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Ground State Wavefunctions of some Conjugated Carbon Compounds — NPSO Method

By

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The method of Non-Paired Spatial-Orbitals is applied to the π-systems of fulvene, hexatriene and butadiene in their ground states. This type of treatment which was found to be so successful for benzene proves to be satisfactory for these typical non-alternant and polyolefinic systems. Ways for determining *a priori* the adjustable parameters which appear in the wavefunction are examined and a procedure for setting up the non-pairing function without using any adjustable parameters is proposed.

Die NPSO Methode wird auf die π-Systeme von Fulven, Hexatrien und Butadien im Grundzustand angewandt. Die beim Benzol erfolgreiche Art der Behandlung erweist sich bei diesen nicht alternierenden und polyolefinischen Systemen als zufriedenstellend. Es werden Wege zur „*a priori*" Bestimmung der Parameter in der Wellenfunktion geprüft und ein Verfahren zur Aufstellung der NPSO's ohne Benutzung von anzupassenden Parametern vorgeschlagen.

La méthode des orbitales spatiales non-appariées (NPSO) est appliquée aux systèmes π de fulvène, hexatriène et butadiène dans leurs états fondamentaux. Ce procédé qui a eu de tel succès au cas de benzène, ce montre satisfaisant par ces systèmes typiques non-alternant et polyéniques. On examine des possibilités par ajuster *a priori* les paramètres dans la fonction d'onde, et on propose une méthode pour obtenir la fonction NPSO sans faire usage d'aucun paramètre ajustable.

Introduction

In a previous paper [6] the method of Non-Paired Spatial-Orbitals (NPSO) was applied to the π-system of benzene. We used the non-empirical interaction integrals of PARR, CRAIG and ROSS [22] and the computational framework of GOEPPERT-MAYER and SKLAR [11]. The results were highly encouraging; a conclusion which may be expected to remain valid when better values are used for the integrals which appear in the energy expression [26, 7, 8].

In the NPSO method, the π-electrons are assigned as far as possible to spatial orbitals localised separately in different "bonding regions" between adjacent carbon nuclei. Anti-symmetric wavefunctions are formed for the ground and lower excited states which are eigenfunctions of the spin and symmetry operators [6, 9]. For several states of benzene this treatment was shown to give a lower energy than that afforded using a wavefunction of comparable complexity constructed according to various other methods. In particular, the ground state energy given by this treatment is lower than that calculated by the quite extensive configuration interaction (CI) treatment of PARR, CRAIG and ROSS [22] and that

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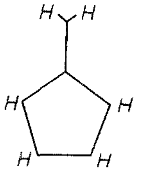
given by an Alternant Molecular Orbital calculation (AMO) in which different mixing parameters were used for different pairs of orbitals [*12*]. The energy obtained with the NPSO function was only 0.09 eV above that given by a "complete" CI treatment, which represents the limit for any treatment using the same basis set of $2p\pi$ atomic orbitals and the same integrals [*19*].

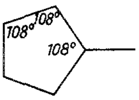
The aim of the present paper is to extend these calculations to some very different π-systems. Our purpose is three-fold: (i) to show first that essentially the same description which was used for benzene can be employed successfully with non-alternant and polyolefinic hydrocarbons; (ii) to examine whether, for different molecules, all the parameters which specify the groundstate wavefunction may be determined *a priori* without great inaccuracy, so that we may hope to write successful wavefunctions for complex systems with no adjustable parameters, and (iii) to demonstrate that calculations on systems less symmetrical than benzene are by no means excessively laborious.

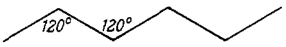
The energies for the non-pairing wavefunctions for the ground states of fulvene, hexatriene and butadiene have been calculated and are compared with those calculated using molecular orbital and valence bond wavefunctions.



The non-alternant molecule fulvene, (C_6H_6) shows only weakly aromatic characteristics. Its chemistry includes both addition and substitution reactions [*4, 1*]. Its resonance energy too is much less than that of benzene. The permanent dipole moment of fulvene [*27*] is believed to be largely a feature of the π-electron distribution in the molecule. Coupled with the information that there is little charge alternation on the hydrogen bearing ring carbon atoms, (from proton magnetic resonance experiments on substituted fulvenes [*25*] this provides a sensitive test of the one electron distribution implied by a trial wavefunction. If such a wavefunction also has a low energy then it is likely that the two-electron distribution is also satisfactorily represented, and that the wavefunction will give a good account of several electronic properties.

For fulvene and hexatriene few comparable studies have appeared in the literature. For these systems containing six carbon atoms we have assumed bond lengths of 1.393 Å throughout; the bond angles have been given the values shown below:





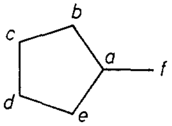
It seemed important not to predispose the systems to some particular electronic distribution by making some bonds shorter than others. Comparisons can be made more easily between different systems in this way and, in any case, the slight differences between these and the true lengths would not alter the results greatly. A computer programme was written to calculate the integrals rapidly by the same method as that used by PARR, CRAIG and ROSS [*22*].

For the 4-carbon system butadiene, on the other hand, the observed dimensions and the integrals of PARR and MULLIKEN were used [*23*].

Wave-Functions

Fulvene

The atomic orbitals of fulvene have been labelled as follows:



and all possible Slater determinants written corresponding to the assignment of three electrons of α-spin wavefunction and three of β-spin wavefunction to each of the two equivalent sets of non-paired orbitals:

$$a + kb, \quad b + kc, \quad c + kd, \quad d + ke, \quad e + ka, \quad a + kf$$

and

$$ka + b, \quad kb + c, \quad kc + d, \quad kd + e, \quad ke + a, \quad a + kf\,.$$

Application of the spin [*18*] and symmetry [*16*] projection operators generates eigenfunctions corresponding to pure spin and symmetry states. In general several independent eigenfunctions can be written for each species and the best wavefunction is a combination of these. The function formed by minimising the energy of a linear combination:

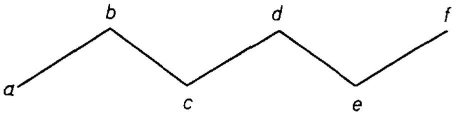
$$^n\Psi^\gamma = a_1^n\,\Psi_1^\gamma + a_2^n\,\Psi_2^\gamma + \ldots\ldots$$

with respect to the adjustable parameters $a_1, a_2, \ldots$ will be described as the NPSO full spin-CI function. (n here refers to the multiplicity and γ to the symmetry of the wavefunction.) The eigenfunctions $^n\Psi_1^\gamma$, $^n\Psi_2^\gamma$ etc. for all systems could be generated rapidly in this way using a simple computer programme.

Hexatriene and Butadiene

For a long chain compound such as hexatriene with n carbon atoms bearing $2p\pi$ orbitals there are only $(n - 1)$ "bonding regions". Corresponding to these, there are orbitals of the form $x + ky$ where x and y are adjacent atomic orbitals. The orbital that is chosen last is a simple atomic orbital, (any one is independent of the NPSOs already chosen), the one used being that which overlaps the other NPSOs to the smallest extent. This is the orbital on the atom at the end of the chain. The basic set of six NPSOs for hexatriene

is: $\quad a, \quad a + kb, \quad b + kc, \quad c + kd, \quad d + ke, \quad e + kf, \quad k > 1$



(before normalising). The NPSO wave function also includes determinants based on the set of equivalent NPSOs formed from this set by application of the covering operations of the group to which the molecule belongs, i. e.

$$f, \quad f + ke, \quad e + kd, \quad d + kc, \quad c + kb, \quad b + ka\,.$$

A similar procedure was used for butadiene.

Results

In Tab. 1 the results of the NPSO treatment are compared (*a*) with those of molecular orbital self consistent field (SCF–LCAO–MO) calculations carried out using Roothaan's scheme [24] and (*b*) with simple "Heitler-London" valence bond (VB) calculations.

Although a "complete" MO–CI treatment was not carried out for fulvene and hexatriene, (it would have required an excessive amount of labour), it is evident, considering the NPSO and SCF–LCAO–MO figures for all the systems together, that the former has taken account of most of the correlation energy. This is shown to be true for butadiene by the figures in Tab. 1 and also for benzene when the difference in energies is 3.00 eV.

Table 1. *Energies (in* eV*) for the ground state wavefunctions of three molecules calculated using various treatments*

Treatment	Fulvene ($^1A_1$) Energy + 6 W_{2p}	Hexatriene (^1A_g) Energy + 6 W_{2p}	Butadiene (^1A_g) Energy + 4 W_{2p}
NPSO full spin CI* for $k = k_{\min}$, (No. of adj. parameters)	− 117.33(5)	− 100.42(5)	− 51.20(2)
SCF-LCAO-MO method [24]	− 113.83**	− 96.40***	− 48.93 [23]
Heitler-London VB, principle structure	− 114.92	− 97.96	− 43.37
Complete MO–CI (No. of adj. parameters)	–	–	− 51.28(11)****
Difference $E_{\mathrm{NPSO}}-E_{\mathrm{SCF}}$	− 3.50	− 3.91	− 2.27

* The matrix elements of the energy between pairs of Slater determinants were determined and the secular determinant set up and solved using a Ferranti Mercury computer.

** Berthier's results [2] for a similar calculation assuming a slightly different geometry gave a very close figure for the energy: 6 W_{2p} − 113.93 eV and almost the same wavefunction.

*** The authors gratefully acknowledge the use of a programme written by Dr. M. Green for computing these figures.

**** In the course of the study it became apparent that some of Fain and Matsen's results [10] for the complete treatment of butadiene and its positive ion using the same set of integrals are in error and their work has been repeated in full for this study.

Some more detailed results for butadiene are summarised in Tab. 2. This system is sufficiently small to allow a wide variety of calculations to be made rapidly without excessive labour, but the results are probably typical of larger systems.

The first group in the table are single determinant molecular orbital functions. The two constants k and λ could be adjusted to minimise the energy of a single Slater determinant independently of one another, (row 1). The two orbitals are orthogonal by symmetry and this function thus reduces to the SCF–LCAO–MO function [23]. Such a function grossly overestimates both the negative one-electron terms and the positive two-electron terms (see columns 4 and 5). The parameters k and λ which minimise the energy are close to those which would be deduced using Hückel's method. The next three rows show the effect on the energy of approximating their values by the Hückel coefficients. The method appears to be very satisfactory in this case. Wheland's method [28] (row 5), which takes account of the finite overlap integral between adjacent atomic orbitals gives no numerical improvement on the more approximate method.

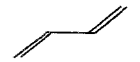
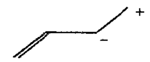
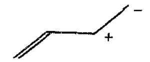
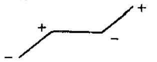
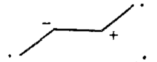
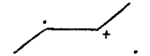
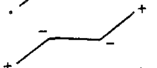
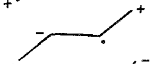
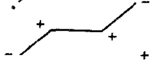
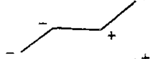
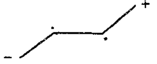
Table 2. *Approximate Treatments of Butadiene. (Energies in* eV *relative to* 4 W_{2p}*)*

Approximate Function	No. of adj. parameters	Energy	Core Term	Coulomb Term	k	λ	Row
MO Functions:							
$\mid(a + kb + kc + d)^2(a + \lambda b - \lambda c - d)^2\mid$ SCF–LCAO–MO, k, λ adjustable.	2	−48.939	−98.55	49.61	1.36	0.80	1
k = Hückel value, λ varied.	1	−48.854	—	—	1.62	0.79	2
k varied, λ = Hückel value.	1	−48.675	—	—	1.45	0.62	3
Hückel MO.	0	−48.649	−98.21	49.56	1.62	0.62	4
Wheland MO.	0	−48.171	−96.44	48.17	1.15	0.54	5
VB Functions:							
Resonance between two *H–L* Covalent structures.	1	−49.436	−91.96	42.53	—	0.16	6
Principle *H–L* structure.	0	−49.366	−91.87	42.51	—	—	7
COULSON-FISCHER, $\mid(a + kb)(ka + b)(c + kd)(kc + d)\mid$ + etc. λ is mixing parameter.	2	−51.084	−95.99	44.91	0.17	0.1	8
Principle term in above *C–F*.	1	−51.058	−95.99	44.93	0.17	—	9
NPSO Functions:							
$\mid a(a + kb)(b + kc)(c + kd)\mid$ Full spin-CI.	2	−51.202	−96.13	44.93	0.33	0.1	10
Single component of above generated by "method 3".	1	−51.197	−96.13	44.93	0.33	—	11
Complete MO–CI treatment.	11	−51.277	−96.09	44.71	—	—	12

The simple Heitler-London VB method, (rows 6 and 7), is more successful than the SCF–LCAO–MO function as regards estimating the total energy, but the error is in the opposite sense, since both one and two-electron terms are underestimated. The singlet diradical structure:

contributes very little to the wavefunction. Indeed a complete valence bond calculation, in which resonance is allowed between all possible covalent and singly and doubly charged ionic structures, shows that this structure is less important than the singly charged ionic forms. The weights (squares of the coefficients of each type of structure in the complete wavefunction), are shown in Tab. 3. Such a complete VB–CI calculation is entirely equivalent to a complete MO–CI calculation and involves 11 adjustable constants, (see last row of Tab. 2).

Table 3. *Weights, (without normalising), of covalent and ionic structures in a complete valence bond calculation for butadiene*

Weight	*Structure*
3,988	
0,456	
0,392	
0,083	
0,056	
0,055	
0,046	
0,037	
0,019	
0,019	
0,002	
0,001	

The "Coulson-Fischer" function was constructed in a way similar to that suggested by these authors for the hydrogen molecule [*3*]. A function of the correct spin and symmetry properties based on the orbitals:

$$a + kb, \quad ka + b, \quad c + kd, \quad kc + d \qquad (1)$$

was generated. Two independent eigenfunctions of ^1A_g symmetry can be written. For the calculation in row 8 the admixture of these two was allowed to vary as well as the correlation parameter k. For row 9 the spin combination which is antisymmetric in the exchange of the first and second pairs of the orbitals (1) was selected. It is a very close approximation to the first. The energy of these functions is quite close to that of the complete treatment, and the distribution between one and two electron terms is fairly satisfactory.

The NPSO functions (rows 10 and 11) approach the complete MO–CI wavefunction even more closely, and give a surprisingly good account of both one and two-electron terms. The first function is the NPSO full spin-CI function, and the second generated by "method 3" which will be described later.

Resonance Energies

The figures for the π-electron energies of hexatriene, fulvene, and benzene differ by the resonance energy and a further positive term for the "self-repulsion" of the sigma core, which is, of course, less for the open structure of hexatriene than for the other two systems. The latter term is implicit in the coulomb integral α of semi-empirical molecular orbital theory. One may assume [*21*] that the repulsion between carbon centres X and Y is just the coulomb repulsion integral xx/yy, i.e. the positive charge distribution is just that of the negative distribution which would be necessary to neutralise the site. The figures for the NPSO functions taken together suggest that the *vertical* resonance energies of fulvene and benzene are about $1\frac{1}{2}$ and $2\frac{1}{2}$ eV above that of hexatriene. These are very satisfactory figures [*20*] in view of the crudeness of the last stage in the calculation, and possible differences in kinetic energy which are only included in an obscure manner in the Goeppert-Mayer and Sklar approximation.

Dipole Moment of Fulvene

For fulvene the π-component of the dipole moment computed from the NPSO-full spin-CI wavefunction using the expression:

$$\mu = \frac{\int \Psi^* \hat{\mu}\, \Psi\, d\tau}{\int \Psi^* \Psi\, d\tau} \quad (\hat{\mu} \text{ is the dipole moment operator})$$

is 1.1 Debye, in excellent agreement with the experimental figure [*27*] for the total moment of 1.1 D. In Tab. 4 the π-component of the dipole moment of the NPSO full-spin CI function is shown for various values of the constant k, ($k_{\min} = 4.2$). The π-moment for a single electron in the exocyclic bond is shown below for the same values of k. Evidently the system behaves as if the whole of the dipole moment is localised in the exocyclic bond.

Table 4. *The dipole moment of fulvene is close to that of a single electron in the exocyclic double bond*

k	3.00	3.50	3.75	4.00	4.25	4.75	5.50
NPSO full spin-CI dipole moment	1.55	1.31	1.21	1.12	1.05	0.92	0.78
Dipole of isolated exocyclic bond	1.62	1.36	1.26	1.17	1.09	0.96	0.81

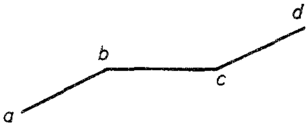
The covalent valence bond function gives a zero dipole moment, whereas a simple Hückel calculation leads to one which is greatly in excess of the observed moment [*29*]. An SCF–LCAO–MO treatment is the least complex which is necessary to give a reasonable estimate of the moment of this π-system [*15*].

Evidently then none of the special effects of non-alternancy reduce the effectiveness of the NPSO treatment which is as successful for calculating electronic properties for the pseudo aromatic fulvene and the polyolefinic hexatriene as it was for benzene. The NPSO full spin-CI function provides a very satisfactory account of the complete wavefunction since the number of adjustable parameters is small and the energy very low. We can however simplify the treatment even further by using empirical and *a priori* arguments to determine the values of the adjustable parameters which define the wavefunction. If the energy determined in this way is not too high we might expect to calculate reasonable values for other observable properties without passing through the intermediate state of a (laborious) energy calculation. Such simplifications are essential in any case if calculations are to be made on much larger systems. Preliminary investigations of this problem have already been made [*6*, *13*].

A Priori Approximations to the NPSO Full Spin-CI Function

Method 1

The first method is crude but very simple. The Slater determinants from which the NPSO function is constructed can be classified according to the numbers of pairs of similar spin functions in adjacent spatial orbitals. A wavefunction is constructed using only those determinants in which the minimum number of pairs bear similar spin functions. For long chain and even membered ring compounds one set of determinants can be written in which no pair of adjacent NPSO's has the same spin function thus for butadiene:



$$\begin{vmatrix} (a) & (a+kb) & (b+kc) & (c+kd) \\ \alpha & \beta & \alpha & \beta \end{vmatrix}, \quad \begin{vmatrix} (a+kb) & (a) & (c+kd) & (b+kc) \\ \alpha & \beta & \alpha & \beta \end{vmatrix}$$

$$\begin{vmatrix} (ka+b) & (kb+c) & (kc+d) & (d) \\ \alpha & \beta & \alpha & \beta \end{vmatrix}, \text{ and } \begin{vmatrix} (kb+c) & (ka+b) & (d) & (kc+d) \\ \alpha & \beta & \alpha & \beta \end{vmatrix}$$

are of this type.

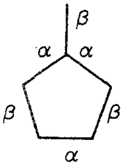
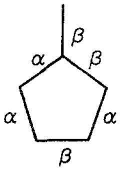
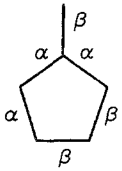
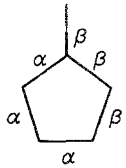
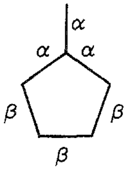
For fulvene all the determinants have at least one pair of adjacent NPSO's bearing the same spin function. In this case determinants such as:

$$\begin{vmatrix} (a+kb) & (b+kc) & (c+kd) & (d+ke) & (e+ka) & (a+kf) \\ \alpha & \beta & \alpha & \beta & \alpha & \beta \end{vmatrix}$$

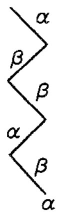
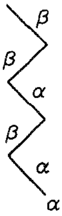
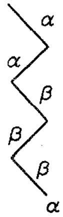
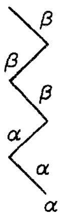
must be used.

Table 5. *Mean squares of the coefficients of determinants of different types in the* NPSO *full spin*-CI *function for* $k = k_{\min}$, *fulvene and hexatriene*

Fulvene

No. of pairs of adjacent NPSOs with same spin function	1	2	3	4	5
Example					
Relative weight	3.55	1.56	0.73	0.10	0.07

Hexatriene

No. of pairs of adjacent NPSOs with same spin function	0	1	2	3	4
Example					
Relative weight	1.70	0.88	0.21	0.05	0.00

These are the determinants which are emphasised in the qualitative double-puartet [*17*] interpretation of the wavefunction. For benzene [*6*] such determinants are found to dominate the wavefunction derived in the full calculation.

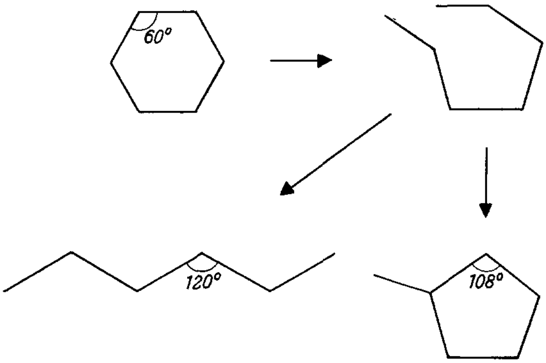
However functions corresponding to pure spin states cannot be formed from such determinants alone; i.e. they cannot be eigenfunctions of the operator $\hat{S}^2$.

Tab. 6 shows that for these systems the energy determined from such functions is a good deal lower than that found using an SCF–LCAO–MO function. It should be emphasised that calculations can be made rapidly with these functions since only four matrix elements of the energy are necessary. Minimising the energy of this simple function with respect to k gives a reasonable value for this constant for use in a more complete calculation.

Tab. 5 shows the mean squares of the coefficients, (weights), of each type of determinant for fulvene and hexatriene in the NPSO full spin-CI treatment, and an example of each. The determinants in which the spin functions alternate between adjacent NPSOs dominate the wavefunction.

Method 2

The projection operator may be applied directly to one of the determinants which involve the maximum alternation of spin function, giving a function which is rigorously an eigenfunction of $\hat{S}^2$. This formally correct method is however rather inflexible. For example it fails to show any change in the spin combination as the benzene π-system is (hypothetically) converted to fulvene and hexatriene:



A similar inflexible projection operator method has been proposed for use with the alternant molecular orbital method. Although the results of this method (Tab. 6) provide an improvement on method 1, they are still not as good as one might hope, and can be improved by making a more reasonable assumption about the spin combination.

Method 3

If we start with the wavefunction from method 1 for ethylene or the "allyl$^+$" π-system, and make it antisymmetric in the exchange of electrons between the pair of NPSOs we derive a function representing the ground state. Let us examine the possibility that the ground state of a poly-electronic system is closely represented by a function which is antisymmetric in the exchange of the maximum number of pairs of electrons in adjacent NPSOs. Such a function reduces to the

Heitler-London valence bond form when $k \to \infty$ [5]. In each case, (see Tab. 6), this function gives an energy very close to that of the NPSO full spin-CI treatment. For benzene too the difference, 0.048 eV for $k = 4$, is small. Indeed it seems most reasonable to suppose that the ground state is a state in which there is the maximum spin-pairing between electrons in spatially adjacent orbitals.

Table 6. *Energies of approximate* NPSO *functions and* SCF–LCAO–MO *functions compared to those obtained using the* NPSO *full spin-*CI *treatment (in* eV*)*

Function	Fulvene	Hexatriene	Butadiene
NPSO full spin-CI $k = k_{\min}$ ($k_{\min}$ approx)	0.00(4.2)	0.00(3.9)	0.00(3.3)
NPSO full spin-CI $k = 4$	0.00	0.01	—
Method 1, $k = k_{\min}$	1.81(4.2)	1.95(3.3)	—
„ $k = 4$	1.82	2.08	—
Method 2, $k = k_{\min}$	0.55(4.6)	0.52(3.7)	—
„ $k = 4$	0.58	0.53	—
Method 3, $k = k_{\min}$	0.16(4.0)*	0.26(3.9)	0.00(3.3)
„ $k = 4$	0.16	0.27	—
SCF–LCAO–MO	3.50	3.91	2.27

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* The two ways of making the function antisymmetric in three pairs of adjacent NPSOs are not quite equivalent, but have been combined with equal weights for simplicity.

A fourth method, which was found to be very successful for benzene [6], is to decompose the single determinant ground state molecular orbital function into determinants based on NPSOs, dropping all those in which one or more pairs of electrons are confined to the same orbital. This is best applied when the MOs are determined solely by symmetry and has not been used here, where they are not.

The Space Constant k

Provided that k is chosen to be near the value which minimises the energy we find empirically that, (cf. reference [6]):

1. The spin combination changes only very slightly as k changes. Any of the methods 1, 2, or 3 can be used successfully to determine the spin combination for an arbitrary value of k near the minimum. Tab. 7 gives examples of the coefficients a_1 to a_5 for fulvene and hexatriene, which define the NPSO full spin-CI function for the ground state at arbitrary values of k.

2. $\left(\frac{\delta E}{\delta k}\right)_{a_n}$ is small. Thus if k is chosen anywhere near $k_{\min}$ the energy and wavefunction are not greatly affected. The energies of NPSO full spin-CI functions for the ground state are also shown in Tab. 7 for arbitrary values of k about the minimum.

3. The value of k which minimises the energy of the NPSO full spin-CI function for hydrocarbon π-systems of different types and geometries are all close to 4.0. Using this value for k and the spin combination determined by method 3, (antisymmetric pairs), for all systems investigated gives a function with a very low

energy*. The values of $k_{\min}$ appropriate to a variety of systems, and the error in the energy made by assuming a value of $k = 4$ are shown in Tab. 8.

Table 7. *Energies (in* eV *relative to* 6 W_{2p}*), and coefficients for the* NPSO *full spin*-CI *functions of (i) fulvene and (ii) hexatriene in their ground states*

k	Energy	a_1*	a_2	a_3	a_4	a_5
(i) 2	− 116.04	.2281	,6522	.0566	.6971	.1829
3	− 117.11	.1105	.4834	.1585	.5636	.6414
3.5	− 117.28	.0840	.4358	.1646	.5262	.7065
3.75	− 117.31	.0747	.4183	.1659	.5133	.7270
4	-117.33_0	.0672	.4038	.1665	.5028	.7429
4.25	-117.33_1	.0610	.3917	.1668	.4941	.7556
4.75	− 117.30	.0512	.3725	.1667	.4803	.7747
5.5	− 117.21	.0407	.3517	.1658	.4653	.7942
(ii) 2	− 98.92	.0150	.0488	.2039	.1384	.9678
3	− 100.22	.0061	.0384	.1570	.1288	.9784
3.5	− 100.37	.0048	.0373	.1512	.1292	.9793
4	− 100.41	.0059	.0375	.1502	.1316	.9791
5	− 100.32	.0053	.0371	.1482	.1333	.9792

* See Appendix for definition of functions associated with a_i.

Table 8. $k_{\min}$ *for the* NPSO *full spin*-CI *treatments of various molecules*

Molecule	$k_{\min}$	Error (in eV) in assuming $k = 4$	Source
Benzene	3.7	0.02	Ref. [*6*]
Fulvene	4.2	0.00	Present Calcs.
Hexatriene	3.9	0.01	Present Calcs.
Butadiene	3.3	—	Present Calcs.
Allyl rad.	3.6	—	Ref. [*14*]
Allyl$^+$	4.0	—	Ref. [*14*]
Ethylene, $R = 1.393$ Å	3.5	0.01	Present Calcs.

These results confirm that it is possible to write an accurate wavefunction for the ground states of these complex molecules without passing through the laborious intermediate state of making an energy calculation.

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Appendix

This Appendix gives the NPSO wave functions of (*i*) Fulvene, and (ii) Hexatriene to be associated with the coefficients a_i in Tab. 7.

The NPSO type orbitals are numbered as follows:

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* For calculations using "empirical integrals" the best value for this constant may be different [*7*], but an equally satisfactory one may be chosen.

Fulvene ($k > 1$) 1, $a + kb$; 2, $b + kc$; 3, $c + kd$; 4, $d + kc$;
5, $c + ka$; 6, $a + kf$; 7, $ka + b$; 8, $kb + e$;
9, $kc + d$; 10, $kd + e$; 11, $ke + a$; 12, $a + kf$.

Hexatriene ($k > 1$) 1, a; 2, $a + kb$; 3, $b + kc$; 4, $c + kd$; 5, $d + kc$;
6, $e + kf$; 7, $ka + b$; 8, $kb + c$; 9, $kc + d$;
10, $kd + e$; 11, $ke + f$; 12, f.

The appropriate NPSO π-wave functions for the ground states of Fulvene and Hexatriene are the combinations shown below. The individual determinants (Φ_m) are identified in the table by giving in the topmost row the three NPSOs of the first set (1, 2, 3, 4, 5 and 6) with which α-spin wave functions are associated, the three others being associated with β-spin wave functions. The coefficients with which each of these appear in the ${}^1\Psi_i^{1A_1}$ functions are tabulated (Tab. 9). To obtain the coefficients of the second set (7, 8, 9, 10, 11, and 12) the appropriate symmetry operation is applied and the coefficients are carried over without change of sign. For Fulvene the symmetry operation is reflection in the plane at right angles to the plane of the molecule and for Hexatriene rotation about the two-fold axis.

Table 9

	123	124	125	126	134	135	136	145	146	156	234	235	236	245	246	256	345	346	356	456
Φ_m	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
${}^1\Psi_1$	−3	−1	1	−1	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1	−1	1	−1	−3
${}^1\Psi_2$	0	−4	−2	2	−2	−1	1	−1	1	2	2	1	−1	1	−1	−2	2	−2	−4	0
${}^1\Psi_3$	0	0	−2	−2	0	−1	−1	1	1	0	0	1	1	−1	−1	0	−2	−2	0	0
${}^1\Psi_4$	0	0	0	0	−2	−1	1	1	−1	−2	−2	−1	1	1	−1	−2	0	0	0	0
${}^1\Psi_5$	0	0	0	0	0	−1	−1	−1	−1	0	0	−1	−1	−1	−1	0	0	0	0	0

References

[1] Bergman, E. D.: Prog. Org. Chem. **3**, 81 (1955).
[2] Berthier, G.: J. Chim. Physique **50**, 344 (1953).
[3] Coulson, C. A., and I. Fischer: Phil. Mag. **40**, 386 (1949).
[4] Day, J. H.: Chem. Rev. **53**, 167 (1953).
[5] Eyring, H., J. Walter, and G. E. Kimball: Quantum Chemistry. New York: John Wiley 1944.
[6] Empedocles, P. B., and J. W. Linnett: Proc. Roy. Soc. A **282**, 166 (1964).
[7] — — To be published.
[8] — To be published.
[9] — D. Phil. Thesis. Oxon 1965.
[10] Fain, J. and F. A. Matsen: J. chem. Physics **26**, 376 (1957).
[11] Goeppert-Mayer, M., and A. L. Sklar: J. chem. Physics **6**, 645 (1938).
[12] de Heer, J.: J. Physic. Chem. **66**, 2288 (1962).
[13] Hirst, D. M., and J. W. Linnett: J. Chem. Soc. **1962**, 1035.
[14] — — J. Chem. Soc. **1963**, 1068.
[15] Kon, H.: J. Chem. Physics **23**, 1176 (1955) and ref. **18**.
[16] Landau, L. D., and E. M. Lifshitz: Quantum Mechanics. Oxford: Pergamon Press 1960.
[17] Linnett, J. W.: J. Amer. Chem. Soc. **83**, 2643 (1961).
[18] Lowdin, P. O.: Adv. Chem. Phys. **2**, 207 (1959).
[19] Moskowitz, J. W., and M. P. Barnett: J. chem. Physics **39**, 1557 (1963).

[*20*] Mulliken, R. S., and R. C. Parr: J. Chem. Physics **19**, 1271 (1951).
[*21*] Pariser, R., and R. G. Parr: J. Chem. Physics **23**, 711 (1955).
[*22*] Parr, R. G., D. P. Craig, and I. G. Ross: J. chem. Physics **18**, 1561 (1950).
[*23*] —, and R. S. Mulliken: J. chem. Physics **18**, 1338 (1950).
[*24*] Roothaan, C. C. J.: Rev. Mod. Physics **23**, 69 (1951).
[*25*] Smith, W. B., and B. A. Shoulders: J. Amer. Chem. Soc. **86**, 3118 (1964).
[*26*] Stewart, E. T.: J. chem. Soc. **1959**, 70.
[*27*] Thiec, J., and J. Wieman: Bull. Soc. Chim. Fr. **1956**, 177.
[*28*] Wheland, G. W.: J. Amer. Chem. Soc. **63**, 2025 (1941).
[*29*] —, and D. E. Mann: J. Chem. Physics **17**, 264 (1949).

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