

THE HYPERFINE COUPLING CONSTANTS OF THE FIVE LOWEST STATES OF CH: AN AB INITIO MRDCI STUDY

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The isotropic (a_{iso}) and the anisotropic (a_{aniso}) hyperfine coupling constants of the five lowest states of the CH molecule, $X^2\Pi$, a $^4\Sigma^-$, $A^2\Delta$, $B^2\Sigma^-$ and $C^2\Sigma^+$ have been calculated. The agreement with experimental data is excellent for a_{aniso} and within about 8% for a_{iso} . Differences in the values for the various states are discussed at the RHF and CI levels. For $X^2\Pi$ and $A^2\Delta$ the effects of the doubly occupied shells are studied. It turns out that in these states the contributions of the 1σ and 2σ shells to a_{iso} are opposite in sign.

1. Introduction

A direct measurement of the unpaired spin distribution in a molecule is given by the isotropic and anisotropic hyperfine coupling constants (hfcc). For a nucleus N they are defined as [1,2]

$$a_{iso} = \frac{4}{3} \pi g_e g_N \beta_e \beta_N \Sigma^{-1} \langle qA\Sigma | \sum_i \delta(r_{iN}) S_{zi} | qA\Sigma \rangle, \quad (1)$$

$$a_{aniso} = \frac{3}{2} g_e g_N \beta_e \beta_N \Sigma^{-1} \times \langle qA\Sigma | \sum_i \frac{3 \cos^2 \theta - 1}{r_i^3} S_{iz} | qA\Sigma \rangle. \quad (2)$$

It is seen that a_{iso} is proportional to the net unpaired spin density at the nucleus N and that a_{aniso} gives a measure of the spatial distribution of the spin density at the nucleus N.

Because of the delta function, only orbitals with a non-vanishing spin density at the nucleus can contribute. For atoms, only s orbitals, and for diatomic molecules only σ orbitals possess this property. Therefore, in systems in which these orbitals are doubly occupied the value of a_{iso} depends solely on electron correlation. On the other hand, for systems

which possess a single orbital of this type, such as the lithium atom, the importance of electron correlation is expected to be smaller but not negligible [3]. For a_{aniso} the influence of electron correlation is small, but its value is quite sensitive to the composition of the basis set [4]. For the carbon hydride radical the ground state $X^2\Pi$ is derived from the electron configuration (core) $\sigma_p^2 \pi^1$ where the core is $\sigma_s^2 \sigma_s^2$ having all σ -type orbitals doubly occupied. The four lowest excited states, a $^4\Sigma^-$, $A^2\Delta$, $B^2\Sigma^-$ and $C^2\Sigma^+$ are derived from (core) $\sigma_p^1 \pi^2$, having one σ orbital singly occupied. Therefore, the CH molecule should be a good system to study the various factors effecting the hyperfine coupling constants (hfcc).

Previous ab initio calculations on CH dealing with the hyperfine structure of the molecule have been carried out on the ground state and the $A^2\Delta$ state [2,5].

Experimentally the carbon hydride radical has been the subject of many spectroscopic as well as astrophysical investigations. Using various techniques the hfcc for the hydrogen center of $X^2\Pi$, $A^2\Delta$ and $C^2\Sigma^+$ [6-8] were measured. For the carbon center no experimental data are available.

In the present work we discuss several aspects of our study on the hfcc of the five lowest states of the

CH molecule. A more detailed representation of our results will be given elsewhere [7].

2. Method

The basis set for carbon consists of the (13s8p) primitive Gaussian of van Duijneveldt [10] in a [8s5p] contraction, augmented by two d and one polarization function. The exponents of the d functions, 1.5 and 0.4, were energy optimized, while the exponent of the f function (0.7) was taken from the literature [11]. No further basis functions, e.g. p, d functions with higher exponents, were added, because for NH it was found that their effects on the hfcc are small [12].

For hydrogen we used the (8s) basis set of van Duijneveldt in a [5s] contraction, augmented by two p polarization functions with exponents 1.4 and 0.25 [13].

The calculations were performed with the MRDCI package of Buenker and Peyerimhoff [14,15]. The $a^4\Sigma^-$ MOs were used in all calculations, because in this state π_x and π_y orbitals are symmetrically occupied. All calculations were performed at the experimental equilibrium distance [16].

The quality of the basis set and the CI calculations can be judged by comparing calculated excitation energies with experimental values as summarized in table 1. With the exception of the $a^4\Sigma^-$ state, the values are about 2% too high. In contrast to this the $a^4\Sigma^-$ is too low, which is probably due to the use of its SCF MOs in all calculations. To gain insight into the spin polarization mechanism, core calculations in which either the 1σ , or $2\sigma_g$ orbital was frozen

[17,18] were performed. For these calculations we used smaller basis set including only one d polarization function with an exponent of 0.6. No f function was used. The values for the Hartree-Fock approximation were obtained by performing CI calculations with a very high selection threshold.

3. Results and discussion

The RHF results are summarized in table 2. The table contains the hfcc formulae of the various states which result if the HF wavefunctions given by Raftery et al. [19] are used. In addition, expectation values for the RHF approximation, calculated by using the $a^4\Sigma^-$ MOs, are also given. The results of the CI calculations are collected in table 3. From experimental work the hfcc at the hydrogen center are known for $X^2\Pi$, $A^2\Delta$ and $C^2\Sigma^+$. For comparison they are summarized together with the theoretical values of Kristiansen et al. [2] in table 4. The core calculations, performed for $X^2\Pi$ and $A^2\Delta$, are given in table 5.

A comparison of the RHF values with the CI results or experimental data shows that the RHF approximation is able to explain the qualitative differences between the hfcc of the various states, and furthermore, the a_{aniso} results are in moderate to good agreement with experiment. Smaller differences in a_{aniso} , e.g. between $A^2\Delta$ and $C^2\Sigma^+$, are reproduced by the CI method only. Using the CI method the a_{aniso} values are in excellent agreement with experiment, deviations lying within the experimental error bars (table 4). In addition to the values given in table 4, Kristiansen et al. [2] calculated the hfcc of the carbon center for $X^2\Pi$. They obtained $a_{\text{aniso}} = -131$ MHz, so that for both centers the theoretical results agree with each other. An analysis of our results shows that both RHF and CI methods predict large differences between the a_{aniso} values for the various excited states at the carbon center but very small ones for those at the hydrogen center. For hydrogen this trend is confirmed by the experimental data.

A full interpretation of these effects will be given elsewhere [9]. From a theoretical point of view a_{iso} is the more difficult property to calculate. It depends very strongly on correlation effects. Because in $X^2\Pi$ all σ orbitals are doubly occupied, the RHF values

Table 1
Excitation energies (in eV) of the various states of the CH molecule

Electron configuration	State	Excitation energy	
		exp. [16]	this work
$\sigma^2\pi^1$	$X^2\Pi$	0.0	0.0
	$a^4\Sigma^-$	0.72	0.65
$\sigma^1\pi^2$	$A^2\Delta$	2.88	2.93
	$B^2\Sigma^-$	3.23	3.30
	$C^2\Sigma^+$	3.94	4.01

Table 2

Summary of the calculated hfcc within the RHF approach. \hat{O} is defined using eq. (1) or (2)

Configuration	Wavefunction [19]	Formula of hfcc	a_{aniso} (MHz)		a_{iso} (MHz)	
			^{13}C	^1H	^{13}C	^1H
X $^2\Pi$	$ \sigma\delta\pi^+\rangle$	$\langle\pi^+ \hat{O} \pi^+\rangle$	-129	54	0	0
a $^4\Sigma^-$	$ \sigma\pi^+\pi^-\rangle$	$\frac{2}{3}\langle\pi^+ \hat{O} \pi^+\rangle + \frac{1}{3}\langle\sigma \hat{O} \sigma\rangle$	-41	54	425	84
A $^2\Delta$	$ \sigma\pi^+\pi^-\rangle$	$\langle\sigma \hat{O} \sigma\rangle$	137	51	1276	253
B $^2\Sigma^-$	$6^{-1/2}(\sigma\pi^+\pi^-\rangle - \sigma\pi^-\pi^-\rangle - \sigma\pi^+\pi^-\rangle)$	$\frac{2}{3}\langle\pi^+ \hat{O} \pi^+\rangle - \frac{1}{3}\langle\sigma \hat{O} \sigma\rangle$	-218	56	-425	-84
C $^2\Sigma^+$	$2^{-1/2}(\sigma\pi^+\pi^-\rangle - \sigma\pi^-\pi^-\rangle)$	$\langle\sigma \hat{O} \sigma\rangle$	137	51	1276	253

Table 3

Summary of the calculated hfcc using the CI wavefunction

	^{13}C		^1H	
	a_{aniso}	a_{iso}	a_{aniso}	a_{iso}
X $^2\Pi$	-127.5	36	58.8	-53
a $^4\Sigma^-$	-37.4	363	56.1	101
A $^2\Delta$	152.1	865	61.4	533
B $^2\Sigma^-$	-221.1	-90	50.7	-337
C $^2\Sigma^+$	154.2	764	65.4	569

Table 4

Hyperfine coupling constants a_{aniso} and a_{iso} (in MHz) of the hydrogen center given by the literature

	Theoretical ^{a)}		Experimental	
	a_{aniso}	a_{iso}	a_{aniso}	a_{iso}
X $^2\Pi$	58.1	-59	57.2 ^{b)}	-58 ^{a)}
A $^2\Delta$	63.7	531	61.1 (± 2) ^{c)}	583 (± 1) ^{b)}
C $^2\Sigma^+$			56.6 (± 7) ^{d)}	620 (± 3.5) ^{c)}

^{a)} Ref. [2]. ^{b)} Ref. [6]. ^{c)} Ref. [7]. ^{d)} Ref. [8].

Table 5

Summary of the core calculations for the X $^2\Pi$ and the A $^2\Delta$ (a_{iso} given in MHz)

Correlated shell	X $^2\Pi$		A $^2\Delta$	
	^{13}C	^1H	^{13}C	^1H
$3\sigma_p$	73	21	1234	217
$2\sigma_s/3\sigma_p$	137	-58	804	544
$1\sigma_s/3\sigma_p$	-49	20	1321	220

of a_{iso} of both centers are zero, so that here a_{iso} results from correlation effects only. For the excited states the σ_p orbital is singly occupied, so that the RHF approximation predicts a_{iso} to be different from zero. As a comparison with the CI results reveals, corrections due to correlation effects are about 50%.

Using the CI method the deviations from experiment are about 8% with the absolute value always calculated too low. As was shown in a previous paper [17], a_{iso} depends strongly upon the SAF selection threshold used in the CI calculations [15]. We expect that improvement of the CI calculations by incorporating more of the less important SAFs which were previously neglected should improve the agreement with experiment. A full discussion of this problem will be given elsewhere.

The improvement in the RHF values by the CI method arises out of two sources. First of all instead of using optimized MOs for each state the RHF values are obtained by using the a $^4\Sigma^-$ MOs. The magnitude of this error can be seen by a comparison with the study of Kristiansen et al. [2], who used many-body perturbation theory (MBPT) to third order. Their first-order value is in better agreement with experiment than our RHF results (by about 20%). A study of this error is possible by using natural orbitals (NO). The second source consists of contributions from doubly occupied σ shells, which are completely neglected within the RHF approximation. These effects can be studied by performing core calculations [18], which are summarized in table 5. Since the correlation effects for a_{aniso} are small, only the a_{iso} values are given.

To separate the contribution of the three σ -type shells we performed three core calculations in which

we either correlated the $3\sigma_p$ shell only or the $3\sigma_p$ shell together with one of the two σ_s shells. The π shells are correlated in each calculation. Clearly not incorporated in these core calculations is the intershell correlation between the $1\sigma_s$ and $2\sigma_s$, for example, but these effects are smaller.

For $X^2\Pi$ a comparison with all-electron CI calculations (table 3) shows a large positive contribution of the $3\sigma_p$ shell for the carbon center. If in addition the $2\sigma_s$ shell is also correlated, a_{iso} further increases. If $1\sigma_s$ instead of $2\sigma_s$ is correlated a_{iso} becomes negative, which points to a large negative contribution from the $1\sigma_s$ shell.

For hydrogen it can be seen from table 5 that the $1\sigma_s$ contribution is nearly zero. The dominant contribution arises out of the $2\sigma_s$ shell, which possesses a negative sign, while the $3\sigma_p$ contribution is positive but less important. The situation is similar to that of the $X^3\Sigma^-$ state of NH [12]. For $A^2\Delta$ the picture changes. For both centers, contributions from the $1\sigma_s$ and $2\sigma_s$ shells change in sign. Since the $3\sigma_p$ orbital is only singly occupied the RHF approximation gives the dominant effect (in contrast to the ground state), but the contributions of the lower shells cannot be neglected. Correlating the $3\sigma_p$ shell, a_{iso} is corrected to smaller values at both centers (relative to the RHF results, table 2). If the $2\sigma_s$ shell is also correlated the value for carbon decreases while that for hydrogen increases. A correlation of $1\sigma_s$ instead of $2\sigma_s$ increases a_{iso} of the carbon center slightly while again the contribution to the hydrogen center is nearly zero. A full explanation of the various effects will be given in the more detailed presentation of our study [9].

4. Summary

In the present paper we have discussed the hfcc for the five lowest states of the CH molecule. For the anisotropic interaction our results are in excellent agreement with experiment. Correlation effects are small in all states. For the isotropic constant a_{iso} , which is more difficult to calculate, the overall deviations are only about 8%. Here, for ground and excited states, the spin polarization contributes about 50%.

Our core calculations for $X^2\Pi$ reveal that the mechanism is similar to that of the $X^3\Sigma^-$ state of the

NH molecule. For the heavier center a positive contribution from the $2\sigma_s$ and $3\sigma_p$ shells and a negative one from the $1\sigma_s$ shell is found. For the hydrogen center the $1\sigma_s$ contribution is nearly zero, whereas the $2\sigma_s$ contribution is negative and dominates the value of a_{iso} , while the $3\sigma_p$ contribution is smaller in magnitude and of opposite sign. For $A^2\Delta$ the signs of the inner shell contributions change. The importance of the individual contributions differs from that of the ground state.

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