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Relationes

The Method of Non-Paired Spatial Orbitals

II. The Benzyl Radical

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The calculation of non-paired spatial orbitals and alternant molecular orbital wavefunctions for the benzyl radical is described. The NPSO and AMO methods give comparable energy lowerings which indicate that they make substantial allowance for electron correlation. The calculated spin densities are not in very good accord with experiment and it is thought that this reflects inadequacies in the integral approximations used.

1. Introduction

In a recent paper [1] we have described the extension of the method of non-paired spatial orbitals (NPSO) to the ten electron π-systems of naphthalene and azulene and compared the NPSO method with the alternant molecular orbital (AMO) calculations of Pauncz and his coworkers [2, 3]. Applications of the NPSO method to open shell systems have so far been restricted to three electron systems [4, 5]. We describe in this paper the application of the method to the seven electron π-system of the benzyl radical.

The benzyl radical continues to be of great interest to theoretical chemists (e.g. [6–8]) on account of the discrepancy between the calculated spin densities and the experimental proton hyperfine coupling constants. Suggestions for resolving this discrepancy have recently been put forward [7, 8].

The AMO method has had limited application to open shell systems and spin density calculations. Apart from calculations on the allyl radical [9, 10] and trimethylene methyl [11] in which the energies were optimised, the only other AMO calculations on such systems seem to be spin density calculations [12, 13] in which the AMO parameters were determined by criteria other than minimum energy. We therefore performed AMO calculations on the benzyl radical both for comparison with the NPSO results and for their intrinsic interest.

Molecular orbital calculations were also made in order to assess the lowering in energy resulting from the use of correlated wavefunctions.

2. Methods

a) Molecular Orbital Calculations

We performed three types of MO calculations. The crudest method used was to calculate the eigenvectors of the overlap matrix. This procedure yields the Hückel-Wheland orbitals [16] and is considerably inferior to self-consistent field

(SCF) methods. For open shell SCF calculations, one has the choice between the restricted Hartree-Fock (RHF) method [14] and the unrestricted Hartree-Fock (UHF) method [15] which makes allowance for electron correlation by using different orbitals for the α and β electrons. The UHF method has the disadvantage that the wavefunction is not a spin eigenfunction. Both methods were used in this work.

A regular geometry was assumed with bond lengths of 1.40 Å. Two sets of calculations were made using the Ruedenberg method [16] and the Goeppert-Mayer Sklar (GMS) [17] method for the calculation of one electron integrals. All overlap integrals were included and the two electron integrals were calculated from accurate Coulomb integrals by the Mulliken approximation. The integrals used are tabulated in the Appendix.

b) Alternant Molecular Orbital Method

Calculations were made by the methods described by Pauncz [18] using the eigenvectors of the overlap matrix as starting orbitals. If the molecular orbitals are denoted $\varphi_i\,(i=1,2\ldots 7)$ in order of ascending energy, the alternant molecular orbitals ψ_j and $\overline{\psi}_j\,(j=1,2,3)$ are given by

$$\psi_j=\cos\theta\varphi_j+\sin\theta\varphi_{8-j}\,, \tag{1}$$

$$\overline{\psi}_j=\cos\theta\varphi_j-\sin\theta\varphi_{8-j}\,, \tag{2}$$

where θ is a parameter which is varied to minimise the energy. It is usual to report the optimum value of θ in terms of a parameter λ which is, in fact, $\cos 2\theta$. ψ_4 is simply the non-bonding orbital φ_4. The wavefunction is then given by

$$\Psi=O_D A[\psi_1\psi_2\psi_3\psi_4\overline{\psi}_1\overline{\psi}_2\overline{\psi}_3]\,, \tag{3}$$

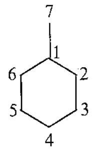
where O_D is a doublet projection operator and A is the antisymmetrizer. Spin densities were calculated using the methods of Pauncz [18] and Harris [19]. It should be noted that there are typographical errors in Eq. (6.72) of Ref. [18]. The correct formula is

$$\begin{aligned}\langle\Psi|F_z|\Psi\rangle=\frac{1}{2}\,\frac{S}{S+1}\Bigg\{\sum_{i=1}^{\nu}\Bigg[\sum_{r=0}^{\nu-1}(-1)^r C_r\,{}^iS_r[|a_{\rm I}(0)|^2\\ -|\overline{a}_{\rm I}(0)^2]-\sum_{r=0}^{\nu-1}(-1)^{r+1}C_{r+1}\,{}^iS_r[-2|a_{\rm I}(0)|^2+a_{\rm I}^*(0)\,\overline{a}_{\rm I}(0)\,\lambda_i\\ +\overline{a}_{\rm I}^*(0)\,a_{\rm I}(0)\,\lambda_i]\Bigg]+\sum_{i=\nu+1}^{\mu}|\psi_i(0)|^2\sum_{r=0}^{\nu}(-1)^r(C_r-2C_{r+1})\,S_r\Bigg\}.\end{aligned} \tag{4}$$

c) Method of Non-Paired Spatial Orbitals

Wavefunctions in the NPSO method are constructed by the application of symmetry and spin projection operators to a single determinantal wavefunction formed by assigning electrons as far as possible to semi-localized bonding orbitals. This is done in such a way as to span the bonding regions of the molecule and as far as possible so that electrons in adjacent semi-localized bonding orbitals have opposite spins.

The wavefunctions for the benzyl radical are constructed from the $2p\pi$ orbitals χ_i located on the carbon atoms. The numbering scheme is shown in the figure



Two choices are possible for the initial single determinantal NPSO wavefunctions for this species, namely:

Function A

$$\begin{aligned}\Psi_{\mathrm{I}(A)} = A[(\chi_1 + k\chi_2)\,\alpha(\chi_3 + k\chi_4)\,\alpha(\chi_5 + k\chi_6)\,\alpha \\ (\chi_1 + k\chi_7)\,\alpha(\chi_2 + k\chi_3)\,\beta(\chi_4 + k\chi_5)\,\beta(\chi_6 + k\chi_1)\,\beta]\end{aligned} \tag{5}$$

and Function B

$$\begin{aligned}\Psi_{\mathrm{I}(B)} = A[(\chi_1 + k\chi_2)\,\alpha(\chi_3 + k\chi_4)\,\alpha(\chi_5 + k\chi_6)\,\alpha \\ (k\chi_1 + \chi_7)\,\alpha(\chi_2 + k\chi_3)\,\beta(\chi_4 + k\chi_5)\,\beta(\chi_6 + k\chi_1)\,\beta]\,.\end{aligned} \tag{6}$$

In these functions k is a parameter to be varied to minimise the energy.

As discussed in Paper I, a wavefunction transforming as one of the irreducible representations of the point group of the molecule may be generated by the application of a symmetry projection operator. Applying the operator for the B_2 representation gives, for function A, the wavefunction

$$\Psi_{(A)} = [\Psi_{\mathrm{I}(A)} + \Psi_{\mathrm{II}(A)}]\,, \tag{7}$$

where

$$\begin{aligned}\Psi_{\mathrm{II}(A)} = A[(k\chi_2 + \chi_3)\,\alpha(k\chi_4 + \chi_5)\,\alpha(k\chi_6 + \chi_1)\,\alpha \\ (\chi_1 + k\chi_7)\,\alpha(k\chi_1 + \chi_2)\,\beta(k\chi_3 + \chi_4)\,\beta(k\chi_5 + \chi_6)\,\beta]\,.\end{aligned} \tag{8}$$

The wavefunction for function B is derived similarly.

A doublet wavefunction is generated by applying a doublet projection operator O_D to wavefunction (7)

$${}^2\Psi_{(A)} = O_D[\Psi_{\mathrm{I}(A)} + \Psi_{\mathrm{II}(A)}]\,. \tag{9}$$

The difficulties of including full spin projection in the calculation were discussed in Paper I. With full spin projection the energy would be given by

$$E = \frac{\langle(\Psi_{\mathrm{I}} + \Psi_{\mathrm{II}})|H|O_D(\Psi_{\mathrm{I}} + \Psi_{\mathrm{II}})\rangle}{\langle(\Psi_{\mathrm{I}} + \Psi_{\mathrm{II}})|O_D(\Psi_{\mathrm{I}} + \Psi_{\mathrm{II}})\rangle} \tag{10}$$

because the spin projection operator is idempotent and commutes with the Hamiltonian operator H. The difficulty lies in the calculation of $\langle\Psi_{\mathrm{I}}|H|O_D\Psi_{\mathrm{II}}\rangle$. We performed four sets of calculations with varying degrees of spin annihilation.

1. *No Spin Projection*

These calculations were made with wavefunction (7). The transformation of King *et al.* [20] was used for the calculation of integrals between individual Slater determinants.

2. *Spin Annihilation*

The quartet component was annihilated from the wavefunction $(\Psi_\mathrm{I} + \Psi_\mathrm{II})$ using the modification of the method of Amos and Hall [21] discussed in Paper I. In this approximation

$$E = \frac{\langle \Psi_\mathrm{I} | H | A'_Q \Psi_\mathrm{I} \rangle + \langle \Psi_\mathrm{I} | H | A'_Q \Psi_\mathrm{II} \rangle}{\langle \Psi_\mathrm{I} | A'_Q \Psi_\mathrm{I} \rangle + \langle \Psi_\mathrm{I} | A'_Q \Psi_\mathrm{II} \rangle}, \tag{11}$$

where A'_Q represents annihilation of the quartet component.

3. *Partial Spin Projection*

An improvement on method 2 is to use the energy expression

$$E = \frac{\langle \Psi_\mathrm{I} | H | O_D \Psi_\mathrm{I} \rangle + \langle \Psi_\mathrm{I} | H | A'_Q \Psi_\mathrm{II} \rangle}{\langle \Psi_\mathrm{I} | O_D \Psi_\mathrm{I} \rangle + \langle \Psi_\mathrm{I} | A'_Q \Psi_\mathrm{II} \rangle}. \tag{12}$$

4. *Spin Projection in Diagonal Term of Energy Expression*

In view of the fact that methods 2 and 3 involve considerable computation, we suggested in Paper I that a reasonable way of doing the calculation would be to use the energy expression

$$E = \frac{\langle \Psi_\mathrm{I} | H | O_D \Psi_\mathrm{I} \rangle + \langle \Psi_\mathrm{I} | H | \Psi_\mathrm{II} \rangle}{\langle \Psi_\mathrm{I} | O_D \Psi_\mathrm{I} \rangle + \langle \Psi_\mathrm{I} | \Psi_\mathrm{II} \rangle}. \tag{13}$$

We included this method in order to see whether our assertion was true in the case of the benzyl radical. In the calculation of the integrals $\langle \Psi_\mathrm{I} | H | O_D \Psi_\mathrm{I} \rangle$ and $\langle \Psi_\mathrm{I} | H | A'_Q \Psi_\mathrm{I} \rangle$ the orbitals were first transformed to "corresponding" [21] or "paired" orbitals [22] and the formulae of Harris [19] were then used. In the integrals $\langle \Psi_\mathrm{I} | H | A'_Q \Psi_\mathrm{II} \rangle$, $A'_Q \Psi_\mathrm{II}$ was expressed as a sum of Slater determinants and the method of King *et al.* [20] was used for each individual integral in the expression.

3. Results

The results of the energy calculations using both sets of integral approximations are given in Table 1. The pattern of the results is roughly the same for both methods of calculating the one electron integrals. We examined two different integral approximations because in our initial UHF calculations using the Ruedenberg method, we obtained unreasonable orbitals although the energy was of the correct order. The same behaviour was observed with the GMS integrals. The UHF results must therefore be regarded with suspicion. Several possible explanations for the anomalous orbitals were considered but did not resolve the matter. The SCF program behaved perfectly normally for closed shell calculations on naphthalene and azulene [1].

The results in Table 1 indicate that NPSO functions of type A are more successful in lowering the energy than those of type B. The performance of the NPSO method is comparable with that of the AMO method for this system. Both methods give substantially lower energies than the RHF method, showing that they are effective in allowing for electron correlation.

Table 1. Energies for wavefunctions for the benzyl radical

	Ruedenberg one electron integrals		Goeppert-Mayer Sklar one electron integrals	
Method	Energy (eV)	k	Energy (eV)	k
Molecular orbital				
Eigenvectors of overlap matrix	−303.9154		−218.8816	
RHF	−305.6740		−219.8315	
UHF	−308.8357		−223.1363	
Alternant molecular orbital method	−308.6701	0.5866[a]	−223.5855	0.5898[a]
NPSO (function A)				
1	−308.6047	4.2	−223.0043	4.99
2	−309.4675	4.83	−223.8714	5.78
	(−309.4167	4.0)	(−223.7067	4.0)
3	−309.5968	4.85	−223.9927	5.75
	(−309.5413	4.0)	(−223.8199	4.0)
4	−309.1104	4.87	−223.5265	5.8
	(−309.0564	4.0)	(−223.3551	4.0)
NPSO (function B)				
1	−307.5750	0.236	−222.2996	0.227
2	−308.3498	0.208	−223.0785	0.2005
	(−308.3075	0.25)	(−223.0169	0.25)
3	−308.4520	0.209	−223.1799	0.20
	(−308.4090	0.25)	(−223.1173	0.25)
4	−307.9956	0.205	−222.7274	0.197
	(−307.9477	0.25)	(−222.6590	0.25)

[a] This value is $\lambda = \cos 2\theta$.

The results for the NPSO functions using methods 2, 3, 4 (energy expressions (11–13)) follow the pattern we observed for naphthalene and azulene and support our suggestion that calculations using energy expression (13) are a reasonable approximation. The use of methods 2 and 3 (i.e. with more complete annihilation of the quartet component) produces only a slight improvement in the energy and the value of k changes very little. The optimum values for k are also in the region of 4 (or 0.25) and the results for these values show that no serious errors would be introduced by the assumption of $k = 4$ (or 0.25). Thus, the results of our present calculations are in accord with the suggestion of Empedocles and Linnett [23]. We feel that we can now write down reasonable NPSO functions for larger systems such as polycyclic aromatic hydrocarbons on the basis of the calculations for smaller systems [1, 23].

The diagonal elements of the calculated spin density matrices are given in Table 2 for the NPSO function A obtained by methods 3 and 4. Function B gave spin densities which were not in accord with experiment and must therefore be rejected. The pattern of the spin densities calculated by the NPSO method is in poor accord with the observed hyperfine coupling constants [24]. The method

Table 2. Calculated spin densities for the benzyl radical

Method	ϱ_1	ϱ_2	ϱ_3	ϱ_4	ϱ_7
	a) Ruedenberg one electron integrals				
RHF	0.006	0.065	0.000	0.030	0.850
AMO	−0.264	0.451	−0.270	0.455	0.537
NPSO (function A)					
3	−0.589	0.696	−0.594	0.687	0.709
4	−0.483	0.616	−0.501	0.604	0.658
	b) Goeppert-Mayer Sklar one electron integrals				
RHF	0.002	0.031	0.000	0.014	0.960
AMO	−0.263	0.450	−0.269	0.454	0.538
NPSO (function A)					
3	−0.619	0.718	−0.618	0.711	0.722
4	−0.516	0.641	−0.530	0.631	0.673
Experimental[a] hyperfine coupling constants (gauss)		5.14	1.75	6.14	16.35

[a] Ref. [24].

grossly overestimates the spin densities on the ring atoms. The RHF and AMO spin densities are also not in very good agreement with experiment.

There are several possible explanations for the poor results for the spin density calculations. The assumption of a regular geometry appears to be an invalid assumption [7, 8] but would not be expected to distort seriously the results. The present calculations are the only published calculations on the benzyl radical which have used the Ruedenberg or the GMS one electron integrals and included all the two electron integrals. It would appear that these approximations do not yield good results for spin density calculations. The omission of full spin projection may be a reason for the poor performance of the NPSO method. This neglect seems to have only a small effect on the energy but may have a more profound effect on the spin density distribution.

4. Conclusion

The calculations presented in this paper indicate that the use of NPSO wavefunctions for the benzyl radical leads to considerably lower energies than those given by molecular orbital methods which do not allow for electron correlation. Using one adjustable parameter, the NPSO and AMO methods give comparable lowerings. Although on the energy criterion the NPSO method seems to be successful in allowing for electron correlation, the calculated spin densities are in poor accord with experiment. On the basis of our calculations it seems that the use of the Ruedenberg and GMS methods for one electron integrals and the use of theoretical values for Coulomb integrals is much less successful than the use of semi-empirical methods [6].

Appendix

Table 3 contains the integral values used in these calculations. The orbital exponents for the carbon atom were those quoted by Ruedenberg [16].

Table 3

			One electron integral (eV)	
	Overlap integral	Coulomb integral (eV)	Ruedenberg approximation	GMS approximation
11	1.0	17.227026	-70.476281	-56.533172
22	1.0	17.227026	-64.635252	-52.514399
33	1.0	17.227026	-62.783655	-50.654663
44	1.0	17.227026	-62.351705	-50.220483
77	1.0	17.227026	-53.508749	-43.192025
12	0.246821	9.028474	-18.248177	-15.286945
13	0.034704	5.651135	- 2.011101	- 2.011578
14	0.015452	4.949867	- 0.892108	- 0.892315
37	0.001934	3.799537	- 0.100433	- 0.100458
47	0.000585	3.367587	- 0.030258	- 0.030260
17			-17.179095	-14.217767
23			-17.602871	-14.641567
24			- 1.945002	- 1.945453
25			- 0.869352	- 0.869559
26			- 1.984626	- 1.985087
27			- 1.834309	- 1.834756
34			-17.321058	-14.359686
35			- 1.920368	- 1.920836
36			- 0.869352	- 0.869559

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