333. *Electronic Structure of Trimethylenemethyl,* $C(CH_2)_3$

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Complete configuration interaction (CI) treatments have been carried out for the π-electron systems of $C(CH_2)_3$, $C(CH_2)_3^+$, and $C(CH_2)_3^{2+}$. Energies, and overlap with the above CI functions, have also been calculated by using the approximate wave functions based on (i) a molecular orbital treatment, (ii) a valence bond treatment, and (iii) the treatment first used by Hirst and Linnett and described by them as non-pairing. It is shown that (iii) provides the best simple representation of the electronic structure. The effect of branching in a molecule on the adjustable parameter in (iii) and transferability of this parameter from one molecule to another have also been examined.

During the last few years, the method of assigning every electron to a different spatial orbital, even if the spins are different, has been applied to molecules, radicals, and ions in this laboratory in two general directions. Towards a better qualitative description of electronic structure, the double-quartet (DQ) theory[1] has been suggested, according to which the Lewis octet is treated as two quartets of electrons instead of four pairs. For the quantitative treatment, the so-called non-pairing method has been used.[2-4] In order to make it clear that this procedure implies only an absence of spatial pairing, it is intended to call this the method of non-paired spatial orbitals (NPSO) meaning that a pair of electrons is never assigned to the same spatial orbital (*i.e.*, no two electrons are given the same spatial function). It does not involve pairing in molecular orbitals as in the MO method, or in bonds or lone-pairs as in the valence-bond (VB) method. While the double-quartet

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[1] Linnett, *Nature*, 1960, **187**, 859; Green and Linnett, *J.*, 1960, 4959; Linnett, *J. Amer. Chem. Soc.*, 1961, **83**, 2643; Linnett, *Nature*, 1963, **199**, 168; Hirst, Hopton, and Linnett, *Tetrahedron*, 1963, **19**, suppl. 2, 15; Linnett, *J.*, 1963, 4663; Linnett, " Electronic Structure of Molecules," Methuen, London, 1964.

[2] Hirst and Linnett, *Proc. Chem. Soc.*, 1961, 427; *J.*, 1962, 1035, 3844; 1963, 1068.

[3] Hopton and Linnett, *J.*, 1962, 1553; Gould and Linnett, *Trans. Faraday Soc.*, 1963, **59**, 1001; Empedocles and Linnett, *Proc. Chem. Soc.*, 1963, 303; Linnett and Sovers, *Discuss. Faraday Soc.*, 1963, **35**, 58.

[4] Unpublished results, Empedocles, Part II Thesis, Oxford, 1962.

theory has been applied to many molecules, comparatively few species have been treated quantitatively by the NPSO method.

In this Paper, we report some recent results which extend the NPSO method from the allyl radical [2] and butadiene [4] to trimethylenemethyl, $C(CH_2)_3$ (Y), and its ions. The results will be compared with those obtained with the other approximations, namely MO and VB, and with the complete CI treatment. In order to investigate the possibility of ultimately extending the NPSO method to more complicated molecules we have also examined the effect of the branching in this molecule on the NPSO parameter k, and the transferability of this parameter from one molecule to another.

Outline of Treatment.—The quantum-mechanical treatment of all three species studied, Y, Y^+, and Y^{2+}, is the same as that used for the allyl system.[2] The following assumptions are made: (1) a fixed geometry for the nuclei in question, a planar aromatic structure, and (2) sigma–pi separability. Only the four $2p\pi$-orbitals on the carbon atoms are considered, designated by a, b, c, and x, where x refers to the central atom. The three species are treated as 4-, 3-, and 2-electron problems, respectively. Then all the Slater determinants (ϕ) are formulated and the symmetry functions (ψ) constructed as proper linear combinations of the ϕ's. The Hamiltonian used here is an approximate one, which was introduced by Goeppert-Mayer and Sklar,[5] used by Parr and Crawford,[6] and involves penetration integrals. The best wave functions $\Psi'_{\mathrm{CI}} = \sum_n c_n\psi_n$ are obtained by solving the usual secular equation. The computational details are given in Appendix A.

The approximate wave functions which are being compared are all of the form $\Psi'(k) = \sum_n f_n(k)\psi_n$, in which the coefficients $f_n(k)$ are defined by the particular approximate function (see later). Once the matrix elements between the ψ's have been evaluated the energy $E'(k)$ can be minimised with respect to k. The relevant matrix elements between the ψ's which constitute the ground state Ψ'_{CI} are tabulated in Appendix B.

The MO wave functions are built from the one-electron molecular orbitals, a_1: $a + b + c + kx$, and e: $2a - b - c$ and $b - c$. For example, for Y^{2+}, $\Psi'_{\mathrm{MO}}{}^{2+},(k) = (a + b + c + kx,\ a + b + c + kx)$, where the symbol (m, n) represents the Slater determinant:

$$\frac{1}{\sqrt{2}}\begin{vmatrix} m(1)\alpha(1) & n(1)\beta(1) \\ m(2)\alpha(2) & n(2)\beta(2) \end{vmatrix}.$$

Here, k replaces $\sqrt{3}$, the value from Hückel MO and is an adjustable parameter.

The VB functions used in this work are of the Coulson–Fischer type,[7] which is a special case of the method of different orbitals for different spins. The parameter k connects the Heitler–London treatment ($k = 0$) with the bond orbital treatment ($k = 1$).

The NPSO functions will be presented in the corresponding sections below.

Trimethylenemethyl.—Complete treatment. The basis set of determinantal functions, in which the four atomic functions are associated with α, β, α, and β spin functions in that order, is:

$\phi_1 = (a,b,c,x)$; $\phi_2 = (a,c,b,x)$; $\phi_3 = (b,a,c,x)$; $\phi_4 = (a,b,x,c)$; $\phi_5 = (x,b,c,a)$; $\phi_6 = (b,a,x,c)$; $\phi_7 = (a,a,c,b)$; $\phi_8 = (a,b,c,c)$; $\phi_9 = (b,a,c,c)$; $\phi_{10} = (a,b,b,c)$; $\phi_{11} = (c,b,b,a)$; $\phi_{12} = (a,a,b,c)$; $\phi_{13} = (b,a,x,x)$; $\phi_{14} = (a,c,x,x)$; $\phi_{15} = (c,a,x,x)$; $\phi_{16} = (b,c,x,x)$; $\phi_{17} = (c,b,x,x)$; $\phi_{18} = (a,b,x,x)$; $\phi_{19} = (a,b,b,x)$; $\phi_{20} = (x,b,b,a)$; $\phi_{21} = (x,c,c,a)$; $\phi_{22} = (a,a,b,x)$; $\phi_{23} = (a,a,x,b)$; $\phi_{24} = (b,b,x,c)$; $\phi_{25} = (b,c,c,x)$; $\phi_{26} = (x,c,c,b)$; $\phi_{27} = (b,b,c,x)$; $\phi_{28} = (a,a,c,x)$; $\phi_{29} = (a,a,x,c)$; $\phi_{30} = (a,c,c,x)$; $\phi_{31} = (a,a,b,b)$; $\phi_{32} = (a,a,c,c)$; $\phi_{33} = (b,b,c,c)$; $\phi_{34} = (a,a,x,x)$; $\phi_{35} = (b,b,x,x)$; $\phi_{36} = (c,c,x,x)$.

The 36 states are found to be $5{}^1A_1 + {}^1A_2 + 7{}^1E + {}^3A_1 + 4{}^3A_2 + 5{}^3E + {}^5A_2$ and the energies of the best wave functions, listed as $E - 4W_{2p}$ in rydbergs, are summarized in

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[5] Goeppert-Mayer and Sklar, *J. Chem. Phys.*, 1938, **6**, 645.

[6] Parr and Crawford, *J. Chem. Phys.*, 1948, **16**, 526.

[7] Coulson and Fischer, *Phil. Mag.*, 1949, **40**, 386.

Table 1. The ground state is a $^3A_2$, state, with $E_{\text{CI}} = 4W_{2p} - 3{\cdot}75381$ rydbergs, and the corresponding normalized best function is:

$$\Psi_{\text{CI}} = 0{\cdot}30461\ \psi_1 + 0{\cdot}05994\ \psi_2 + 0{\cdot}09117\ \psi_3 + 0{\cdot}02659\ \psi_4,$$

where $\psi_1 = \phi_1 - \phi_2 - \phi_3 + \phi_4 + \phi_5 - \phi_6$;
$\psi_2 = \phi_{12} - \phi_7 + \phi_{10} - \phi_{11} + \phi_8 - \phi_9$;
$\psi_3 = \phi_{16} - \phi_{17} + \phi_{18} - \phi_{13} - \phi_{14} + \phi_{15}$;
$\phi_4 = -\phi_{28} + \phi_{19} + \phi_{22} - \phi_{30} + \phi_{27} + \phi_{25} + \phi_{29} - \phi_{20} - \phi_{23} + \phi_{21} - \phi_{24} - \phi_{26}$.

Molecular orbital.

$$\begin{aligned}\Psi_{\text{MO}}(k) &= (a + b + c + kx,\ a + b + c + kx,\ 2a - b - c,\ b - c)\\ &\qquad - (a + b + c + kx,\ a + b + c + kx,\ b - c,\ 2a - b - c)\\ &= 4k\psi_1 + 6\psi_2 + 2k^2\psi_3 + 2k\psi_4.\end{aligned}$$

Valence bond.

$$\begin{aligned}\Psi_{\text{VB}}(k) &= (\mathbf{E} + \mathbf{C}_3{}^1 + \mathbf{C}_3{}^2)[(a + kx,\ x + ka,\ b,\ c,) - (x + ka,\ a + kx,\ c,\ b)]\\ &= (1 + k^2)\psi_1 + k\psi_2 + k\psi_3,\end{aligned}$$

where $\mathbf{E}$, $\mathbf{C}_3{}^1$, and $\mathbf{C}_3{}^2$ are the identity, 120° rotation, and 240° rotation symmetry operators, respectively.

NPSO. The basic function for the NPSO treatment is of the same type that worked well in the cases of the allyl radical [2] and butadiene,[4] namely, $(a,\ x + ka,\ c + kx,\ b + kx)$.

For any four-electron system with $S_Z = 0$, there are three independent combinations of spin assignments which are eigenfunctions of S^2 with an eigenvalue of $S = 1$:

$$\sigma_1 = \alpha\beta\alpha\beta - \beta\alpha\beta\alpha;\quad \sigma_2 = \alpha\beta\beta\alpha - \beta\alpha\alpha\beta;\quad \sigma_3 = \alpha\alpha\beta\beta - \beta\beta\alpha\alpha.$$

Corresponding to these,

$$\begin{aligned}\Psi_{\text{I}} &= (\mathbf{E} + \mathbf{C}_3{}^1 + \mathbf{C}_3{}^2)[(a,\ x + ka,\ c + kx,\ b + kx) - (x + ka,\ a,\ b + kx,\ c + kx)]\\ &= \psi_1 + k\psi_2 + k\psi_3 + k^2\psi_4;\\ \Psi_{\text{II}} &= (\mathbf{E} + \mathbf{C}_3{}^1 + \mathbf{C}_3{}^2)[-(a,\ x + ka,\ b + kx,\ c + kx) + (x + ka,\ a,\ c + kx,\ b + kx)]\\ &= \psi_1 + k\psi_2 + k\psi_3 + k^2\psi_4;\\ \Psi_{\text{III}} &= (\mathbf{E} + \mathbf{C}_3{}^1 + \mathbf{C}_3{}^2)[-(a,\ c + kx,\ x + ka,\ b + kx) + (c + kx,\ a,\ b + kx,\ x + ka)]\\ &= \psi_1 + 2k\psi_3.\end{aligned}$$

Any linear combination of Ψ_{I}, Ψ_{II}, and Ψ_{III} is an eigenfunction of S^2 with $S = 1$. Since σ_1 and σ_2 are symmetric, Ψ_{I} and Ψ_{II} are equal and have equal weight. Therefore, the general NPSO function is:

$$(1 - |\,\theta\,|)(\Psi_{\text{I}} + \Psi_{\text{II}}) + \theta\Psi_{\text{III}},\ \text{with} -1 \leqslant \theta \leqslant +1.$$

To avoid introducing this additional parameter θ for energy minimization, we make use of the spin projection operator,[8] $\mathbf{O}$. For four-electron systems with $S_Z = 0$, $^3\mathbf{O} = \frac{1}{8}S^2(6 - S^2)$, and

$$^3\mathbf{O}(\alpha\beta\alpha\beta) = \tfrac{1}{2}(\alpha\beta\alpha\beta - \beta\alpha\beta\alpha).$$

Since $\Psi_{\text{I}} = \Psi_{\text{II}}$, the projected function corresponds to the special case in which $\theta = 0$, *i.e.*,

$$\Psi_{\text{NPSO}}(k) = \psi_1 + k\psi_2 + k\psi_3 + k^2\psi_4.$$

The justification for this procedure is discussed later.

Results.—The results of these one-parameter energy minimizations are listed in Table 2, in which the optimum values of k are shown in the first column, the energies, $E - E_{\text{CI}}$ in

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[8] Löwdin, *Adv. Chem. Phys.*, 1959, **2**, 309.

rydbergs, in the second, and the difference from unity of the overlap integrals $\int\Psi_{CI}\Psi'd\tau$ in the last. The overlap integrals have been calculated with the normalized best function Ψ_{CI} and the normalized approximate function Ψ' in order to show how closely the latter approximate the former. It places the three approximate functions in the same order as the energies do, both showing that the NPSO method is superior.

TABLE 1

Energies ($E - nW_{2p}$) in rydbergs, for the best CI wave functions (n equals the number of π-electrons)

	Sym. class	Energy	Sym. class	Energy	Sym. class	Energy	Sym. class	Energy
$C(CH_2)_3$ ...	5^1A_1	−3·18127	7^1E	−3·68267	4^3A_2	−3·75381	5^3E	−3·50035
		−2·72752		−2·93627		−2·79860		−3·01453
		−2·46431		−2·87551		−2·72025		−2·76265
		−1·89277		−2·48124		−2·06417		−2·36338
		−1·46663		−2·30767				−2·25142
				−1·76275	$^1A_2$	−2·50300		
	$^3A_1$	−2·52329		−1·54449			$^5A_2$	−3·38728
$C(CH_2)_3^+$ ...	4^2A_1	−3·52860	7^2E	−3·85353	2^4A_2	−3·67329		
		−3·00121		−3·47962		−2·96827		
		−2·55805		−3·14258				
		−2·13720		−2·77023	^4E	−3·34875		
				−2·64505				
	2^2A_2	−3·46477		−2·34332				
		−2·29251		−2·03993				
$C(CH_2)_3^{2+}$	4^1A_1	−3·46747	3^1E	−3·05182	$^3A_2$	−2·60936		
		−2·67067		−2·52391				
		−2·22504		−1·66463	2^3E	−3·05519		
		−1·62841				−2·74632		
			$^3A_1$	−2·89665				

TABLE 2

Results obtained with various one-parameter approximate functions compared to the best CI function. In the last column, values of the difference from unity of the overlap integral $S = \int\Psi_{CI}\Psi'd\tau$ are listed

Species	Method	k	$E - E_{CI}$	$1 - S$
Y	MO	2·89390	0·10896	0·0577
	VB	0·28367	0·01054	0·0045
	NPSO	0·26052	0·00295	0·0014
Y^+	MO	2·34547	0·12016	0·0782
	VB	0·17259	0·20827	0·2749
	NPSO	0·70241	0·03013	0·0238
Y^{2+}	MO	2·76412	0·03174	0·0103
	VB	0·13534	0·07758	0·0301
	NPSO	0·87719	0·01491	0·0058

Trimethylenemethyl Positive Ion.—Complete treatment. The basis set of Slater determinants for this species is:

$$\phi_1 = (a,b,c);\quad \phi_2 = (b,c,a);\quad \phi_3 = (c,a,b);\quad \phi_4 = (x,a,b);\quad \phi_5 = (x,b,c);\quad \phi_6 = (x,c,a);$$
$$\phi_7 = (x,b,a);\quad \phi_8 = (x,c,b);\quad \phi_9 = (x,a,c);\quad \phi_{10} = (a,x,b);\quad \phi_{11} = (b,x,c);\quad \phi_{12} = (c,x,a);$$
$$\phi_{13} = (a,a,b);\quad \phi_{14} = (b,b,c);\quad \phi_{15} = (c,c,a);\quad \phi_{16} = (a,a,c);\quad \phi_{17} = (b,b,a);\quad \phi_{18} = (c,c,b);$$
$$\phi_{19} = (a,a,x);\quad \phi_{20} = (b,b,x);\quad \phi_{21} = (c,c,x);\quad \phi_{22} = (x,x,a);\quad \phi_{23} = (x,x,b);\quad \phi_{24} = (x,x,c).$$

Here, the three atomic orbitals in each case are associated with the α, β, and α spin functions in that order. The 24 states and the energies of the best functions, listed as $E - 3W_{2p}$, are given in Table 1. The ground state is a ^2E state, with $E_{CI} = 3W_{2p} - 3{\cdot}85353$ rydbergs, and the pair of ground-state wave functions are not unique. If they are chosen such that they are symmetric and antisymmetric with respect to reflection in a plane through the *atoms a* and x and perpendicular to the plane of the four carbon atoms (σa) then the normalized ground-state wave functions are:

$$\begin{aligned}\Psi_{\mathrm{CI}}{}^{+}(\sigma_{\mathrm{a}} = +1) = {} & 0{\cdot}21409\,\psi_9 + 0{\cdot}08320\,\psi_{10} + 0{\cdot}15901\,\psi_{11} \\ & + 0{\cdot}00656\,\psi_{12} + 0{\cdot}00731\,\psi_{13} + 0{\cdot}01432\,\psi_{14} + 0{\cdot}10655\,\psi_{15};\end{aligned}$$

$$\begin{aligned}\Psi_{\mathrm{CI}}{}^{+}(\sigma_{\mathrm{a}} = -1) = {} & 0{\cdot}12361\,\psi_{16} + 0{\cdot}14410\,\psi_{17} + 0{\cdot}09180\,\psi_{18} \\ & + 0{\cdot}01136\,\psi_{19} + 0{\cdot}00422\,\psi_{20} + 0{\cdot}02481\,\psi_{21} + 0{\cdot}18455\,\psi_{22},\end{aligned}$$

where $\psi_9 = \phi_1 - \phi_2$;
$\psi_{10} = 2\phi_5 - \phi_4 - \phi_6 + 2\phi_8 - \phi_7 - \phi_9$;
$\psi_{11} = \phi_4 - \phi_6 - \phi_7 + \phi_9 + 2\phi_{10} - 2\phi_{12}$;
$\psi_{12} = 2\phi_{13} - \phi_{14} - \phi_{15} + 2\phi_{16} - \phi_{17} - \phi_{18}$;
$\psi_{13} = \phi_{14} - \phi_{15} - \phi_{17} + \phi_{18}$;
$\psi_{14} = 2\phi_{19} - \phi_{20} - \phi_{21}$;
$\psi_{15} = -2\phi_{22} + \phi_{23} + \phi_{24}$;
$\psi_{16} = 2\phi_3 - \phi_1 - \phi_2$;
$\psi_{17} = \phi_4 - \phi_6 + \phi_7 - \phi_9$;
$\psi_{18} = -2\phi_5 + \phi_4 + \phi_6 + 2\phi_8 - \phi_7 - \phi_9 - 4\phi_{11} + 2\phi_{10} + 2\phi_{12}$;
$\psi_{19} = -\phi_{14} + \phi_{15} - \phi_{17} + \phi_{18}$;
$\psi_{20} = 2\phi_{13} - \phi_{14} - \phi_{15} - 2\phi_{16} + \phi_{17} + \phi_{18}$;
$\psi_{21} = -\phi_{20} + \phi_{21}$;
$\psi_{22} = \phi_{23} - \phi_{24}$.

In the symbols ψ's and ϕ's used in this and the following sections, the superscripts $^{+}$ and $^{2+}$ have been omitted for convenience since there should be no confusion. It should be clear from the superscript on the symbol Ψ or Φ (see Discussion) which ψ's are involved.

Molecular orbitals.

$$\begin{aligned}\Psi_{\mathrm{MO}}{}^{+}(k) &= (a + b + c + kx,\ a + b + c + kx,\ b - c) \\ &= \tfrac{1}{2}[2\psi_{16} + k\psi_{17} + k\psi_{18} + 3\psi_{19} + \psi_{20} + 2k\psi_{21} + 2k^2\psi_{22}].\end{aligned}$$

Valence Bond.

$$\begin{aligned}\Psi_{\mathrm{VB}}{}^{+}(k) = {} & (\mathbf{C}_3{}^1 - \mathbf{C}_3{}^2)[(a + kx,\ x + ka,\ b) + (x + ka,\ a + kx,\ b) \\ & + (a + kx,\ x + ka,\ c) + (x + ka,\ a + kx,\ c)] \\ = {} & \tfrac{1}{2}[(1 + k^2)\psi_{17} - (1 + k^2)\psi_{18} - 4k\psi_{19} - 4k\psi_{22}].\end{aligned}$$

NPSO. The simplest NPSO function is constructed with the basic function $(a + kx,\ b + kx,\ c + kx)$. Because of the symmetry in such a function, it is independent of the combination of spin assignments, except for a multiplicative constant.

$$\begin{aligned}\Psi_{\mathrm{NPSO}}{}^{+}(k) &= (\mathbf{C}_3{}^1 - \mathbf{C}_3{}^2)[(a + kx,\ b + kx,\ c + kx) + (a + kx,\ c + kx,\ b + kx)] \\ &= \tfrac{1}{2}[2\psi_{16} + 3k\psi_{17} + k\psi_{18} + 6k^2\psi_{22}].\end{aligned}$$

Results. The results are shown in Table 2, where the energies are listed as $E - E_{\mathrm{CI}}$. We see that in this case, the NPSO method gives a much better wave function, both in energy and in overlap with the best CI function, than the other two methods.

Trimethylenemethyl Doubly-positive Ion.—Complete treatment. The basic set of functions is:

$\phi_1 = (a,b,)$; $\phi_2 = (b,c)$; $\phi_3 = (c,a)$; $\phi_4 = (b,a)$; $\phi_5 = (c,b)$; $\phi_6 = (a,c)$; $\phi_7 = (a,x)$; $\phi_8 = (b,x)$; $\phi_9 = (c,x)$; $\phi_{10} = (x,a)$; $\phi_{11} = (x,b)$; $\phi_{12} = (x,c)$; $\phi_{13} = (a,a)$; $\phi_{14} = (b,b)$; $\phi_{15} = (c,c)$; $\phi_{16} = (x,x)$.

where the symbol (m, n) has been defined in the section on outline of treatment. The 16 states and the energies of the best functions, listed as $E - 2W_{2p}$ are shown in Table 1.

The ground state is a $^1A_1$ state with $E_{CI} = 2W_{2p} - 3{\cdot}46747$ rydbergs. The normalized wave functions of the ground state is:

$$\Psi_{CI}{}^{2+} = 0{\cdot}06745\,\psi_1 + 0{\cdot}23135\,\psi_2 - 0{\cdot}00484\,\psi_3 + 0{\cdot}39273\,\psi_4,$$

where $\psi_1 = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6$;
$\psi_2 = \phi_7 + \phi_8 + \phi_9 + \phi_{10} + \phi_{11} + \phi_{12}$;
$\psi_3 = \phi_{13} + \phi_{14} + \phi_{15}$;
$\psi_4 = \phi_{16}$.

Molecular orbital.

$$\begin{aligned}\Psi_{MO}{}^{2+}(k) &= (a + b + c + kx,\ a + b + c + kx)\\ &= \psi_1 + k\psi_2 + \psi_3 + k^2\psi_4.\end{aligned}$$

Valence bond.

$$\begin{aligned}\Psi_{VB}{}^{2+}(k) &= (\mathbf{E} + \mathbf{C}_3{}^1 + \mathbf{C}_3{}^2)[(a + kx,\ ka + x) + (ka + x,\ a + kx)]\\ &= (1 + k^2)\psi_2 + 2k\psi_3 + 6k\psi_4.\end{aligned}$$

NPSO.

$$\begin{aligned}\Psi_{NPSO}{}^{2+}(k) &= (\mathbf{E} + \mathbf{C}_3{}^1 + \mathbf{C}_3{}^2)[(a + kx,\ b + kx) + (b + kx,\ a + kx)]\\ &= \psi_1 + 2k\psi_2 + 6k^2\psi_4.\end{aligned}$$

Results. The results are compared with the complete treatment in Table 2, with the energies expressed as $E - E_{CI}$. The NPSO function again fares better than the other two, all on the same, one-parameter, level of approximation.

DISCUSSION

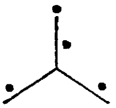
The NPSO function for Y has been obtained by using the spin projection operator. Table 3 gives some of the more common projected spin functions.

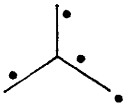
TABLE 3

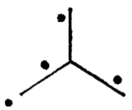
Spin functions obtained by using the projection operator

$$\begin{aligned}
{}^1\mathbf{O}\alpha\beta &= \tfrac{1}{2}(\alpha\beta - \beta\alpha)\\
{}^3\mathbf{O}\alpha\beta &= \tfrac{1}{2}(\alpha\beta + \beta\alpha)\\
{}^2\mathbf{O}\alpha\beta\alpha &= \tfrac{1}{3}(2\alpha\beta\alpha - \beta\alpha\alpha - \alpha\alpha\beta)\\
{}^4\mathbf{O}\alpha\beta\alpha &= \tfrac{1}{3}(\alpha\beta\alpha + \beta\alpha\alpha + \alpha\alpha\beta)\\
{}^1\mathbf{O}\alpha\beta\alpha\beta &= \tfrac{1}{6}(2\alpha\beta\alpha\beta + 2\beta\alpha\beta\alpha - \alpha\alpha\beta\beta - \beta\beta\alpha\alpha - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta)\\
{}^3\mathbf{O}\alpha\beta\alpha\beta &= \tfrac{1}{2}(\alpha\beta\alpha\beta - \beta\alpha\beta\alpha)\\
{}^5\mathbf{O}\alpha\beta\alpha\beta &= \tfrac{1}{6}(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha + \alpha\alpha\beta\beta + \beta\beta\alpha\alpha + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta)\\
{}^2\mathbf{O}\alpha\beta\alpha\beta\alpha &= \tfrac{1}{6}(3\alpha\beta\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha + \alpha\alpha\beta\alpha\beta + \beta\alpha\alpha\alpha\beta - \beta\alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha\beta - \alpha\alpha\beta\beta\alpha - \alpha\beta\beta\alpha\alpha - \alpha\alpha\alpha\beta\beta -\\
&\quad \beta\beta\alpha\alpha\alpha)\\
{}^1\mathbf{O}\alpha\beta\alpha\beta\alpha\beta &= \tfrac{1}{12}(3\alpha\beta\alpha\beta\alpha\beta - 3\beta\alpha\beta\alpha\beta\alpha + \alpha\beta\beta\alpha\beta\alpha - \beta\alpha\alpha\beta\alpha\beta + \beta\alpha\beta\alpha\alpha\beta - \alpha\beta\alpha\beta\beta\alpha + \beta\alpha\alpha\beta\beta\alpha - \alpha\beta\beta\alpha\alpha\beta +\\
&\quad \alpha\alpha\beta\alpha\beta\beta - \beta\beta\alpha\beta\alpha\alpha + \beta\alpha\beta\beta\alpha\alpha - \alpha\beta\alpha\alpha\beta\beta + \beta\beta\alpha\alpha\beta\alpha - \alpha\alpha\beta\beta\alpha\beta + \beta\alpha\alpha\alpha\beta\beta - \alpha\beta\beta\beta\alpha\alpha +\\
&\quad \alpha\alpha\beta\beta\beta\alpha - \beta\beta\alpha\alpha\alpha\beta + \beta\beta\beta\alpha\alpha\alpha - \alpha\alpha\alpha\beta\beta\beta)
\end{aligned}$$

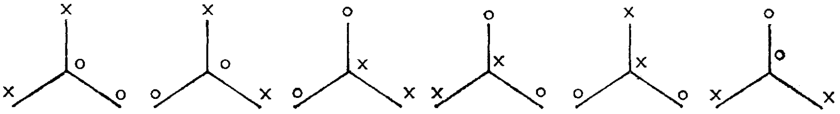
The one-parameter NPSO wave functions for the allyl system used by Hirst and Linnett [2] are seen to be precisely those corresponding to the projected spin functions. The arbitrary use of the projection operator can be justified *a posteriori* by the fact that the wave functions thus projected have extremely good, though not the best, energies for the allyl, butadiene, and trimethylenemethane systems.


(I)


(II)

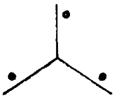

(III)

The spatial part of Ψ_{NPSO} corresponds to formulæ (I), (II), and (III). For each structure, there are six ways of assigning the spin functions such that $S_Z = 0$. For instance, for (I), there are the following:

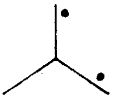


The projection operator in this calculation essentially eliminates the last pair and gives equal weights to the first four.*

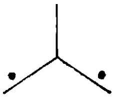
The NPSO function for Y^+ is represented by formula (IV) and that of Y^{2+} by (V), VI), and (VII).



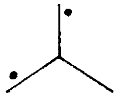
(IV)



(V)



(VI)



(VII)

For these functions, there is no ambiguity in the spin assignments, though for different reasons. Table 2 shows that for these species the NPSO method gives considerably lower energies than MO and VB treatments, especially for Y^+. The values of the NPSO parameter k at the minimum energies are not too far from unity. And, if k is arbitrarily set equal to 1, one obtains an energy of $3W_{2p} - 3{\cdot}79977$ rydbergs for Y^+, and $2W_{2p} - 3{\cdot}44946$ rydbergs for Y^{2+}, both better than either MO or VB with one-parameter variation. Therefore, for the π-electrons in these ions, the NPSO picture of a one-electron bond for each of the carbon–carbon bonds in Y^+ and $\frac{2}{3}$ of a one-electron bond in Y^{2+} are better than the VB representation of $\frac{1}{3}$ of a two-electron bond in both Y^+ and Y^{2+}.

Other NPSO Functions.—The NPSO functions presented so far are by no means unique. Other NPSO functions, to which the symbol Φ is given, have also been tested. Some of them give better energies than the $\Psi_{\mathrm{NPSO}}(k)$, and some, worse. A few of them will be discussed below.

For Y, we tried a NPSO function with the parameter $\theta = 0{\cdot}5$:

$$\Phi_1(k) = 0{\cdot}5(\Psi_{\mathrm{I}} + \Psi_{\mathrm{II}} + \Psi_{\mathrm{III}}) = \tfrac{3}{2}\psi_1 + k\psi_2 + 2k\psi_3 + k^2\psi_4,$$

as well as one which is similar to the VB function:

$$\begin{aligned}\Phi_2(k) &= (\mathbf{E} + \mathbf{C}_3{}^1 + \mathbf{C}_3{}^2)[(x + ka,\ a + kx,\ b + kx,\ c + kx) \\ &\qquad\qquad - (a + kx,\ x + ka,\ c + kx,\ b + kx)] \\ &= (1 + k^2)\psi_1 + k\psi_2 + (2k + k^3)\psi_3 + k^2\psi_4.\end{aligned}$$

The energies obtained are $4W_{2p} - 3{\cdot}75088$ and $4W_{2p} - 3{\cdot}74920$ rydbergs, respectively, compared to $4W_{2p} - 3{\cdot}75085$ rydbergs for $\Psi_{\mathrm{NPSO}}(k)$.

For Y^+, the Φ^+ functions tested are all special cases of a two-parameter NPSO function obtained by using the spin projection operator and starting with $(a + k_1x,\ b + k_2x,\ c + k_2x)$ as the basic determinant. This general NPSO function, antisymmetric with respect to σ_a (one member of the ^2E pair), has the form:

$$\Phi^+(k_1, k_2) = 6\psi_{16} + (6k_2 + 3k_1)\psi_{17} + (2k_2 + k_1)\psi_{18} + (12k_1k_2 + 6k_2{}^2)\psi_{22}.$$

The energies, $E - 3W_{2p}$, in rydbergs for the special cases of $k_1 = 0$, $k_1 = 1$, $k_1 = 1/k_2$, $k_2 = 0$, and $k_2 = 1$ are $-3{\cdot}83065$, $-3{\cdot}82464$, $-3{\cdot}83371$, $-3{\cdot}79000$, and $-3{\cdot}82733$, respectively. The NPSO function $\Psi_{\mathrm{NPSO}}{}^+(k)$, used in the previous section, with an energy of $3W_{2p} - 3{\cdot}82341$ rydbergs, is just the special case of $\Phi^+(k_1, k_2)$ with $k_1 = k_2$.

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* In these formulæ crosses represent electrons having one spin and circles those having the other. A dot represents a single electron, the spin not being specified. For a more detailed description see J. W. Linnett, "The Electronic Structure of Molecules," Methuen, 1964.

Similarly, the NPSO function for Y^{2+} was generalized as a two-parameter function and various special cases were tested.

$$\Phi^{2+}(k_1, k_2) = (\mathbf{E} + \mathbf{C}_3{}^1 + \mathbf{C}_3{}^2)[(a + k_1x,\ b + k_2x) + (b + k_2x,\ a + k_1x)]$$
$$= \psi_1 + (k_1 + k_2)\psi_2 + 6k_1k_2\psi_4.$$

The energies for the special cases with $k_1 = 1$ and $k_1 = 1/k_2$ are $2W_{2p} - 3{\cdot}45311$ and $2W_{2p} - 3{\cdot}46735$ rydbergs, respectively, compared to $2W_{2p} - 3{\cdot}45256$ rydbergs for $\Psi_{\text{NPSO}}{}^{2+}$, *i.e.*, $\Phi^{2+}(k_1, k_2)$ with $k_1 = k_2$.

Effect of Branching.—Before considering the effect of branching of a molecule on the NPSO parameter k, we must go back to the straight-chain species, the allyl radical, as a basis of comparison, and examine how k varies down the chain. In other words, instead of starting with $(a,\ b + ka,\ c + kb)$ as the basic determinantal function,[2] we now use $(a,\ b + k_1a,\ c + k_2b)$, and obtain

$$\tfrac{2}{3}\psi_1 + k_1\psi_2 + k_2\psi_3 + k_1k_2\psi_4,$$

where the symmetry spin orbitals in this function are those defined by Hirst and Linnett.[2] From the coefficients of the best function, in place of $k = 0{\cdot}277$ * the best values for k_1 and k_2 are now 0·241 and 0·293, respectively.* Therefore, for a normal straight-chain neutral hydrocarbon, the NPSO parameter k is expected to increase slowly down the chain. The minimum energy is not particularly sensitive to such a variation in k since the one-parameter variation for the allyl radical already yields an energy which is only 0·00080 rydbergs above the best energy from the complete CI treatment.

Now, if the same is done for Y, *i.e.*, replacing k with k_1 and k_2, we get

$$\Phi(k_1, k_2) = (\mathbf{E} + \mathbf{C}_3{}^1 + \mathbf{C}_3{}^2)[(a,\ x + k_1a,\ c + k_2x,\ b + k_2x) - (x + k_1a,\ a,\ b + k_2x,\ c + k_2x)]$$
$$= \psi_1 + k_1\psi_2 + k_2\psi_3 + k_1k_2\psi_4.$$

A two-parameter variation yields a minimum energy of $4W_{2p} - 3{\cdot}75329$ rydbergs at $k_1 = 0{\cdot}21589$ and $k_2 = 0{\cdot}31822$.

At first glance, these values of k_1 and k_2 appear surprising, since we expect that the effect of branching in a molecule is such that the electrons tend to stay apart thereby increasing k_1 and decreasing k_2 with respect to the straight chain. However, if we carry out a two-parameter variation on one of the other NPSO functions tested, the one with $\theta = 0{\cdot}5$ arbitrary, *i.e.*,

$$\Phi_1(k_1, k_2) = \tfrac{3}{2}\psi_1 + k_1\psi_2 + 2k_2\psi_3 + k_1k_2\psi_4,$$

we find that the minimum energy is $4W_{2p} - 3{\cdot}75243$ rydbergs at $k_1 = 0{\cdot}33664$ and $k_2 = 0{\cdot}24553$. Therefore, we are forced to conclude that the variation in k is strongly governed by the choice of combination of spin assignments. Happily, the energy is not very sensitive to such variations.

Transferability of NPSO Parameter.—A satisfactory feature exists in the values of the NPSO parameter k, in that, for the cases investigated as far, the optimum values of k are all fairly close to 0·3. The best values of k for the projected NPSO function are 0·2769 for allyl radical, 0·30 for butadiane, and 0·2605 for trimethylenemethane.

Moreover, in these calculations, the energy is not very sensitive to small variations in k. At $k = 0{\cdot}3$ for Y, the energy is $4W_{2p} - 3{\cdot}74953$ rydbergs, which is still lower than those for the MO and VB functions *with* energy minimization.

These two facts, (1) that the parameter k is relatively constant, and (2) that the energy is not very sensitive to small changes in k, suggest the possibility of extending the NPSO method to more complicated molecules for which energy minimization may be too involved

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* These best values of k, k_1, and k_2 are slightly different from those in ref. 2 (0·279, 0·243, and 0·298) because they have been obtained by starting with the more accurate integrals over atomic orbitals used in this work.

or not even feasible. Empedocles and Linnett[3] have applied the NPSO method to the benzene molecule with considerable success.

We thank the N.A.T.O. for a postdoctoral fellowship (to D. P. C.) and many colleagues for helpful discussions.

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[*Received, February* 14*th*, 1964.]

APPENDIX A

The Hamiltonian operator used in this work was reviewed in detail by Daudel *et al.*[9] The method of evaluating the matrix elements between the symmetry spin orbitals from the integrals over atomic orbitals was clearly explained by Eyring *et al.*[10] and Slater.[11] Therefore, in this appendix, we are concerned only with the integrals over the π-atomic orbitals, which are summarized in Table 4.

TABLE 4

Integrals over atomic orbitals used in this work

Overlap	$\langle a \mid b \rangle = 0{\cdot}0388688$	$\langle a \mid x \rangle = 0{\cdot}2599520$
Penetration (rydbergs)	$(a \mid xx) = 0{\cdot}062831$	$(x \mid ab) = 0{\cdot}023403$
	$(a \mid bb) = 0{\cdot}000976$	$(a \mid xb) = 0{\cdot}002848$
	$(a \mid ax) = 0{\cdot}138783$	$(a \mid bc) = 0{\cdot}000153$
	$(a \mid ab) = 0{\cdot}007990$	
Repulsion (rydbergs)	$(aa \mid aa) = 1{\cdot}244672$	$(aa \mid bb) = 0{\cdot}416771$
	$(aa \mid xx) = 0{\cdot}663676$	$(ab \mid cx) = 0{\cdot}006081$

All others given by ref. 16.

Throughout this work, we used Slater-type π-atomic orbitals with exponent $\rho = Zr = 8{\cdot}37$ and $Z = 3{\cdot}18$. The overlap integrals were calculated by use of Roothaan's formula.[12] The penetration integrals were all evaluated using Sklar's formulæ[13] as corrected by Parr and Crawford and Parr, Craig, and Ross.[14] The one-centre electron-electron repulsion integral was calculated exactly. The two-centre coulombic repulsion integrals were evaluated with Roothaan's formula[12] and checked by numerical interpolation of Kotani's table.[15] The two-centre repulsion integrals were taken from the accurate computations of Karplus and Shavitt.[16] The four-centre repulsion integral was taken as the average of the values obtained by the Sklar and Mulliken approximations.

All the computations were performed on a Mercury Ferranti computer at the Oxford University Computing Laboratory.

APPENDIX B

The matrix elements between the symmetry spin orbitals which constitute the ground state of Y, Y^+, and Y^{2+} are listed in Tables 5, 6, and 7, respectively.

TABLE 5

Matrix elements between $^3A_2$ symmetry spin orbitals of Y

i	j	S_{ij}	$H_{ij} - 4S_{ij}W_{2p}$ (trydbergs)	i	j	S_{ij}	$H_{ij} - 4S_{ij}W_{2p}$ (trydbergs)
1	1	6·348055	−23·331388	2	3	1·123632	−5·102685
1	2	3·105652	−12·371176	2	4	3·105652	−11·185776
1	3	2·881640	−11·682657	3	3	5·542639	−17·394102
1	4	1·498176	−6·753633	3	4	2·881640	−10·605259
2	2	6·437877	−19·405956	4	4	11·197933	−30·882274

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[9] Daudel, Lefebvre, and Moser, " Quantum Chemistry," Interscience Publishers Inc., New York, 1959, pp. 486 ff.

[10] Eyring, Walter, and Kimball, " Quantum Chemistry," John Wiley & Sons Inc., New York, 1960, pp. 240, 241.

[11] Slater, " Quantum Theory of Molecules and Solids," Vol. 1, McGraw-Hill Book Company Inc., New York, 1963, Appx. 9, pp. 285 ff.

[12] Roothaan, *J. Chem. Phys.*, 1951, **19**, 1445.

[13] Sklar and Lyddane, *J. Chem. Phys.*, 1939, **7**, 374.

[14] Parr and Crawford, *J. Chem. Phys.*, 1948, **16**, 1049; Parr, Craig, and Ross, *ibid.*, 1950, **18**, 1561.

[15] Kotani *et al.*, " Table of Molecular Integrals," Maruzen Co. Ltd., Tokyo, 1955.

[16] Karplus and Shavitt, *J. Chem. Phys.*, 1963, **38**, 1256.

TABLE 6

Matrix elements between one of the sets of ^2E symmetry spin orbitals of Y^+

i	j	S_{ij}	$H_{ij} - 3S_{ij}W_{2p}$ (rydbergs)
16	16	5·999648	−20·611823
16	17	1·499088	−6·239956
16	18	4·846870	−20·496267
16	19	0·241573	−1·058507
16	20	0·672444	−2·896364
16	21	0·058268	−0·293713
16	22	0·389691	−1·890982
17	17	3·714628	−12·973275
17	18	1·169073	−5·677140
17	19	−0·422006	+1·478817
17	20	1·499088	−5·634553
17	21	0·019535	−0·070269
17	22	0·499696	−2·074401
18	18	40·797719	−150·29575
18	19	4·846870	−18·536159
18	20	4·846870	−18·605908
18	21	1·169073	−5·195947
18	22	4·497264	−18·556524
19	19	4·223913	−11·290823
19	20	0·241573	−0·998567
19	21	1·018815	−3·420010
19	22	0·389691	−1·744974
20	20	11·326851	−28·722191
20	21	0·058268	−0·281354
20	22	0·389691	−1·773754
21	21	1·867082	−4·967565
21	22	0·499696	−1·868725
22	22	1·922262	−6·407065

TABLE 7

Matrix elements between the $^1A_1$ symmetry spin orbitals of Y^{2+}

i	j	S_{ij}	$H_{ij} - 2S_{ij}W_{2p}$ (rydbergs)
1	1	6·493620	−18·204786
1	2	3·361920	−12·291553
1	3	0·475490	−1·751757
1	4	0·405450	−1·774067
2	2	7·682776	−25·608114
2	3	1·680960	−5·490175
2	4	1·559712	−5·902922
3	3	3·009065	−5·681360
3	4	0·202725	−0·826049
4	4	1·000000	−3·114366