, 1), to which a p-function with orbital exponent 0.875 was added to give ⟨H/2, 1⟩.

The main part of the calculations were performed at the IBM Research Laboratory, San José, on an IBM 360/91 computer with the program system REFLECT [7]. This program was further developed to include full use of C_{2v} symmetry both in integral calculation and in SCF symmetry blocking.

3. Applications to Ethylene

All the calculations on ethylene were carried out with the following geometry: $r(\mathrm{CC}) = 2.5510$, $r(\mathrm{CH}) = 2.0236$ bohrs, $\angle \mathrm{HCH} = 117°$. The molecule belongs to the point group D_{2h}. We have chosen a coordinate system with the z-axis along the CC bond and the x-axis perpendicular to the molecular plane. With this choice the electronic configuration is $(1a_g)^2\,(1b_{1u})^2\,(2a_g)^2\,(2b_{1u})^2\,(1b_{2u})^2\,(3a_g)^2\,(1b_{3g})^2\,(1b_{3u})^2$, the last orbital being the π-orbital.

3.1. Ground State Properties: Basis Set Dependency

The different kinds of basis sets employed and the notations used below are collected in Table 2. The basis denoted *Apd* is sufficiently accurate to serve as a measure on the goodness of the other basis sets. Unprimed letters *A*, *B*, *C*, *D* are used for atom-optimized sets and primed, *B'*, *D'*, for ethylene-optimized sets. Lower case letters, *p*, *d*, indicate polarization functions added to the original set.

Calculated values of total energies are listed in Table 3. It is seen that the substantial improvement of 0.07 hartrees in going from the basis *D* to *D'* is reduced to a minor improvement of 0.01 hartrees of *B'* compared to *B*. The role of polarization functions however is almost equally important in all three cases *C*, *B* and *B'*. Hence these functions do not merely serve as a necessary enlargement of the basis but describe a real polarization though with very low population, ca. 0.01 of an electron at each "polarized" atom. It should also be noted that the basis *B'pd* is almost as good as *Apd*, cf. also below.

Table 2. Gaussian basis sets

Notation	Optimized for	Size	
A	Atoms	(C/11, 6),	(H/5)
Ap	Atoms	(C/11, 6),	(H/5, 1)
Ad	Atoms	(C/11, 6, 1),	(H/5)
Apd	Atoms	(C/11, 6, 1),	(H/5, 1)
Bpd, etc.	Atoms	(C/9, 5, 1),	(H/4, 1)
B'pd, etc.	Ethylene	(C/9, 5, 1),	(H/4, 1)
Cp, etc.	Atoms	(C/7, 3),	(H/4, 1)
D, Ref. [3]	Atoms	(C/8, 4),	(H/4)
D', Ref. [3]	Ethylene	(C/8, 4),	(H/4)

The orbital energies are very similar for all basis sets. Therefore only the results from *B*, *B'pd* and *Apd* are listed in Table 4. Their connection with ionization energies will be discussed below.

A property which shows a more pronounced sensitivity towards the choice of basis are Mulliken's [8] population numbers. This sensitivity is apparent both in subpopulation and total populations. Some results from the population analysis are displayed in Figs. 1 and 2. Fig. 1 shows gross atomic, *N*(X), net atomic, *n*(X), and overlap populations, *n*(XY), obtained in the various cases.

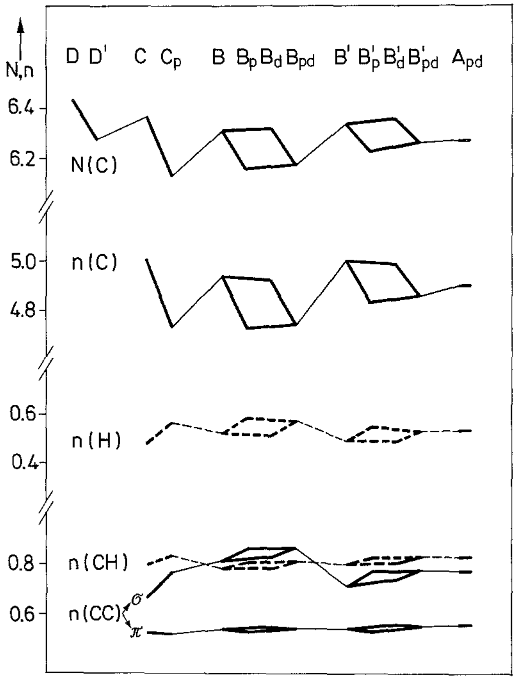

Fig. 1. Total populations of ethylene in various basis sets: gross atomic: *N*(C); net atomic: *n*(C) solid line, *n*(H) broken line; overlap *n*(CC) solid line, *n*(CH) broken line

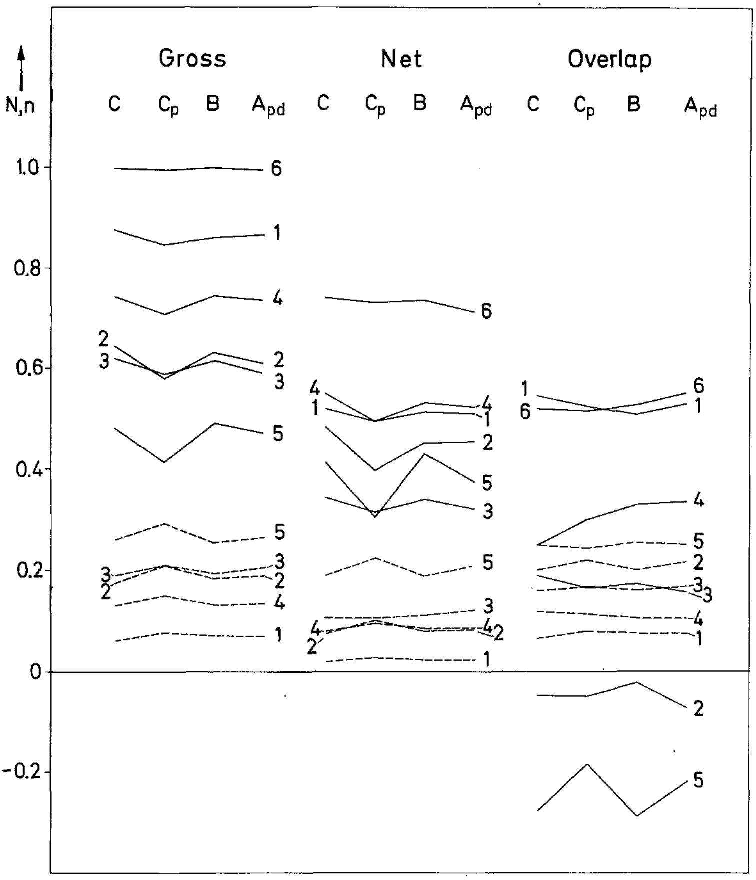

Fig. 2. Orbital populations of ethylene: Solid lines: $N(\mathrm{C})$, $n(\mathrm{C})$, $n(\mathrm{CC})$; broken lines $N(\mathrm{H})$, $n(\mathrm{H})$, $n(\mathrm{CH})$. The numbers indicate the various valence orbitals, 6 being the outermost (π) orbital, cf. Table 4

Comparison of the ethylene-optimized basis B' to B without polarization functions only indicates a slightly better agreement with the *Apd* basis. The only obvious advantage of B' over B is that B' gives $n(\mathrm{CH}) > n(\mathrm{CC}\sigma)$ in accord with the *Apd* basis. If $n(\mathrm{XY})$ can be interpreted as a measure of the strength of the XY bond, this result is also in agreement with experiments, since energy [9] and force constant [10] of the average CH bond are slightly larger than those of the CC single bond.

Polarization functions have similar effects in all the cases, C, B and B', cf. Fig. 1. Addition of p to the hydrogen basis invariably increases not only gross and net atomic populations on hydrogen but also the overlap populations both in CH and CC bonds. These p-functions have a larger effect on all depicted populations than addition of carbon d-functions. For studies of population-dependent properties an addition of polarization functions only on hydrogen may therefore be of interest. However it must be kept in mind that a formally balanced basis with polarization functions on all atoms, in the present case on

Table 3. Total energy (in hartrees) of ethylene in different basis sets. For notations, see Table 2

Basis	No polariz. function	$+p$	$+d$	$+p+d$
A	—	—	—	-78.0623
B'	-78.0160	-78.0306	-78.0423	-78.0508
B	-78.0060	-78.0287	-78.0327	-78.0471
C [6]	-77.9464	-77.9685	—	—
D' [3]	-77.9083	—	—	—
D [3]	-77.8399	—	—	—

Table 4. Orbital energies (in eV) of ethylene in different basis sets

No.	UAO	D_{2h}	Calculation				Exptl. Vertical IP [18]
			$-\varepsilon(B)$	$-\varepsilon(B'pd)$	$-\varepsilon(Apd)$	ΔE (SCF)	
—	—	$1a_g$	305.772	305.818	305.625	298.586	
—	—	$1b_{1u}$	305.730	305.778	305.582	—	
1	$2s\sigma_g$	$2a_g$	28.250	27.972	28.066	—	23.7
2	$2p\sigma_u$	$2b_{1u}$	21.751	21.698	21.778	20.985	19.2
3	$2p\pi_y$	$1b_{2u}$	17.671	17.478	17.586	16.758	15.9
4	$3d\sigma_g$	$3a_g$	16.042	15.881	16.011	14.405	14.8
5	$3d\pi_{yz}$	$1b_{3g}$	13.925	13.913	14.006	13.313	12.4
6	$2p\pi_x$	$1b_{3u}$	10.192	10.054	10.128	8.906	10.5

both hydrogen and carbon, is necessary for a good description of other properties. This is borne out e.g. by Table 3 showing that addition of carbon *d*-functions in all cases means a larger improvement of the total energy than addition of hydrogen *p*-functions. This result is in complete accord with previous studies of the role of polarization functions, see e.g. Millie and Berthier [11].

Figure 2 shows some examples of orbital populations. It is seen that the general picture is the same for all basis sets, but that there are considerable variations concerning the details, much more pronounced than the variations of the orbital energies, cf. Table 4. This underlines the danger of drawing any conclusion from small population differences.

3.2. *Ionized States of Ethylene*

As is well known, orbital energies, $-\varepsilon_i$, are frequently used as a measure of ionization potentials with reference to Koopmans' theorem. The shortcoming of this measure can be described as rearrangement energy and change in correlation. Although these effects may amount to a few eV's the grouping and the order of the energy levels is in most cases correctly reproduced by the ε-values. The rearrangement can be accounted for by separate SCF calculations for each ionized level. In the present study such calculations were performed in the *Apd*

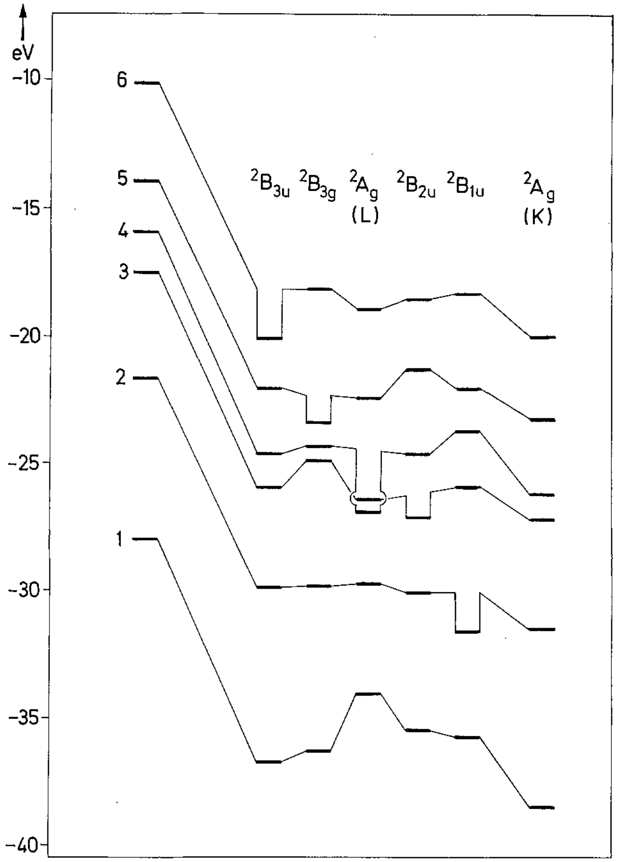

Fig. 3. Values of ε for ethylene. The numbers refer to the various valence orbitals, cf. Table 4. Values referring to the neutral molecule (to the outermost left) and to various ionized states

basis for the main part of the ionic states that can be described by singly ionized configurations. Ionization potentials, ΔE(SCF), obtained as the difference in total energy between the ion and the neutral molecule are listed in Table 4. In almost all cases the values of ΔE(SCF) are closer to the experimental IP values than are the $-\varepsilon_i$'s.

In spite of the deficiency of the ε-values it is interesting to see how these quantities will change upon ionization. The ε-values obtained for the different states are displayed in Fig. 3. It is perspicuous that upon ionization of a valence orbital the ε-values of all subsistently doubly filled orbitals are shifted by almost the same amount, the average shift of a valence orbital being 8.4 eV and of an inner orbital (not displayed in Fig. 3) 9.4 eV. This invariability is particularly interesting, since Koopmans' theorem does not apply to these ε's. Using similar assumptions it can be shown that the ionization potential is the sum of the ε-value and an exchange integral. Experience shows that MO exchange integrals are fairly constant within the valence shell. This indicates the utility of the independent particle model for a first estimate of the energies involved in multiple ionization.

Figure 3 also shows that ε of the singly occupied orbital is shifted by about 10 eV. Since this ε-value does submit to Koopmans' theorem, it could be foreseen that this shift should be different from the other valence orbital shifts. When an inner orbital is ionized (the ^2A_g state furthest to the right in Fig. 3), the average valence orbital shift is 10 eV, whereas the $1a_g$ orbital itself (not displayed) is shifted by 40 eV. It should be noted that this kind of ionized configuration with retention of the g, u-restriction for each orbital does not correctly describe the experimental situation of K shell ionization since the physical process leaves a vacancy in a localized orbital, cf. Bagus and Schaefer [12].

Another point to be noted from the values displayed in Fig. 3 is that after ionization the level order remains unchanged except for the ^2A_g state, where the vacancy is in the $3a_g$ orbital. The coupling between the $3a_g$ and the $2a_g$ levels is seen to be exceptionally strong, the pronounced raising of the $2a_g$ level being counterbalanced by a more than average lowering of the $3a_g$ level. The result is a reversal of the order between the $3a_g$ and the adjacent $1b_{2u}$ level.

4. Applications to Acetylene

A comparison between ethylene and acetylene is clearly of interest for chemical reasons. The comparison is also informative from the technical point of view since McLean and Yoshimine [13] have carried out a very accurate calculation on acetylene, estimated to lie 0.001 hartrees from the Hartree-Fock limit.

All our calculations on acetylene were carried out with the same geometry as adopted by McLean and Yoshimine, i.e.: $r(\text{CC}) = 2.2810$, $r(\text{CH}) = 2.0020$ bohrs. The electronic configuration of the ground state is $(1\sigma_g)^2\,(1\sigma_u)^2\,(2\sigma_g)^2\,(2\sigma_u)^2\,(3\sigma_g)^2\,(1\pi_u)^4$. Eight different basis sets were employed: four of type B' and four of type A, cf. Table 2. Some results are listed in Tables 5, 6, 7 and 8.

Total energies are displayed in Table 5. For comparison results from McLean and Yoshimine [13] and Snyder and Basch [14] are also included. Again polarization functions improve the energy substantially (0.03 hartrees) in both basis sets, B' and A. It is also seen that the Apd basis is very close to the Hartree-Fock limit.

Table 6 shows some typical values of orbital energies. The proximity of the Apd basis to the Hartree-Fock limit also in this respect is clear.

Total and orbital populations are listed in Tables 7 and 8. Again the values of these quantities are rather sensitive to the choice of basis. As an example, the

Table 5. Total energy (in hartrees) of acetylene in different basis sets

Basis	No polariz. function	$+p$	$+d$	$+p+d$
A	−76.8133	−76.8227	−76.8423	−76.8482
B'	−76.8016	−76.8100	−76.8275	−76.8328
Ref. [13]	—	—	—	−76.8540
Ref. [14]	−76.7919	—	—	—

Table 6. Orbital energies (in eV) of acetylene in different basis sets

Orbital	Calculation $-\varepsilon$					Exptl.
UAO	*B′*	*B′p*	*B′pd*	*Apd*	Ref. [13]	Vertical IP [18]
$1\sigma_g$	306.531	306.569	306.283	305.999	305.958	—
$1\sigma_u$	306.434	306.471	306.186	305.898	305.857	—
$2s\sigma_g$	28.234	28.295	27.909	28.041	28.016	23.4
$2p\sigma_u$	20.777	20.735	20.863	20.949	20.948	18.6
$3d\sigma_g$	18.520	18.473	18.415	18.560	18.579	16.7
$2p\pi_u$	11.178	11.168	11.044	11.148	11.166	11.4

Table 7. Total populations of acetylene in different basis sets. Gross atomic $N(X)$, net atomic $n(X)$ and overlap $n(XY)$ populations

Population	Ref. [14]	*B′*	*B′p*	*B′pd*	*Apd*
N(C)	6.258	6.270	6.201	6.206	6.217
N(H)	0.742	0.730	0.799	0.794	0.783
n(C)	4.905	4.883	4.794	4.765	4.836
n(H)	0.380	0.395	0.439	0.438	0.399
n(CC)	1.984	2.110	2.093	2.120	1.992
n(CH)	0.753	0.689	0.740	0.741	0.814
$n(\sigma;$ CC)	0.860	1.000	0.981	0.953	0.812
$n(\pi;$ CC)	1.123	1.116	1.112	1.158	1.180

Table 8. Orbital populations of acetylene

Basis	Population	Orbital			
		$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$1\pi_u$
B′	N(C)	0.986	0.657	0.628	1.000
	N(H)	0.014	0.343	0.372	—
	n(C)	0.626	0.405	0.410	0.721
	n(H)	0.010	0.161	0.224	—
	n(CC)	0.710	0.140	0.144	0.558
	n(CH)	0.016	0.338	0.334	—
Apd	N(C)	0.955	0.629	0.640	0.996
	N(H)	0.045	0.371	0.360	0.004
	n(C)	0.565	0.435	0.440	0.698
	n(H)	0.014	0.180	0.205	0.000
	n(CC)	0.720	−0.002	0.094	0.590
	n(CH)	0.050	0.396	0.356	0.006

CC overlap population of the $2\sigma_u$ orbital is changed from +0.140 in the *B′* basis to −0.002 in the *Apd* basis. The corresponding values of the $3\sigma_g$ orbital are +0.144 and +0.094.

5. Applications to Benzene

Benzene has frequently been chosen as a test molecule for the evaluation of theoretical methods. Besides, this molecules is of considerable interest by itself. Schulman *et al.* [3] have applied their minimal basis to benzene and also employed an extended basis [15]. An even larger basis has been used by Buenker *et al.* [16] in an *ab initio* study of the benzene spectrum. Very recently, Almlöf *et al.* [17] have performed *ab initio* calculations on azabenzenes, including the unsubstituted parent molecule, employing the above-mentioned (C/7, 3) basis [1].

The present calculations on benzene were carried out with the following geometry: $r(\mathrm{CC}) = 2.6323$, $r(\mathrm{CH}) = 2.0409$ bohrs. On account of the size of the molecule the choice of basis set had to be much more restrictive than for acetylene and ethylene. Only the bases B' and $B'p$ were used. Some results are listed in Tables 9, 10 and 11.

Table 9 presents the total energies obtained. For comparison also some results from previous calculations [3, 15, 16, 17] are included. From Tables 3 and 5 it can be seen that for molecules with two carbon atoms the B' basis gives rise to total energy values less than 0.06 hartrees, or 0.7‰ above the Hartree-Fock limit. With the reasonable assumption that the accuracy is comparable in the case of benzene, the total energy of the $B'p$ basis is likely to be less than 0.15 hartrees or 0.6‰ above the Hartree-Fock limit, which is estimated to be close to −230.82 hartrees.

Table 9. Total energy (in hartrees) of benzene in different basis sets

Contr. basis	⟨C/2, 1⟩ ⟨H/1⟩	⟨C/3, 2⟩ ⟨H/1⟩	⟨C/3, 1⟩ ⟨H/1⟩	⟨C/4, 2⟩ ⟨H/2, 1⟩	B'	$B'p$
Ref.	[3]	[15]	[16]	[17]	Present work	
Energy	−230.318	−230.463	−230.375	−230.476	−230.658	−230.679

Table 10. Orbital energies (in eV) of benzene

Orbital			Calculation −ε		Exptl. Vertical
UAO	m	D_{6h}	B'	$B'p$	IP [18]
		$1a_{1g}$	306.11	306.15	—
		$1e_{1u}$	306.10	306.13	—
		$1e_{2g}$	306.06	306.10	—
		$1b_{1u}$	306.05	306.08	—
$2s$	0	$2a_{1g}$	31.533	31.562	25.8
$2p$	1	$2e_{1u}$	27.762	27.759	22.7
$3d$	2	$2e_{2g}$	22.489	22.456	19.2
$3s$	0	$3a_{1g}$	19.457	19.415	17.0
$4f$	3	$2b_{1u}$	17.463	17.423	15.5
$4f'$	3	$1b_{2u}$	16.930	16.904	14.9
$3p$	1	$3e_{1u}$	16.091	16.079	14.0
$2p\pi$	0	$1a_{2u}$	13.705	13.699	12.5
$4d$	2	$3e_{2g}$	13.392	13.376	11.8
$3d\pi$	1	$1e_{1g}$	9.199	9.191	9.3

Orbital energies are listed in Table 10. A comparison between calculated orbital energies and vertical ionization potentials has recently been made by Almlöf *et al.* [17]. These authors have suggested an empirical correction of the ε-values for adjustment to vertical ionization potentials. After addition of the correction terms, they found the following order of the lowest ionization potentials: $\pi(1e_{1g})$, $\pi(1a_{2u})$, $\sigma(3e_{2g})$.... Lindholm *et al.* [18], on the other hand, interpret their measurements as supporting the order π, σ, π, ... This is also the calculated order both in the present work and in Ref. [17] before correction. The calculated energy difference: $\varepsilon(3e_{2g})-\varepsilon(1a_{2u})$ is found to have almost the same value in the bases B'(0.31 eV) and $B'p$(0.32 eV) as in Ref. [17] (0.36 eV). Therefore the present results cannot contribute any new argument to this controversy.

In the first column of Table 10, the united atom assignments of the various orbitals are listed. The table also includes the m-values given by Slater [19]. His discussion of the band structure of benzene can now be illustrated both by experimental [18] and calculated values. These values are displayed in Fig. 4. It is seen that the over-all picture is similar to that given by Slater. The virtual orbital energies, included in Fig. 4, are of course an artefact and are strongly basis dependent. It is however interesting that disregarding the highest depicted empty band, both experiments and calculations support Slater's general picture. A closer analysis of the calculated orbitals reveals, however, that the kind of bonding, proposed by Slater for the σ-bands, is not borne out by the calculations. This conclusion is based upon the assumption that overlap populations are of some guidance concerning bonding properties. Although well aware of the weakness of this assumption, we expect it to be valid for the present analysis, vide infra. Orbital populations from the B' basis are collected in Table 11. The total populations from the $B'p$ basis are also given. The details of the $B'p$ population are rather similar to those of the B' basis, the essential difference being a slight increase in some orbital n(H)-values, particularly in the second band. These values are the source of the increase by 0.062 of the total n(H) population shown in the

Table 11. Orbital (B' basis) and total (B' and $B'p$ bases) populations of benzene

Orbital			Populations					
m	D_{6h}	No.	n(C)	n(H)	n(CC)	n(CH)	N(C)	N(H)
0	$2a_{1g}$	1	0.162	0.003	0.126	0.011	0.323	0.010
1	$2e_{1u}$	2	0.193	0.007	0.109	0.024	0.313	0.020
2	$2e_{2g}$	3	0.192	0.013	0.083	0.040	0.229	0.034
3	$1b_{2u}$	6	0.225	0.000	0.129	0.000	0.333	0.000
0	$3a_{1g}$	4	0.126	0.049	0.043	0.091	0.233	0.100
1	$3e_{1u}$	7	0.163	0.069	0.065	0.076	0.226	0.108
2	$3e_{2g}$	9	0.221	0.077	0.003	0.093	0.235	0.099
3	$2b_{1u}$	5	0.174	0.073	−0.035	0.155	0.199	0.135
0	$1a_{2u}$	8	0.191	—	0.112	—	0.333	—
1	$1e_{1g}$	10	0.275	—	0.095	—	0.333	—
Total B'			4.963	0.458	1.088	0.722	6.234	0.766
Total $B'p$			4.850	0.520	1.115	0.751	6.163	0.837

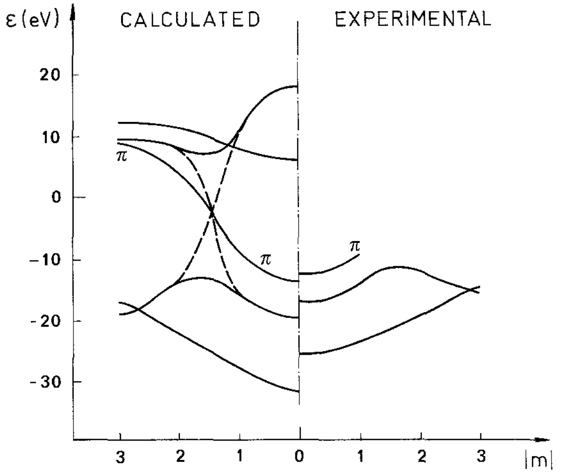

Fig. 4. Energy "bands" of benzene obtained by plotting ε against (cylindrical) |*m*|-values. All bands but one are of σ-type

table. In particular, the orbital *n*(CC) and *n*(CH) values were almost identical in the two bases *B*′ and *B*′*p*. Table 11 shows that *n*(CC) is considerable for the first valence band whereas *n*(CH) is very small. This is valid for the whole band if we assign the $1b_{2u}$ orbital to the first band. However according to Table 10 we have found $\varepsilon(1b_{2u}) > \varepsilon(2b_{1u})$. This fact seems to invalidate our assignment of $1b_{2u}$ to the lowest valence band. On the other hand, experiments [18] show that these two orbitals are almost (accidentally) degenerate. Moreover, calculations on the azabenzenes, see e.g. Ref. [17], on toluene, fluorobenzene, etc., in all cases to our knowledge have given $\varepsilon(1b_{2u}) < \varepsilon(2b_{1u})$ in support of our assignment. We therefore conclude that the lowest valence band is CC-bonding. Table 11 also shows that the next valence band is mainly CH-bonding, although the first two orbitals are somewhat CC-bonding as well. The third (π) band is obviously CC-bonding. The advantage of grouping the orbitals into bands is indicated by these population numbers. An arrangement of the orbitals according to increasing ε-values (sequential numbers in the third column of Table 11) would have obscured the regularity of the overlap populations. A similar regularity is brought out by the orbital contour maps, cf. Ref. [17]. It is found that all orbitals belonging to the first band have extreme values in CC-regions (atomic and/or bond regions) whereas those of the second band have nodal surfaces close to the carbon nuclei and extreme values in the CH bond directions. Hence these contour maps strongly support our conclusions about bonding properties. In fact, if evidence from contour maps were in contradiction to population numbers we expect contour maps to be the better representatives of the physical situation.

It should be pointed out that the present conclusions concerning bonding and antibonding properties are only in partial agreement with recent publications, e.g. Jonsson and Lindholm [20]. As an example, these authors classify the $2e_{2g}$ orbital as weakly CC-antibonding. The reason seems to be that one orbital in this pair of degenerate orbitals can be represented by an orbital with a nodal surface cutting two CC-bonds. However the population numbers in Table 11, +0.083 for $2e_{2g}$, are the *average* populations in an orbital from the degenerate pair, one contribution being positive and the other negative. Population numbers as well as contour maps show that the positive contribution will dominate for $2e_{2g}$ as well as for e.g. $2e_{1u}$. Hence both should be classified as CC-bonding. Similarly, the pairs $3e_{1u}$ and $3e_{2g}$ are about equally strongly CH-bonding.

6. Corresponding Orbitals

Since results for the various molecules have been obtained with the same basis set B' it is interesting to compare the results. For this purpose we shall give some comments on corresponding orbitals of acetylene and ethylene. As a third member of the series we have chosen N_2, for which results from a (N/9, 5) basis are available [21].

Corresponding molecular orbitals within a series with the same number of heavy atoms are those with the same UAO (United Atom Orbital) description. Extension to cases with different numbers of heavy atoms can be made. Since there is no unique way of doing this we shall not include benzene in our discussion, although an interesting parallelism between orbitals of C_2H_4 and C_6H_6 can be found. Correlation diagrams between corresponding orbital energies in the series C_2 to C_2H_6 have been published by Buenker *et al.* [22]. We shall therefore limit ourselves to a discussion of bonding properties with reference to overlap populations and contour maps. Overlap populations are collected in Table 12. The $2s$ and $2p\pi'$ orbitals are clearly XX bonding within the series. The $2p\pi$ orbital (in the C_2H_4 plane) is also bonding although in C_2H_4 the bonding includes both CC and CH bonds. These conclusions are nicely borne out by the contour maps of Fig. 5. From the map of the $2p\pi$ orbital in C_2H_4 it is easy to predict that the $2p\pi(1b_{2u})$ orbital of C_2H_4 must be not only CC- but also CH-bonding, since this bond is lying in a region which is strongly bonding even before distortion by the addition of a new proton. The character of the $2p\sigma$ and $3p\sigma$ orbitals are not so easily interpreted from the population numbers. These numbers indicate that $2p\sigma$ should be strongly antibonding in N_2, weakly

Table 12. Overlap populations of corresponding valence orbitals

		Molecule		
UAO	n(XY)	N_2[21]	C_2H_2	C_2H_4
$2s$	n(XX)	0.77	0.71	0.51
	n(XH)	—	0.01	0.08
$2p\sigma$	n(XX)	−0.58	0.14	0.02
	n(XH)	—	0.34	0.20
$2p\pi$	n(XX)	0.49	0.56	0.17
	n(XH)	—	—	0.16
$2p\pi'$	n(XX)	0.49	0.56	0.53
	n(XH)	—	—	—
$3d\sigma$	n(XX)	−0.01	0.14	0.33
	n(XH)	—	0.34	0.11

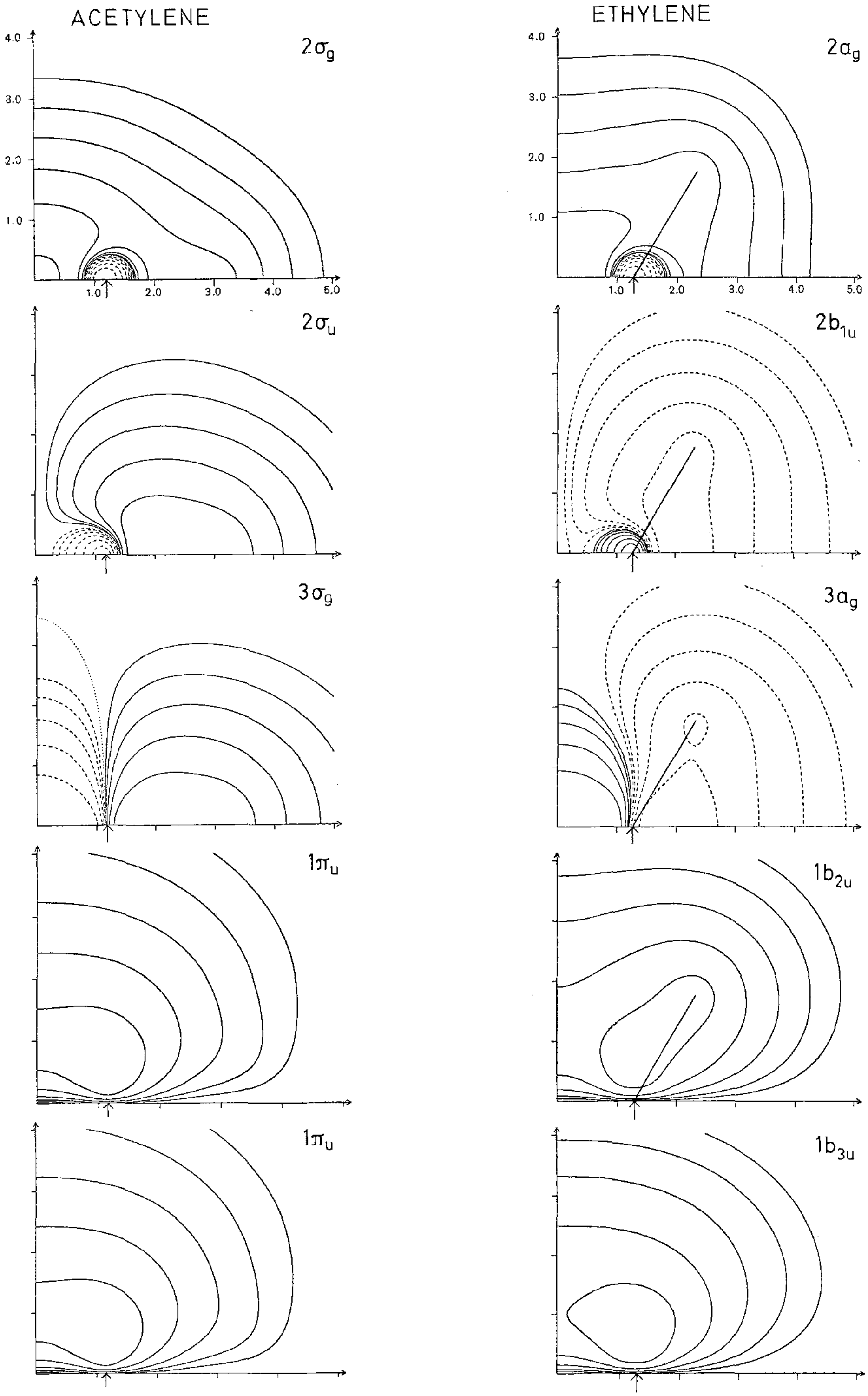

Fig. 5. Contour maps in the molecular plane of pairs of corresponding orbitals. Regions with different signs are indicated by solid and broken lines respectively. The arrows point towards the position of the carbon nucleus on the *z*-axis. The solide line in ethylene maps is drawn along the CH bond

CC-bonding in C_2H_2 and CC-nonbonding in C_2H_4. Similarly the population numbers of $3d\sigma$ indicate this orbital to be non-bonding in N_2, slightly CC-bonding in C_2H_2 and more CC-bonding in C_2H_4. Moreover, according to these numbers the $2p\sigma(2\sigma_u)$ and $3d\sigma(3\sigma_g)$ orbitals of acetylene should be almost identical. However the contour maps of Fig. 5 strongly indicate that $2p\sigma$ is XX-antibonding and $3d\sigma$ XX-bonding throughout the series. In particular, the difference between $2\sigma_u$ and $3\sigma_g$ of C_2H_2 is clearly demonstrated. These results underline the precautions that must be taken at the interpretation of population numbers. In this context it might be mentioned that we have tried to find a correlation between trends in force constants given by trends in vibration frequencies and population numbers. No simple picture emerged from these studies. Our experience points rather towards contour maps as a cheap and quite useful tool for the discussion of bonding properties. We are well aware that these maps cannot give definite answers in all cases and that more elaborate analysis as given e.g. by Buenker *et al.* [22] and by Clementi and Popkie [23] may be useful and sometimes necessary. It is however interesting that our conclusions from contour maps concerning C_2H_2 and C_2H_4 are in full accord with the extensive calculations by Clementi and Popkie [23].

7. Conclusions

The results presented in the preceding Sections show that the "double zeta" basis B' is sufficiently large to give adequate results for several properties of physical interest. However it is also clear that the non-optimized basis B could have been used with practically the same results. Even the smaller (C/7, 3) basis set is seen to be in accord with the B' basis when double-zeta contraction is employed.

As pointed out many times before we have found that population analysis is so strongly basis set dependent that erroneous conclusions might emerge from an improvident application. On the other hand, contour maps seem to be a very useful instrument, both less sensitive to the choice of basis set and more informative about details of the electronic density distribution. The main drawback at present may be the difficulty to publish this information in an inexpensive way.

The usefulness of the corresponding orbital concept has been demonstrated, and might have been pursued further. It seems however to be most efficient for series of about equally sized molecules.

In the case of benzene it has been shown that Slater's energy-band plot is rather useful for classifying bonding properties.

Acknowledgments. We are greatly indebted to IBM World Trade Corporation and to the Swedish IBM Corporation for granting a fellowship to one of us (P.S.) that made it possible to perform the larger part of the calculations at IBM Research Laboratory in San José. Part of this work has been supported by a grant from the Swedish Board for Technical Development and the Swedish Natural Science Research Council. We are grateful to the members of the Stockholm Quantum Chemistry group for unpublished details of their calculations. Thanks are due to Professor E. Lindholm and coworkers for preprints prior to publication.

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