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Further *ab initio* Calculations on the Allyl Radical

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Further *ab initio* calculations of proton coupling constants using the LCGO technique are presented for the allyl radical, showing varying degrees of success.

Es werden weitere *ab initio* Rechnungen für die Proton-Kopplungskonstante angegeben wobei die LCGO-Methode auf das Allylradikal mit unterschiedlichem Erfolg angewandt wird.

Introduction

In a previous publication [1] the results of preliminary *ab initio* calculations of ESR hyperfine coupling constants in the allyl radical were presented. Each Slater type orbital (STO) was represented by a linear combination of two Gaussian orbitals (GTOs), and two different linear combinations (contractions) were reported. Considering the relative lack of sophistication of the wavefunctions employed, the results were found to be in fair agreement with experiment, and compared well with the results obtained from semi empirical calculations.

In this publication we present the results of similar calculations employing more accurate wavefunctions. The reason for extending the calculations by using a larger number of GTOs in the contraction is that, whereas small contractions are clearly very poor for energy calculations, this gives little guide as to their usefulness for the calculation of molecular properties; thus hopefully it should be possible to use very simple wavefunctions for the *ab initio* calculation of certain molecular properties, although the converse may be true.

Method

A number of differet contractions were tried in order to assess the sensitivity of the proton ESR coupling constants. The STO hydrogen exponent was assumed to be 1.2 throughout, instead of the free atom value 1.0; A number of contractions exist in the literature for free atoms, the ones used in the present work being given in Table 1 [2, 3]. Thus each STO was approximated by GTO where $n = 2, 3, 4, 5, 6$ (referred to as A, B, C, D, E) and a further calculation was performed (F) to check that the proton coupling constant calculation is insensitive to the precise form of the carbon $1s$ orbital. For this calculation, the carbon $1s$ orbitals were approximated as 6 GTO whilst the valence orbitals were approximated by 3 GTO.

All integrals were calculated using a version of IBMOL 4 [4] specially rewritten for the University of Manchester ICL 1906 Å computer, running under the GEORGE III operating system [1]. It is unfortunately impossible to report the exact mill times taken for integral calculation, as this figure cannot be obtained

Table 1. Contractions used

H		K_c		S_c		X_c		
d	α	*d*	α	*d*	α	*d*	α	
0.4301	1.2266	0.4301	27.6756	0.7471	0.3412	0.4523	1.1418	A
0.6789	0.2183	0.6789	4.9262	0.2856	0.1296	0.6713	0.2824	
0.1543	3.2078	0.1677	69.6723	-0.2888	8.3652	0.2332	2.3235	B
0.5353	0.5843	0.5434	12.4425	0.7008	0.3794	0.5743	0.5014	
0.4446	0.1581	0.4320	3.2222	0.3734	0.1223	0.4132	0.1318	
0.0568	7.5123	0.0649	158.7920	-0.0874	32.1659	0.0997	4.6202	C
0.2601	1.3747	0.2815	28.8682	-0.2444	5.5509	0.3560	1.0573	
0.5328	0.3819	0.5339	7.8246	0.6465	0.4253	0.5289	0.3113	
0.2916	0.1267	0.2707	2.4906	0.4479	0.1346	0.2545	0.0988	
0.0221	16.2804	0.0267	331.7210	-0.0221	109.0350	0.0437	8.4706	D
0.1354	2.9833	0.1322	60.6526	-0.0994	19.4645	0.1906	1.9972	
0.3318	0.8333	0.3580	16.7641	-0.2188	4.9297	0.4054	0.6365	
0.4826	0.2845	0.4736	5.5702	0.6386	0.4343	0.4439	0.2220	
0.1936	0.1072	0.1632	2.0004	0.4602	0.1366	0.1576	0.0791	
0.0092	33.2684	0.0092	750.6175	-0.0042	73.1160	0.0079	15.4981	E
0.0494	6.0997	0.0494	137.6249	-0.0207	13.4087	0.0514	4.0416	
0.1685	1.7065	0.1685	38.5025	-0.0515	3.7681	0.1898	1.4461	
0.3705	0.5862	0.3705	13.2266	0.3346	0.5389	0.4050	0.6045	
0.4165	0.2276	0.4165	5.1363	0.5621	0.2446	0.4013	0.2764	
0.1303	0.0938	0.1303	2.1154	0.1713	0.1166	0.1052	0.1307	

from the computer to any degree of accuracy. As a rough approximation however, for $n=2$ the two electron integrals took 180 seconds whilst for $n=4$ the mill time was approximately 2000 seconds.

The self consistent field method used to calculate the wavefunctions was the Unrestricted Hartree Fock (UHF) method [5] which averaged 200 sec to obtain accuracy in the density matrices to 5 decimals, depending on the goodness of the initial guesses for the density matrices. As before, the allyl radical was assumed to be planar with regular geometry, all CC bond lengths 1.4 Å, all CH bond lengths 1.08 Å. No attempt was made to find the lowest energy conformation, although it was not expected that any change in geometry would affect the results significantly.

Results and Discussion

The nuclear repulsion energy was 64.83595 a.u., whilst the electronic energies are given in Table 2. The best energy was given by the $n=5$ set, this contraction corresponding to the best $n=5$ contraction for the carbon atom in its ${}^3p$ state [3]. The $n=6$ set was slightly inferior, due to the different method of finding the contraction [2]. For large systems however, the small improvements in energy and wavefunction that result from using $n>4$ seem hardly justifiable in the face of the increased cost of the calculation (proportional to n^4 approximately).

Table 2

Basis	$\langle S^2\rangle_{ba}$	$\langle S^2\rangle_{aa}$	Energy	Density at nucleus
A	1.0252	0.7632	−176.5639	0.262
B	0.9657	0.7548	−179.6109	0.362
C	0.9902	0.7580	−180.6720	0.429
D	0.9954	0.7587	−180.9997	0.495
E	1.0597	0.7679	−180.9893	0.486
F	0.9645	0.7548	−180.7283	0.368

Energies and density at nucleus in atomic units.

Table 3

Basis	1	2	3
A	−26.79	−26.89	+19.06
	− 8.78	− 8.81	+ 6.49
B	−28.35	−28.61	+20.14
	− 9.32	− 9.41	+ 6.86
C	−36.76	−37.14	+26.21
	−12.06	−12.18	+ 8.88
D	−42.45	−42.96	+29.99
	−13.91	−14.08	+10.18
E	−53.95	−54.30	+39.94
	−17.64	−17.76	+13.67
F	−28.33	−28.59	+20.10
	− 9.32	− 9.40	+ 6.78
Experiment	−13.93	−14.83	+ 4.06

Proton coupling constants (gauss).

UHF calculations, as is well known [5] are not accurate descriptions of spectroscopic states, since they are not spin eigenfunctions. Such wavefunctions can be improved by the spin annihilation technique of Amos and Snyder [5]. Values of $\langle S^2\rangle_{ba}$ and $\langle S^2\rangle_{aa}$ in the notation of [5] are given in Table 2: spin annihilation generally makes a large improvement in the value of $\langle S^2\rangle$.

The results for Basis A ($n=2$) were reported previously [1], but unfortunately there was an error in the coupling constants reported in [1], for that particular basis set. We report here the corrected values in Table 3, together with the results for the other basis sets.

In general, the coupling constants calculated *before* spin annihilation are too large, whilst the ones calculated after spin annihilation are in much better agreement with experiment. The results for the central proton become less good as n increases, and a general unwelcome trend is obvious from the table, that the coupling constants increase in modulus as n increases. This is because the one and two electron integrals for all except the carbon 1s orbitals change little as n increases, so consequently the molecular orbital coefficients change little as n increases. However, the density of the hydrogen 1*s* orbital at the nucleus changes by 100%, as can be seen from Table 2. For comparison, the exact value for a Slater hydrogen 1*s* orbital $\sqrt{\zeta^3/\pi\, e^{-r}}$ is $\zeta^3/\pi = 0.55$ for $\zeta = 1.2$. The density at the nucleus is seriously in error, even for the most accurate contraction taken ($n = 5$). Further, the shapes of GTOs and STOs around the nucleus is quite different.

Treating the density at the nucleus as a variable parameter still gives the same overall pattern of coupling constants, and does not correctly reproduce their experimental ratio.

As before [1] we may compare our results with the results of a semi empirical calculation using the Pariser-Parr integrals [6]. The Pariser-Parr model may be regarded as using an *orthogonalised* basis of π type atomic orbitals $(\bar{\varphi}_1 \ldots \bar{\varphi}_m)$ for the construction of π molecular orbitals. These are related to the non-orthogonal $2p_z$ orbitals $(\varphi_1 \ldots \varphi_m)$ by the transformation

$$(\bar{\varphi}_1 \ldots \bar{\varphi}_m) = (\varphi_1 \ldots \varphi_m)\boldsymbol{S}^{-\frac{1}{2}}$$

where $S_{ij} = \langle \varphi_i | \varphi_j \rangle$ is the matrix of overlap integrals. *Ab initio* calculations are generally performed using a non orthogonal basis, for ease of computation, and if $\boldsymbol{P}_1(r)$, $\boldsymbol{Q}_1(r)$ are the one electron charge and spin density functions respectively [7], where

$$\begin{aligned} \boldsymbol{P}_1(r) &= \Sigma\, \varphi_i^*(r)\,(\boldsymbol{P}_1)_{ij}\,\varphi_j(r) \\ \boldsymbol{Q}_1(r) &= \Sigma\, \varphi_i^*(r)\,(\boldsymbol{Q}_1)_{ij}\,\varphi_j(r) \end{aligned} \tag{1}$$

and $\boldsymbol{P}_1$, $\boldsymbol{Q}_1$ are their matrix representations, and also

$$\begin{aligned} \boldsymbol{P}_1(r) &= \Sigma\, \bar{\varphi}_i^*(r)\,(\boldsymbol{P}_1)_{ij}\,\bar{\varphi}_j(r) \\ \boldsymbol{Q}_1(r) &= \Sigma\, \bar{\varphi}_i^*(r)\,(\boldsymbol{Q}_1)_{ij}\,\bar{\varphi}_j(r) \end{aligned} \tag{2}$$

then

$$\begin{aligned} \bar{\boldsymbol{P}}_1 &= \boldsymbol{S}^{\frac{1}{2}}\boldsymbol{P}_1\boldsymbol{S}^{\frac{1}{2}} \\ \bar{\boldsymbol{Q}}_1 &= \boldsymbol{S}^{\frac{1}{2}}\boldsymbol{Q}_1\boldsymbol{S}^{\frac{1}{2}} \end{aligned} \tag{3}$$

so the elements of $\boldsymbol{P}_1$, $\boldsymbol{Q}_1$ obtainable from our *ab initio* calculation by (3) should be directly comparable to the semi empirical results.

For the semi empirical calculation we find

$$\bar{\boldsymbol{P}}_1 = \begin{pmatrix} 1.000 & 0.693 & 0.000 \\ & 1.000 & 0.693 \\ & & 1.000 \end{pmatrix} \quad \bar{\boldsymbol{Q}}_1 = \begin{pmatrix} 0.551 & 0.000 & -0.425 \\ & -0.102 & 0.000 \\ & & 0.551 \end{pmatrix}$$

whilst for the $n = 5$ *ab initio* calculations we obtain

$$\bar{\boldsymbol{P}}_1 = \begin{pmatrix} 1.000 & 0.671 & 0.000 \\ & 1.000 & 0.671 \\ & & 1.000 \end{pmatrix} \quad \bar{\boldsymbol{Q}}_1 = \begin{pmatrix} 0.570 & 0.000 & -0.370 \\ & -0.140 & 0.000 \\ & & 0.570 \end{pmatrix}$$

which compare reasonable well. It is interesting to note that, assuming the proton coupling constants can be calculated using McConnell's relation [8] with a proportionality constant -22.5 gauss, the "experimental" diagonal elements of $\bar{Q}_1$ are 0.58, -0.16 and 0.58, which compare alomost exactly with our calculation. It is also interesting to note that the diagonal elements of $\bar{P}_1$ are 1.000. The discrepancy in the *ab initio* calculation of coupling constants arises because of the relatively inaccurate representation of the σ system.

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