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Use of Orthogonalised Atomic Orbitals in π-Electron Systems

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It is shown that Löwdin-orthogonalised Slater-type orbitals yield reasonable spin densities in the case of the trimethylene-methyl- and allyl radical.

It is well known that the use of an orthogonal set of atomic orbitals leads to great simplifications in the calculation of energies and other properties from molecular wave functions. It has also been shown [1] that, of all possible sets of orthogonalised atomic orbitals (OAO's), the Löwdin orthogonalised atomic orbitals (LOAO's) [2] are closest to the original set of atomic orbitals (AO's) by a least squares criterion. Hence, any loss of physical correspondence in going from the AO's to OAO's is minimized when LOAO's are used. Moreover, the use of LOAO's is closely related to the zero differential overlap approximation [3–5] and may readily lend itself to various treatments.

On the other hand, non-paired spatial orbital (NPSO) wave functions have proved to be remarkably close to configuration-interaction (CI) functions when Slater-type orbitals (STO) are used [6, 7]. It would be natural to ask how accurate NPSO wave functions are when one uses LOAO's. Such a test was suggested by Pauncz [8] and then by Chong [9]. Recently, Duke [10] tested the use of LOAO's on the allyl cation and the diborohydride anion, and concluded that the use of LOAO's in NPSO calculations did not look very promising.

The object of this work is to extend the test to the allyl and trimethylenemethyl radicals. Besides the energies, the spin density matrices for these radicals are also calculated.

The wave functions for allyl have been defined by Hirst and Linnett [6] and by Chong and Linnett [11]. Construction of the $S_z = 1$ component of the ${}^3A_2$ ground state of trimethylenemethyl follows a procedure analogous to the derivation of the $S_z = 0$ component by Chong and Linnett [7]. Thus, the basic NPSO determinant for trimethylenemethyl is chosen to be $(a, b + kx, c + kx, x + ka)$, where x refers to the central atom and the spins are in the order $\alpha\alpha\alpha\beta$. All the necessary integrals have been presented earlier [9, 12, 13].

Spin densities are calculated by the method of McConnell [14] from wave functions using LOAO's. The spin density matrices are then transformed back from the LOAO basis to the STO basis and renormalized (trace equal to unity).

The results are summarized in Tabs. 1 and 2. The experimental spin density for trimethylenemethyl is determined by combining the observed proton hyperfine splitting of Dowd, Gold, and Sachdev [15] with the assumption that $Q = 22.5$ gauss. It can be seen that NPSO wave functions using LOAO's give

Table 1. *Energies of functions using Slater-type orbitals (STO's) and Löwdin orthogonalised orbitals (LOAO's)*

Radical	Function	Energy (hartrees)			
		STO's		LOAO's	
		$E-nW_{2p}$[a]	$E-E_{CI}$	$E-nW_{2p}$[a]	$E-E_{CI}$
Trimethylenemethyl	CI ($S_z = 1$)	-1.87690	—	-1.87690	—
	NPSO ($S_z = 1$)	-1.87544	0.00146	-1.86603	0.01087
Allyl	CI	-1.06310[b]	—	-1.06310	—
	NPSO	-1.06270[b]	0.00040	-1.06204	0.00106
	AMO	-1.06189[b]	0.00121	-1.06217	0.00093
	VB	-1.06061[b]	0.00249	-1.05310	0.01000
	MO	-0.99691[b]	0.06619	-0.99691	0.06619

[a] For trimethylenemethyl, $n = 4$; for allyl, $n = 3$.

[b] Results from Ref. [11].

Table 2. *Comparison of spin density matrix elements (see text for details of present calculations)*

Radical	Function	Elements of spin density matrix[a]			
		ϱ_{aa}	ϱ_{ax}	ϱ_{ac}	ϱ_{xx}
Trimethylenemethyl	CI	0.388	0.000	-0.093	-0.164
	NPSO	0.397	0.021	-0.096	-0.192
	MO	0.333	—	—	0.000
	URHFSCF[b]	0.374	—	—	-0.121
	Experimental	0.396	—	—	-0.187
Allyl	CI	0.614	-0.125	-0.263	-0.229
	NPSO	0.609	-0.014	-0.285	-0.219
	MO	0.500	—	—	0.000
	semi-emperical EHF[c]	0.626	—	—	-0.252
	Experimental[d]	0.581	—	—	-0.162

[a] The central atoms for both radicals are labelled "x" in this table.

[b] A. D. McLachlan: Molecular Physics **5**, 51 (1962).

[c] A. D. McLachlan: Molecular Physics **3**, 233 (1960).

[d] Work of Fessenden. See D. M. Hirst and J. W. Linnett: J. Chem. Soc. (London) **1963**, 1068.

energies inferior to STO-NPSO functions. However, the relatively small sacrifice in the energy, the moderate success in the spin density, and the tremendous simplification in the computations all indicate that the extension of the use of LOAO's to larger π-electron systems appears to be more promising than Duke [10] suggested.

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