

The Hyperfine Coupling Constants of $^{19}\text{F}_2^-$: An Ab Initio MRD-CI Basis Set Study

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Abstract

The isotropic (a_{iso}) and dipolar (A_{dip}) hyperfine coupling constants of $^{19}\text{F}_2^-$ were obtained from MRD-CI wave functions using a variety of basis sets. In series I, increasing numbers of d functions were added to a $5s4p$ contracted Huzinaga/Dunning basis. In series II, the $5s3p$ basis set was uncontracted in several steps until $9s5p$ was reached, to which were added from one to three d -polarization functions. CI parameters (selection thresholds and the number of reference configurations) were also varied. A study of the R dependence of a_{iso} and A_{dip} was performed. The best values obtained at R_e are 260 G for a_{iso} and 308 G for A_{dip} , compared with experimental values of about 280 G for a_{iso} and 320 G for A_{dip} .

1. Introduction

In a recent paper by Karna and Grein [1] (paper I), the isotropic (a_{iso}) and dipolar (A_{dip}) hyperfine coupling constants (HFCC) of ^{19}F , $^{19}\text{F}_2^-$, ^{35}Cl , and $^{35}\text{Cl}_2^-$ in their respective ground states were studied within the unrestricted Hartree-Fock (UHF) formalism. For F and F_2^- , Huzinaga's $9s5p$ basis set [2] was used in various stages of contraction, down to a $5s3p$ contraction as given by Dunning [3]. Polarization and diffuse functions were added.

It was found that A_{dip} changed little with the basis set, whereas a_{iso} decreased by a large amount when going from $5s3p$ to $6s5p2d1f$, the best contracted basis set used. After annihilation of the quartet component, (for simplicity this will be referred to as UHF-AA), a_{iso} for $^{19}\text{F}_2^-$ went from 341.3 G for a $5s3p$ basis set to 317.6 G for $6s5p2d1f$, to be compared with experimental values of 272–284 G [4–6]. For the same changes in basis set, A_{dip} went from 305.7 to 310.0 G, with experimental values ranging from 312 to 324 G [4–6]. The inclusion of d functions was found to be essential, whereas f functions caused negligible changes in the calculated HFCCs. With the uncontracted $9s5p$ basis set, a_{iso} moved slightly away from the experimental value when d functions were added. So the best agreement, 308.7 G, was obtained with $9s5p$. The value of A_{dip} changed little when uncontracted basis sets were used. Since incrementing the larger basis sets brought smaller and smaller changes of a_{iso} , it can be assumed that the above values would not change much if the basis sets were increased further.

The significant discrepancy of a_{iso} obtained by UHFAA from the experimental value indicates that better correlated wave functions are required, as one would expect for a system like F_2^- .

Obviously, UHF methods reproduce the spin density *close to* the nucleus quite well (A_{dip} depends on $1/r^3$) but are unable to describe the spin density *at* the nucleus (δ function for a_{iso}).

Systematic studies of the basis set dependence of a_{iso} for other systems such as ^{14}N using MRSD-CI wave functions were reported by Engels et al. [7] and Feller and Davidson [8]. For $^{19}\text{F}_2^-$, two theoretical studies are available: one by Nguyen and Ha [9] and the other by Carmichael [10]. The latter author used double-zeta plus one d function (DZP) and triple-zeta plus two d function (TZP) basis sets, employing UHF, PUHF, ROHF, SCI, and SDCI wave functions. The effect of diffuse functions was also tested. A more detailed comparison of Carmichael's with our results will be made later. At this time it may be noted that some of the basis sets used here are larger and that a systematic convergence of a_{iso} to the experimental value could be observed as basis sets and CI expansion increased.

In this paper, we follow the procedure used in paper I and Ref. 7. The effects of basis set increases will be studied in two ways: first, by the addition to a fixed s, p basis of one to four d functions, and second by decreasing the amount of contraction in the initially contracted s, p basis set. The effect of CI will be investigated by increasing the number of reference configurations and by decreasing the configuration selection threshold. The isotropic HFCCs will be analyzed by calculating separately the contributions from the $1s$ and $2s$ electrons. Finally, the dependence of a_{iso} and A_{dip} on the internuclear separation will be studied.

2. Basis Sets and Details of Methods

As in paper I, the $9s5p$ basis set for F due to Huzinaga [2] was used in various stages of contraction [3]. Added were a p_{neg} function with $\alpha = 0.074$ [11], and $1d$ [11], $2d$, $3d$, and $4d$ functions [12] (always using 6 components for a d function), with exponents given in Table I. Calculations were performed for the $X^2\Sigma_u^+$ ground state of F_2^- at $R = 1.88 \text{ \AA}$, an SCF optimized value available in the literature [13], and at other distances. The UHF program and spin annihilation techniques were described in paper I. For the CI calculations, MRD-CI [14–18] wave functions were used, together with the hyperfine programming package as described by Engels et al. [7]. There, the integrals for the hyperfine operators are obtained according to Chandra and Buenker [19]. Molecular orbitals obtained for the ground state of F_2^- have been used for the CI expansion. Most calculations were performed with one reference configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^4 3\sigma_u$, but for checking purposes, reference configurations corresponding to the excitations $3\sigma_g \rightarrow 6\sigma_g$ and $3\sigma_g 1\pi_g \rightarrow 3\sigma_u 2\pi_u$ (two configurations) were added. All singly and doubly excited configurations with respect to the reference configurations were generated. From the generated space, all singly excited configurations were retained automatically while the energetically most important doubly excited configurations were selected according to the chosen configuration threshold T . Energies given were extrapolated to $T = 0$.

TABLE I. Exponents of the d functions used in basis set studies of F_2^- .

	Exponent	Ref.
$1d$	0.90	11
$2d$	3.00616	12
	0.83043	
$3d$	4.96494	12
	1.77700	
	0.63601	
$4d$	6.12691	12
	2.45077	
	0.98031	
	0.39212	

Using a fairly large $6s5p2d1f$ basis set, the CI potential curve was calculated for the ground state of F_2^- , resulting in a new and improved value for R_e . For all chosen values of R , a_{iso} and A_{dip} are reported. The number of generated symmetry-adapted functions (SAFs) ranged from 5507 to 445732. From this generated set, using $T = 2\mu\text{hartree}$ ($2\text{--}5\ \mu\text{h}$ with the $6s5p2d1f$ basis set), about 2500–16500 SAFs were selected for actual diagonalization.

3. Results

Effect of Basis Set

Results obtained at $R = 1.88\ \text{\AA}$ with one reference configuration and $T = 2\mu\text{hartree}$ are listed in Tables II and III. In Table II, $1d$, $2d$, $3d$, and $4d$ basis func-

TABLE II. Isotropic (a_{iso}) and dipolar (A_{dip}) hyperfine coupling constants for $^{19}\text{F}_2^-$, using basis sets with increasing numbers of d functions, at $R = 1.88\ \text{\AA}$.

Basis Set ^b	$a_{\text{iso}}(\text{G})$		$A_{\text{dip}}(\text{G})$	
	UHFAA ^c	CI ^d	UHFAA ^c	CI ^d
$5s4p$	342.5	374.4	305.5	301.5
$5s4p1d$	325.1	320.3	306.1	301.0
$5s4p2d$	314.3	279.8	308.1	305.4
$5s4p3d$	317.1	271.2	306.1	306.5
$5s4p4d^e$	317.6	285.1	310.0	307.0

^aThe lowest energies (in hartree) are -198.85438 (UHF) and -199.35572 (CI) for $5s4p4d$.

^b $5s4p$ stands for $5s3p$ (Dunning) + p_{neg} .

^cUHF results after annihilation.

^dCI results for one reference configuration and a selection threshold $T = 2\ \mu\text{hartree}$.

^e $T = 4\ \mu\text{hartree}$.

TABLE III. Isotropic (a_{iso}) and dipolar (A_{dip}) hyperfine coupling constants for $^{19}\text{F}_2^-$, using basis sets of decreasing contraction, at $R = 1.88 \text{ \AA}$.^a

Basis Set	a_{iso} (G)		A_{dip} (G)	
	UHFAA ^b	CI ^c	UHFAA ^b	CI ^c
5s3p	341.3	373.3	305.7	306.4
5s4p	342.8	372.4	304.1	304.7
7s4p	309.2	294.8	303.8	304.8
7s4p1d	308.9	277.9	304.8	304.0
9s5p	308.6	290.6	304.3	304.9
9s5p1d	309.6	278.1	305.0	304.1
9s5p2d	313.1	262.5	305.7	307.6
9s5p3d	317.6	271.4	306.9	308.8

^aThe lowest energies are $E_{\text{UHF}} = 198.83728$ hartree and $E_{\text{CI}} = -199.39023$ hartree for 9s5p3d.

^bUHF results after annihilation.

^cCI results for 1 reference configuration and a selection threshold $T = 2 \mu\text{hartree}$.

tions were added to 5s4p (4p is the Dunning 3p contraction plus p_{neg}). The UHFAA results are given for comparison (UHF results for 5s4p4d were not contained in paper I). It is seen that A_{dip} changes little with basis set, converging to 310 G (UHFAA) and 307 G (CI), whereas a_{iso} undergoes large changes. The UHFAA value of a_{iso} appears converged at the 5s4p3d level (317 G), whereas the CI values first decrease, reaching a minimum for 5s4p3d, and then increase to 285 G for the best basis set of Table II, 5s4p4d. The final CI value of a_{iso} is in good agreement with experimental results. It may be noted that for the 5s4p basis set, a_{iso} (CI) is not as good as a_{iso} (UHFAA) but becomes better than UHFAA with the introduction of d functions.

In Table III, the s, p basis set (9s5p/5s3p) is being uncontracted from 5s3p to 9s5p. (The UHFAA results for 7s4p and 7s4p1d were not contained in paper I.) Whereas A_{dip} remains essentially constant, a_{iso} improves considerably with decreasing contraction, ending at 308.6 G for UHFAA and 290.6 G for CI. Since d functions with contracted basis sets commonly lower a_{iso} , their effect on 7s4p and 9s5p was tested. From 7s4p to 7s4p1d the CI value of a_{iso} is lowered by 17 G, whereas from 9s4p to 9s4p1d a_{iso} (CI) was lowered by about 12 G, and for 9s5p2d by another 16 G, to reach a minimum of 262.5 G. Upon addition of a third d function, however, a_{iso} (CI) moved up to 271.4 G. In contrast, the UHFAA values of a_{iso} always increased upon addition of d functions.

Effect of the Configuration Selection Threshold and the Number of Reference Configurations

As shown in Table IV, the configuration selection threshold T has been decreased in several steps from 10 to 0.001 $\mu\text{hartree}$. Always, a 5s4p1d basis set, as in Table II, was used, with one reference configuration. A noticeable change and improvement occurs for a_{iso} , going from 331 to 314 G. From about 1 μh on, further improvements of a_{iso} are minimal. A_{dip} , on the other hand, remains constant.

TABLE IV. Isotropic (a_{iso}) and dipolar (A_{dip}) CI hyperfine coupling constants for $^{19}\text{F}_2^-$, using various configuration thresholds T , at $R = 1.88 \text{ \AA}$.

T ($\mu\text{hartree}$)	No. of selected SAFs	a_{iso} (G)	A_{dip} (G)
10	4791	331.4	301.3
5	6046	328.1	301.3
2	7797	320.3	301.0
1	9273	316.3	301.0
0.025	15012	315.0	300.9
0.001	17432	314.4	300.9

*The $5s4p1d$ basis set and one reference configuration were used.

Calculations were performed using several reference configurations. All values of Table II were recalculated for four reference configurations, as described in Section 2. The a_{iso} values differ at most by 3 G and are always within 1% of the Table II results. The same is true for A_{dip} . A study done with the $5s4p3d$ basis set and $T = 2 \mu\text{hartree}$, by adding one reference configuration at a time, shows values of a_{iso} going from 281.13 to 281.21 G, and A_{dip} from 306.52 to 306.77 G, without any fluctuations. It shows again that additional reference configurations are not helpful in this case and that the correlation effect is well described by single and double excitations relative to the ground state configuration of F_2^- .

Distance Dependence of Hyperfine Coupling Constants

It could be argued that the basis sets used so far are insufficient to give a reliable value for the equilibrium distance of F_2^- . It can be assumed that diffuse and f functions are required to reproduce the experimental geometry of F_2^- . For this purpose, s and p diffuse functions with exponents 0.036 and 0.029, respectively [11], and one set of f functions with exponent 1.832 [12] were added to the $5s4p2d$ basis set used earlier ($4p$ is the Huzinaga/Dunning $3p$ plus p_{neg}). With this $6s5p2d1f$ basis, CI calculations with one reference configuration and $T = 2.5 \mu\text{hartree}$ were performed as a function of R . The results are listed in Table V. By interpolation, $R_e = 1.896 \text{ \AA}$ is obtained showing a reasonable increase over the SCF optimized value of 1.88 \AA . (Other spectroscopic constants obtained for the ground state of F_2^- are $\omega_e = 636.8 \text{ cm}^{-1}$ and $B_e = 0.4938 \text{ cm}^{-1}$. At R_e , the energy is $-199.37593 \text{ hartree}$.) Carmichael [10] obtained 1.9192 \AA for R_e , optimized by using the DZP basis set with UCISD. At 1.896 \AA the value of a_{iso} is 269.06 and of A_{dip} is 307.1 G.

As a further check on the quality of the CI wave function used for the distance dependence, the adiabatic electron affinity of F_2 was calculated. Using for F_2 the same basis set and the same MOS as for F_2^- , with a selection threshold of $5 \mu\text{hartree}$, and $R_e(\text{F}_2) = 1.411 \text{ \AA}$ [20], a value of 2.34 eV (2.89 eV UHF) was obtained to be compared with an experimental value of 3.08 eV [21].

Whereas diffuse functions and f functions are needed to obtain a good equilibrium value of R , it was noticed above and in other instances [1, 10, 22] that they do not help

TABLE V. Isotropic (a_{iso}) and dipolar (A_{dip}) hyperfine coupling constants for $^{19}\text{F}_2^-$ as functions of bond distance using a $6s5p2d1f$ basis set and $T = 2.5 \mu\text{hartree}$.^a

R (Å)	E (hartree)	a_{iso} (G)	A_{dip} (G)
1.84	-199.37550	312.2	308.6
1.86	-199.37581	296.0	308.0
1.88	-199.37589	280.4	307.5
1.90	-199.37592	266.1	307.0
1.92	-199.37579	252.2	306.5
1.94	-199.37568	239.3	305.9
1.96	-199.37540	227.1	305.4

^aThe number of generated SAFS is 85695, the number of selected SAFS range from 16326 to 16496. The interpolated R_e is 1.896 Å.

improving a_{iso} . Indeed, at $R = 1.88$ Å, a_{iso} of Table V (280.4 G) is nearly identical with a_{iso} of Table II for $5s4p2d$ (279.86). As was pointed out above, the $6s5p2d1f$ basis set used for the optimization of R differs from $5s4p2d$ used in Table II only by addition of diffuse and f functions.

Discussion of Results

At $R = 1.88$ Å, all calculated values of A_{dip} lie between 301 and 310 G. With improving basis sets (Tables II and III), no clear direction of change can be noticed, although there is an indication of a small increase of A_{dip} with addition of polarization functions. Calculated values are slightly below the experimental results, which range from 312 to 324 G. Correlation has no effect on A_{dip} , indicating that the spin density in the vicinity of the nuclei ($1/r^3$) is well described by the UHF_{AA} wave function.

The same cannot be said of the isotropic component a_{iso} . Changes owing to improving basis sets and correlation are large. At $R = 1.88$ Å, UHF_{AA} results converge toward 310–320 G, whereas CI results converge toward 270–285 G.

Following the arguments outlined in paper I, the addition of d functions to an s, p basis set improves the s density in the vicinity of a nucleus. Therefore, the effect of adding d functions should diminish when improving the s, p basis set. Comparing $9s5p$ results of Table III with $5s4p$ results of Table II, the addition of $1d$ lowers a_{iso} (CI) by 12/54 G, $2d$ by an additional 16/40 G, and $3d$ by an additional -9/9 G. The d exponents for $1d, 2d, 3d$ are the same in both sets of calculations. From $7s4p$ to $7s4p1d$, a_{iso} (CI) is lowered by 17 G, a value intermediate between 12 G for $9s5p$ and 54 G for $5s4p$. With these results, the general argument about the effect of d functions given above is verified. It is often stated that the 6-component d functions, as used here, allow for a linear combination $(x^2 + y^2 + z^2) \exp(-ar^2) = r^2 \exp(-ar^2)$, which has s character, and thereby improves the s density at the nucleus. However, this function is zero at $r = 0$ and therefore cannot directly help the density at the nucleus. Since it is capable of introducing a shell structure to the s density, it can thereby modify the $1s$ and $2s$ densities at the nucleus and therefore also the spin densities. In CI terms it means that inclusion of d functions improves the spin polarization from the doubly occupied σ -MOs corresponding to $1s$ and $2s$. As was noted in other studies, p functions, f functions, and diffuse functions have little effect on a_{iso} .

Additional CI calculations were performed in order to study separately the spin polarization contributions of the "1s" and the "2s" electrons to a_{iso} . For calculating the 1s contribution, a_{iso} was evaluated from a CI wave function, where $1\sigma_g$ and $1\sigma_u$ were always kept doubly occupied (frozen). The 1s contribution to a_{iso} was then taken as the difference a_{iso} (all electrons) - a_{iso} [1s], the symbol [1s] indicating the frozen 1s. Similarly, the 2s contribution was obtained from a CI wave function where $2\sigma_g$ and $2\sigma_u$ were kept frozen, and $a_{\text{iso}}^{2s} = a_{\text{iso}}$ (all electrons) - a_{iso} [2s]. Obviously, $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$ are not pure 1s or 2s orbitals but have other σ contributions as well. The results for basis sets corresponding to Table II are shown in Table VI. The all-electron results are repeated in column 2, and the 1s, 2s contributions are given in columns 3 and 4. The "2p" contribution (last column) was obtained as the difference between the all-electron results and the 1s + 2s results. From the method described above for obtaining 1s and 2s contributions, it should be obvious that these are not accurate but approximate values only.

Table VI shows that the 2p contribution remains essentially constant. The 1s contributions are negative and decrease with increasing numbers of polarization functions until they reach a minimum for $5s4p3d$. On the other hand, the 2s contribution is always positive and decreases, until it reaches a minimum for the $5s4p2d$ basis set. So the 1s and 2s contributions, although of opposite sign, move in the same direction, with the one small exception between $2d$ and $3d$. For the N atom, Engels et al. [7] found the 2s contributions to be positive and decreasing with increasing d basis (as observed for F_2^- until $2d$), whereas the 1s contributions were negative but increased with increasing d basis (for F_2^- only found at the very end). For F_2^- , the initial d functions reduce the positive (α) spin density in 2s while at the same time increasing the negative (β) spin density in 1s.

In Table VII, the 1s and 2s contributions to a_{iso} , corresponding to the basis sets used in Table III, are shown. Again, the 1s contributions are negative, decreasing with subsequent uncontractions but increasing slightly when polarization functions are added to the fully uncontracted $9s5p$ basis set. The 2s contributions, which are again positive, decrease both with subsequent uncontractions and with the addition of $1d$ and $2d$ to $9s5p$, whereas $3d$ leads to a slight increase of a_{iso} (2s). The recovery

TABLE VI. Contributions to a_{iso} of $^{19}\text{F}_2^-$ from 1s ($1\sigma_g$, $1\sigma_u$) and 2s ($2\sigma_g$, $2\sigma_u$) electrons, with basis sets corresponding to Table II, at $R = 1.88\text{\AA}$.^a

Basis set	All els	a_{iso} (G)		
		1s	2s	2p ^b
$5s4p$	374.4	-181.8	358.9	197.3
$5s4p1d$	320.3	-199.5	314.8	205.0
$5s4p2d$	279.8	-216.2	290.4	205.6
$5s4p3d$	271.2	-231.0	296.5	205.7
$5s4p4d$	285.1	-219.4	304.7	199.8

^aCI values for 1 reference configuration and $T = 2 \mu\text{hartree}$.

^bEntries for 2p were not calculated separately but are differences between all electron values and 1s + 2s values.

TABLE VII. Contributions to a_{iso} of $^{19}\text{F}_2^-$ from $1s$ ($1\sigma_g, 1\sigma_u$) and $2s$ ($2\sigma_g, 2\sigma_u$) electrons, with basis sets corresponding to Table III, at $R = 1.88\text{\AA}$.^a

Basis set	All els	a_{iso} (G)		
		$1s$	$2s$	$2p^b$
$5s3p$	373.3	-188.0	371.7	189.6
$5s4p$	372.4	-189.7	367.6	194.5
$7s4p$	294.8	-238.0	338.4	194.4
$7s4p1d$	277.9	-237.7	317.1	198.5
$9s5p$	290.6	-240.0	332.9	197.7
$9s5p1d$	278.1	-238.9	314.4	202.6
$9s5p2d$	262.5	-235.0	292.1	205.4
$9s5p3d$	271.4	-228.9	293.3	207.0

^aCI values for 1 reference configuration and $T = 2 \mu\text{hartree}$.

^bDifference between all electron values and $1s + 2s$ values.

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of a_{iso} from 262 to 271 G between $9s5p2d$ and $9s5p3d$ is due mainly to the rise of a_{iso} ($1s$).

Since most basis set and CI dependence studies were performed at 1.88\AA , whereas our optimized R_c is 1.896\AA , both a_{iso} and A_{dip} were recalculated at 1.896\AA , using $9s5p3d$, the best basis set of this paper as far as HFCCs are concerned. The CI results are 260.3 G for a_{iso} and 308.3 G for A_{dip} . The trend toward smaller values of a_{iso} with increasing basis set, as observed before, combined with the decrease of this quantity with R gives a theoretical result about 20 G below the best experimental values. It is not clear at this time whether this discrepancy is due to basis set or CI deficiencies, both of which were tested extensively, or basic theoretical shortcomings.

5. Comparison with Carmichael's Results

One may roughly compare Carmichael's [10] DZ basis set with our $5s4p$ basis, DZP with $5s4p1d$, and TZP with $9s5p2d$, although the actual TZ basis used by Carmichael was not stated. Most of the CI results of this paper correspond to SDCI of Ref. 10. The comparison for a_{iso} , as far as possible, is shown in Table VIII. The numbers obtained in this work are generally higher, probably due to the use of $R = 1.88 \text{\AA}$, compared with 1.919\AA in Ref. 10. The significant difference is seen in the trends. Whereas our results always decrease with improved basis set, Carmichael's UHFPA results change from 286 to 306 G in going from DZP to TZP. Some complications arise due to Carmichael's use of five-component d functions in some instances. Since some basis set and CI details were not given by Carmichael, a final judgment on the relative merits of the two studies cannot be made. However, in the present study, basis sets and CI methods were improved systematically, causing systematic and decreasing changes of the calculated values of a_{iso} and A_{dip} . Carrying this method to the limit of available programming facilities led to nearly converged values of the properties in question.

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TABLE VIII. Isotropic hyperfine coupling constants of F_2^- (in Gauss): comparison between Carmichael's [10] results (first number) and this work (second number).^a

Basis Set ^b	PUHF/UHFAA	SDCI
DZ	-1343	317/374
DZP	286/325	285 ^c /320
TZP	306 ^c /313	-1262

^aDone at $R = 1.919 \text{ \AA}$ (Ref. 10) and at $R = 1.88 \text{ \AA}$ (this work).

^bSee text.

^cFive-component d functions used.

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