

Valence states of carbon in π -electron systems

II. Excited states and ions†

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(Received 23 April 1967)

Changes in atomic orbitals (AO) brought about by changes in molecular wavefunctions are studied by minimizing the energy of carbon in atomic valence states appropriate for ions and excited states of alternant hydrocarbons. It is found that positive-ion and triplet-state $2p\pi$ AO's are more contracted than in alternant hydrocarbon ground states. Negative-ion and excited-singlet $2p\pi$ AO's are more expanded than in the ground states. These AO changes may be negligible for large molecules but are increasingly important for molecules smaller than naphthalene.

1. INTRODUCTION

A basic assumption of π -electron theory [1] is to use the same atomic orbital (AO) for all states of a molecule and for all aromatic carbon atoms in a molecule. We wish to examine this assumption within the framework of the valence state model.

The valence state energy of carbon, according to the recipe given in I [2], contains information about the molecular wavefunction through the π -electron α and β charge densities q_+ and q_- and a parameter δ (which will be explained later):

$$E_{CVS} = E_{C^+} + (q_+ + q_-)\alpha + (q_+q_- + \delta)\gamma. \quad (1)$$

(The quantities (except for δ) in equation (1) are defined by equations (16)–(28) of I.) For alternant hydrocarbon ground states, $q_+ = q_- = \frac{1}{2}$ and $\delta = 0$. Atomic orbitals were obtained in I to varying degrees of approximation by minimizing E_{CVS} for alternant hydrocarbon ground states. In this paper E_{CVS} is minimized for values of q_+ , q_- and δ typical of several π -electron ions and excited states, and the resulting AO's are compared.

The changes in the AO's are presumably indicative of changes which would be found in a full molecular calculation. As mentioned in I, a rigorous, quantitative study of the validity of the valence state model has not yet been given, so one should be cautious in drawing conclusions based upon it. In the valence state model used in this paper there is no provision for charge transfer in the σ bonds (induced by the changes in the π -electronic state). Charge transfer could be incorporated

† Supported in part by the United States Atomic Energy Commission under contract with the Union Carbide Corporation and in part by the National Science Foundation.

into a more refined valence-state model, along with a number of other effects, e.g. non-neglect of overlap.

Moreover, in I, it was found that a single integer n Slater type orbital (STO) did not represent a valence-state AO very well. In this work, however, we are primarily interested in changes in AO's brought about by changes in the molecule. One integer n STO per AO should not be bad for determining small changes in AO's, and so, in the interest of economy, all the calculations described in this paper have been with integer n minimal bases. The reader is referred to I for a discussion of the computational procedures.

2. PARISER'S DISPROPORTIONATION REACTION

The disproportionation reaction of carbon in an ' $(sp^2)^3p_z$ valence state', invented by Pariser [3], $\dot{C} + \dot{C} \rightarrow \ddot{C}^- + C^+$, historically provided a clear rationalization of the low experimental value of γ (equation (19) of I). Changes in σ and π energies and in the correlation energy in this reaction have been calculated by Orloff and Sinanoğlu [4, 5] and by Hermann [6]. For historical continuity, we have also calculated AO's and energies for this reaction. Our method differs from the previous [4-6]† ones in that the $2p\sigma$ and $2p\pi$ AO's were allowed to differ, the energy was not separated into a sum of spectroscopic state energies [4, 5], correct hybridization [vs. Ref. 6] was taken for the σ electrons, and we have not taken correlation into account.

Nevertheless, we feel that Pariser's reaction is *not* the most appropriate way to elucidate either the numerical value of γ or the σ - π changes. The γ appearing in this reaction is a negative carbon ion γ , and negative-ion atomic Hartree-Fock calculations give γ 's about 2 eV lower than for neutral atoms. Moreover, none of the species in this reaction has a valence state equivalent to $E_{CVS-AHC-gs}$ (equation (25) of I). (The neutral species of this reaction has a valence state appropriate for the triplet state of ethylene.) Finally, the change from an atomic positive ion valence state to a negative ion is much more extreme than the local changes around carbon in a molecule.

The charge density parameters appropriate for Pariser's three valence states are:

$$q_+ = q_- = \delta = 0 \quad (\text{positive ion}), \quad (2)$$

$$q_+ = 1, \quad q_- = \delta = 0 \quad (\text{neutral species}), \quad (3)$$

$$q_+ = q_- = 1, \quad \delta = 0 \quad (\text{negative ion}). \quad (4)$$

The results of minimizing E_{CVS} are summarized in table 1. Note the large changes in the $2p\pi$ and $2p\sigma$ orbital exponents from species to species. Note also that the apparent γ of the reaction, $\gamma_{I-A} = I-A = 0.4773 \text{ A.U.} = 12.99 \text{ eV}$, is almost entirely the negative-ion γ (12.30 eV), whereas the neutral species $2p\pi$ AO gives a γ of 16.39 eV. It seems that the closeness of γ_{I-A} to the experimental γ derived from spectra is accidental, and that the experimental γ is low compared to the old theoretical value (16.93 eV) and to that of the neutral species of the reaction (16.39 eV) for other reasons [2, 7].

† There is also a calculation by K. Ohno, 1964, *Theor. chim. acta*, 2, 219, which we have been unable to reproduce.

Energy expression	Total energy	γ	Basis functions \ddagger	ξ orbital exponent	Coefficients for orthogonal atomic orbitals	
					1s	2s
E_{C^+} (positive ion)	-37.0460 290 A.U.		1s 2s 2p σ	5.6760 1.7461 1.7507	0.99690 0.012191	-0.26863 1.03238
$E_{C^+ + \alpha}$ (neutral species)	-37.3655 152 A.U.	0.6023 A.U. 16.39 eV	1s 2s 2p σ 2p π	5.6779 1.6462 1.5666 1.5387	0.99715 0.012260 0.99743	-0.24450 1.02662
$E_{C^+ + 2\alpha + \gamma}$ (negative ion)	-37.2077 181 A.U.	0.4520 A.U. 12.30 eV	1s 2s 2p σ 2p π	5.6817 1.5985 1.4910 1.1548	0.011625	-0.23235 1.02407

\dagger See [2] for definition of symbols.

\ddagger The basis functions are integer n Slater type orbitals.

Table 1. Minimization of valence state energy for species in Pariser's disproportionation reaction \dagger .

3. POSITIVE AND NEGATIVE IONS, TRIPLETS AND EXCITED SINGLET

In the simple Hückel theory one makes the positive ion by removing an electron from the highest filled molecular orbital and the negative ion by adding an electron to the highest unfilled molecular orbital. The ionic ψ_π (cf. equation (2) of I) is a single determinant. If the ionization electron is given β spin (it is no loss of generality to choose β spin) the change in q_- for an atom is \mp the square of the Hückel coefficient of that atom's 2p π -AO in the (highest filled/lowest unfilled) molecular orbital. Thus singly-ionized alternant hydrocarbons are characterized by valence states with:

$$\left. \begin{array}{l} q_+ = \frac{1}{2} \\ q_- = \frac{1}{2} - \Delta \\ \delta = 0 \end{array} \right\} \text{ (positive ion),} \quad (5)$$

$$\left. \begin{array}{l} q_+ = \frac{1}{2} \\ q_- = \frac{1}{2} + \Delta \\ \delta = 0 \end{array} \right\} \text{ (negative ion).} \quad (6)$$

The Δ represents the square of the Hückel coefficient. A typical value for Δ is the reciprocal of the number of aromatic carbon atoms in the molecule. Results of minimizing E_{CVS} for $\Delta = \frac{1}{2}, \frac{1}{5}, \frac{1}{6}$ and $\frac{1}{10}$ are given in tables 2 and 3.

The lowest excited singlet and triplet states \dagger of a molecule in the Hückel theory (but not necessarily lowest in actuality) are obtained by promoting an electron from the highest filled molecular orbital to the lowest unfilled orbital. One of the ψ_π for the triplet is a single determinant, but the ψ_π for the singlet will be the sum of two determinants (in the absence of orbital degeneracy). Symbolically:

$$\psi_\pi\{\text{triplet}\} = \mathcal{A}\{ \dots (\phi_n^\pi \alpha)(\phi_{n+1}^\pi \alpha) \}, \quad (7)$$

$$\psi_\pi\{\text{singlet}\} = \mathcal{A}\left\{ \dots (\phi_n^\pi \phi_{n+1}^\pi) \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \right\}. \quad (8)$$

\dagger These excited singlet states correspond to the p bands of the electronic spectra of aromatic hydrocarbons.

Δ	Total energy	γ	Basis functions	ζ orbital exponent	Coefficients for orthogonal atomic orbitals	
					1s	2s
$\frac{1}{10}$	-37.2191 843 A.U.	0.5119 A.U. 13.93 eV	1s	5.6784	0.99713	-0.25051
			2s	1.6724	0.012065	1.02805
			2p σ	1.6266		
			2p π	1.3080		
$\frac{1}{8}$	-37.2146 659 A.U.	0.5173 A.U. 14.08 eV	1s	5.6782	0.99711	-0.25171
			2s	1.6772	0.012091	1.02832
			2p σ	1.6348		
			2p π	1.3217		
$\frac{1}{6}$	-37.2125 177 A.U.	0.5206 A.U. 14.16 eV	1s	5.6782	0.99709	-0.25234
			2s	1.6795	0.012149	1.02845
			2p σ	1.6388		
			2p π	1.3300		
$\frac{1}{2}$	-37.1976 684 A.U.	0.5742 A.U. 15.62 eV	1s	5.6772	0.99702	-0.25740
			2s	1.7001	0.012205	1.02964
			2p σ	1.6720		
			2p π	1.4670		

Table 2. Minimization of $E_{CVS} = E_{C^+} + (1 - \Delta)\alpha + (\frac{1}{4} - \frac{1}{2}\Delta)\gamma$ for positive ions.

Δ	Total energy	γ	Basis functions	ζ orbital exponent	Coefficients for orthogonal atomic orbitals	
					1s	2s
$\frac{1}{10}$	-37.2342 542 A.U.	0.5023 A.U. 13.67 eV	1s	5.6790	0.99718	-0.24678
			2s	1.6571	0.012009	1.02719
			2p σ	1.5996		
			2p π	1.2833		
$\frac{1}{8}$	-37.2397 470 A.U.	0.5009 A.U. 13.63 eV	1s	5.6792	0.99721	-0.24543
			2s	1.6517	0.011974	1.02690
			2p σ	1.5896		
			2p π	1.2796		
$\frac{1}{6}$	-37.2425 744 A.U.	0.5005 A.U. 13.62 eV	1s	5.6793	0.99721	-0.24479
			2s	1.6489	0.011991	1.02674
			2p σ	1.5843		
			2p π	1.2786		
$\frac{1}{2}$	-37.2707 339 A.U.	0.5040 A.U. 13.71 eV	1s	5.6801	0.99730	-0.23814
			2s	1.6214	0.011913	1.02527
			2p σ	1.5288		
			2p π	1.2878		

Table 3. Minimization of $E_{CVS} = E_{C^+} + (1 + \Delta)\alpha + (\frac{1}{4} + \frac{1}{2}\Delta)\gamma$ for negative ions.

Δ	Total energy	γ	Basis functions	ζ orbital exponent	Coefficients for orthogonal atomic orbitals	
					1s	2s
$\frac{1}{10}$	-37.2315 317 A.U.	0.5105 A.U. 13.89 eV	1s	5.6787	0.99715	-0.24849
			2s	1.6640	0.012059	1.02758
			2p σ	1.6114		
			2p π	1.3042		
$\frac{1}{6}$	-37.2406 809 A.U.	0.5182 A.U. 14.10 eV	1s	5.6786	0.99715	-0.24813
			2s	1.6624	0.012079	1.02749
			2p σ	1.6077		
			2p π	1.3238		
$\frac{1}{5}$	-37.2470 400 A.U.	0.5234 A.U. 14.24 eV	1s	5.6786	0.99715	-0.24791
			2s	1.6614	0.012098	1.02744
			2p σ	1.6051		
			2p π	1.3371		
$\frac{1}{2}$	-37.3655 152 A.U.	0.6023 A.U. 16.39 eV	1s	5.6779	0.99715	-0.24450
			2s	1.6462	0.012260	1.02662
			2p σ	1.5666		
			2p π	1.5387		

Table 4. Minimization of $E_{\text{CVS}} = E_{\text{C}^+} + \alpha + (\frac{1}{2} - \Delta^2)\gamma$ for triplet states.

Δ	Total energy	γ	Basis functions	ζ orbital exponent	Coefficients for orthogonal atomic orbitals	
					1s	2s
$\frac{1}{10}$	-37.2214 113 A.U.	0.5015 A.U. 13.65 eV	1s	5.6787	0.99715	-0.24893
			2s	1.6658	0.012060	1.02768
			2p σ	1.6158		
			2p π	1.2813		
$\frac{1}{6}$	-37.2125 664 A.U.	0.4933 A.U. 13.42 eV	1s	5.6787	0.99715	-0.24930
			2s	1.6675	0.012035	1.02777
			2p σ	1.6198		
			2p π	1.2604		
$\frac{1}{5}$	-37.2065 726 A.U.	0.4876 A.U. 13.27 eV	1s	5.6788	0.99714	-0.24958
			2s	1.6687	0.012041	1.02783
			2p σ	1.6226		
			2p π	1.2458		
$\frac{1}{2}$	-37.1169 349 A.U.	0.3470 A.U. 9.44 eV	1s	5.6782	0.99708	-0.25716
			2s	1.7004	0.011965	1.02964
			2p σ	1.6869		
			2p π	0.8865		

Table 5. Minimization of $E_{\text{CVS}} = E_{\text{C}^+} + \alpha + (\frac{1}{4} + \Delta^2)\gamma$ for singlet states.

Under the simplifying conditions of pairing [8] for alternant hydrocarbons (i.e. the squares of the Hückel coefficients of the highest filled and lowest unfilled molecular orbitals are equal), we obtain the following valence state characterizations:

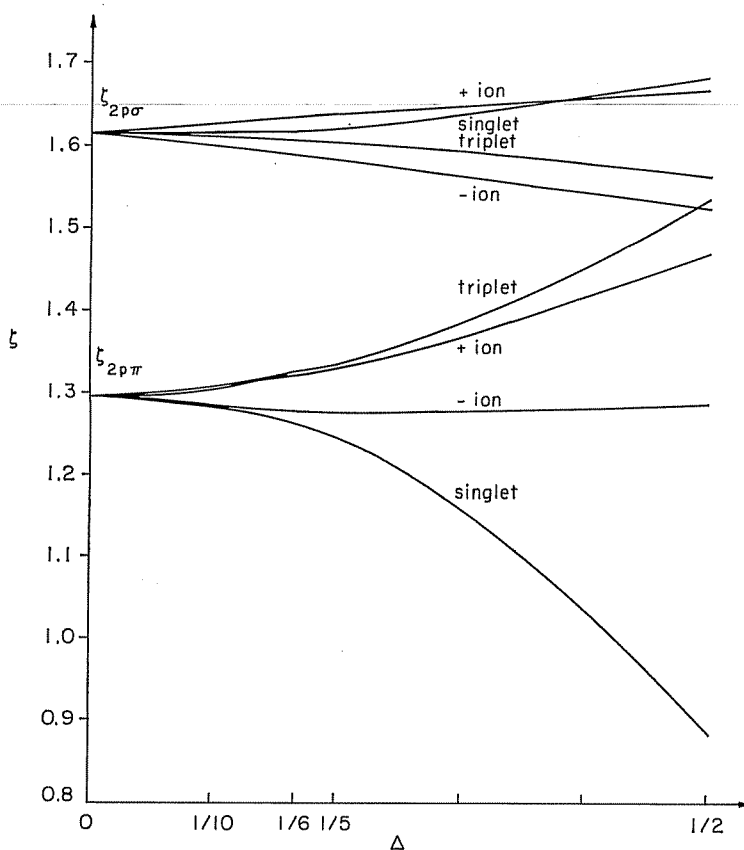
$$\left. \begin{array}{l} q_+ = \frac{1}{2} + \Delta \\ q_- = \frac{1}{2} - \Delta \\ \delta = 0 \end{array} \right\} \text{ (triplets),} \quad (9)$$

$$\left. \begin{array}{l} q_+ = \frac{1}{2} + \Delta \\ q_- = \frac{1}{2} - \Delta \\ \delta = 2\Delta^2 \end{array} \right\} \text{ (singlets).} \quad (10)$$

The $\delta = 2\Delta^2$ for the singlet state brings in the contribution to the valence state energy from the cross term between the two determinants of ψ_π . Results of minimizing E_{CVS} for $\Delta = \frac{1}{2}, \frac{1}{5}, \frac{1}{6},$ and $\frac{1}{10}$ are given in tables 4 and 5.

In the figure, the values of $\zeta_{2p\sigma}$ and $\zeta_{2p\pi}$ versus Δ are plotted for the ions, triplets and singlets. The $\Delta = 0$ data is given in table 1 of I.

As expected, the $2p\pi$ AO's are more contracted† (larger ζ) for positive ions than for negative ions and are more contracted for triplets than for singlets. The



$\zeta_{2p\sigma}$ and $\zeta_{2p\pi}$ as a function of the change Δ in the charge density q for positive ions, negative ions, triplet states, and excited singlet states.

† Compare also with the $E_{CVS-AHC-gs}$ results of table I [2].

$2p\sigma$ AO's behave in the same sense for the ions but in the opposite sense for the triplets and singlets as do the $2p\pi$ AO's. For $\Delta \leq 0.1$, the changes in ζ are less than 2 per cent. Thus for molecules the size of naphthalene or larger, the constancy of the AO's is probably good. But for smaller molecules or for large localized changes, the constancy approximation appears poorer. When $\Delta \sim 0.2$ the change in $\zeta_{2p\pi}$ from triplet to singlet is 8 per cent. The drastic changes when $\Delta \sim 0.5$ (ethylene) suggest that it is a poor approximation to use a single $2p\pi$ AO for the ground state, excited states, and ions of ethylene.

Two other qualitative inferences may be drawn from the figure: the variation in AO between triplet and singlet may account for part of the discrepancies in theoretical singlet-triplet splittings (the rest presumably is due to correlation); the similarity between the triplet and positive-ion $\zeta_{2p\pi}$ curves also suggests that in electron paramagnetic resonance, deviations from McConnell's relation [9] for proton isotropic coupling constants should be similar for triplets and positive ions and in the opposite sense from deviations in negative ions.

Finally, calculations [10] of the π -electron charge density dependence of proton isotropic coupling constants in electron spin resonance, based on the orbitals of tables 2 and 3, are in semi-quantitative agreement with the semi-empirical results of Colpa and Bolton [11].

4. SUMMARY

Minimization of valence state energies leads to carbon atomic orbitals for ions and excited states both different from each other and from ground state AO's. The changes are small (< 2 per cent) when the changes in α or β π -electron charge density are ≤ 0.1 (typical of, say, naphthalene), but they increase very rapidly with charge density changes and are especially large for ethylene. The $2p\pi$ AO's for positive ions and triplet states are contracted and for negative-ion and singlet states are expanded over the neutral ground state alternant hydrocarbon $2p\pi$ AO. It is notable that the negative-ion $2p\pi$ AO's show relatively small changes from the alternant hydrocarbon ground state AO. Calculations on the valence state species in Pariser's disproportionation reaction were also made, but the relevance of this reaction especially to large π -electron molecules is uncertain.

We would like to thank Dr. Malcolm K. Orloff, Professor Robert G. Parr, and Professor Jaroslav Koutecký for helpful conversations. Computations were performed on the CDC 1604-A computer of the Oak Ridge National Laboratory.

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