

Rovibrationally averaged magnetizability, rotational g factor, and indirect spin–spin coupling of the hydrogen fluoride molecule

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The magnetizability tensor, the rotational g factor, and the indirect nuclear spin–spin coupling constant of the hydrogen fluoride molecule have been calculated using large multiconfigurational self-consistent field wave functions and large basis sets. For a critical comparison with experiment, rovibrational corrections have also been calculated. For the magnetizability tensor and the spin–spin coupling constant, we present results with higher precision than available experimental data; for the rotational g factor, our results are in good agreement with experiment. © 1999 American Institute of Physics. [S0021-9606(99)02519-2]

I. INTRODUCTION

For small closed-shell gas-phase molecules, magnetic properties can nowadays be calculated routinely with such an accuracy that rovibrational effects can be expected to be the main reason for discrepancies between theory and experiment.^{1–6} There are several reasons for this development. First, the basis-set convergence of many magnetic properties has been dramatically improved by the efficient implementation of London orbitals for nuclear shieldings and magnetizabilities^{7–12} and the introduction of the similarly constructed rotational London orbitals for rotational g factors and spin-rotation constants.¹³ Second, for most of the important second-order magnetic properties of closed-shell systems, efficient implementations exist for the analytical evaluation of the magnetic properties for a wide variety of wave functions of different computational cost and accuracy.^{11–19} For a meaningful comparison of calculated magnetic properties with experiment, it is usually necessary to compute corrections due to molecular rotations and vibrations.

For diatomic molecules, several methods have been developed for calculating rovibrational averages of molecular properties.^{20–22} The approach taken here may be regarded as an extension of the perturbation technique of Buckingham²⁰ and is based on a method for including the anharmonicity of the potential in the calculation of intermolecular vibrational frequencies.²³ In the high-temperature limit, a rovibrationally

averaged property $\langle \Omega \rangle$ of a heteronuclear diatomic molecule is in this scheme obtained as¹

$$\langle \Omega(T) \rangle = \Omega_{\text{eff}} + \frac{B_{\text{eff}} \Omega''_{\text{eff}}}{\omega_{\text{eff}}} \left(\frac{1}{2} + \frac{e^{(-hc\omega_{\text{eff}}/kT)}}{1 - e^{(-hc\omega_{\text{eff}}/kT)}} \right) + \frac{4kT}{hcB_{\text{eff}}} \left(\frac{B_{\text{eff}}}{\omega_{\text{eff}}} \right)^2 \Omega'_{\text{eff}}, \quad (1)$$

where B is the rotational constant, ω the harmonic frequency, and T the temperature, and where we have truncated the expansion at second order. The derivatives are here given as $\Omega' = (\partial\Omega/\partial\xi)$ and $\Omega'' = (\partial^2\Omega/\partial\xi^2)$, respectively, where $\xi = (r - r_{\text{eff}})/r_{\text{eff}}$. The subscript eff indicates that the quantities are calculated at a variationally determined effective geometry.²³ We note that the effective geometry r_{eff} depends on the isotopomer and that its determination is more complicated than a normal geometry optimization.¹ By shifting the geometry, the contribution from the first order mechanical anharmonicity vanishes. This is also noted in a similar expression to Eq. (1) in Ref. 24 which is based on the delta approximation.²⁵ Although the method is more expensive than the traditional approach,²⁰ it appears to converge faster with respect to the property derivatives included in the expansion Eq. (1), which is particularly important for molecules with soft modes and for molecular complexes.^{1,23} Furthermore, the vibrational part of the wave function is represented by one Gaussian function for each degree of freedom, which will be useful when dynamical approaches are adopted for this model or when larger molecules are studied. In a recent paper,²⁶ higher-order zero-point vibrational contributions to Eq. (1) have been included for different properties at the SCF level. This paper demonstrated that the

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contributions from higher-order terms are smaller than the errors normally obtained from truncation of the basis set and orbital space, even for highly sophisticated quantum chemical calculations.

The purpose of the present paper is to investigate whether it is possible to obtain experimental accuracy for the magnetizability, the rotational g factor, and the indirect nuclear spin–spin coupling constant of the hydrogen fluoride molecule and furthermore to establish whether the main limitations in obtaining an accurate rovibrationally averaged result arise from the treatment of rovibrational effects or from the treatment of the electronic structure. Previously, the nuclear shieldings of HF have been studied by Åstrand and Mikkelsen¹ and the nuclear shieldings and spin-rotation constants by Sundholm, Gauss, and Schäfer.⁵ This work should be regarded as complementary to these studies.

II. RESULTS

We first consider the dependence of the properties on the basis set and the treatment of electron–correlation. Two kinds of basis sets are employed; the atomic natural orbital (ANO) sets of Widmark *et al.*²⁷ and the correlation-consistent sets of Dunning and co-workers.^{28–31} The ANO basis sets are denoted ANO[$6s5p4d/5s4p$], where $6s5p4d$ is the number of contracted orbitals in the fluorine basis and $5s4p$ the number of contracted functions in the hydrogen basis. The correlation-consistent basis sets are denoted xxx -cc-pV n Z and xxx -cc-pCV n Z, respectively, where xxx is the degree of augmentation (aug, daug, taug or no augmentation at all) and $n \in \{D, T, Q, 5\}$. We have used the core-valence xxx -cc-pCV n Z sets for the calculation of the spin–spin coupling constant and the valence xxx -cc-pV n Z sets for the calculation of the magnetizability and rotational g factor.

The orbital spaces of the complete-active-space self-consistent field (CASSCF) (Ref. 32) wave function are denoted $inactive$ CAS active , where inactive represents the inactive orbital space of doubly occupied orbitals and active the space of orbitals with variable occupation numbers. The restricted-active-space SCF (RASSCF) (Refs. 33, 34) spaces are denoted in a similar manner as $inactive$ RAS RAS2 RAS3 , where RAS2 corresponds to the active space of a CASSCF calculation. In this work, we allow single and double excitations out of the RAS1 space, and single and double excitations into the RAS3 space. The orbital spaces, which have been chosen on the basis of the natural occupation numbers of a MP2 calculation,³⁵ are characterized by the number of orbitals in each irreducible representation of the C_{2v} point group. The DALTON program has been used in all the electronic-structure calculations.³⁶

A. Basis set convergence

Our Hartree–Fock (HF) results obtained at the experimental geometry ($r = 1.7325 a_0$) (Ref. 37) are collected in Table I for the ANO and the correlation-consistent basis sets.

For the isotropic magnetizability ξ , the ANO[$6s5p4d/5s4p$] basis is within 0.01 ppm cgs of the basis-set limit. The rotational g factor shows a similar convergence, which is to be expected since the paramagnetic part of the magnetizability tensor and the rotational g tensor

TABLE I. Hartree–Fock magnetic properties of HF for ANO and correlation-consistent^a basis sets.

	ξ /ppm cgs	$\Delta\xi$ /ppm cgs	g	$^1J^{HF}$ /Hz
ANO[$4s3p2d/3s2p$]	−10.448	0.4717	0.7581	596.3
ANO[$4s3p2d1f/3s2p1d$]	−10.449	0.4987	0.7579	197.7
ANO[$5s4p3d/4s3p$]	−10.411	0.5052	0.7621	671.6
ANO[$5s4p3d2f/4s3p2d$]	−10.409	0.5240	0.7617	1013.3
ANO[$6s5p4d/5s4p$]	−10.397	0.5068	0.7620	979.2
ANO[$6s5p4d3f/5s4p3d$]	−10.395	0.5319	0.7626	647.3
ANO uncontracted	−10.393	0.5272	0.7624	649.9
cc-pVDZ	−9.890	0.5540	0.7403	326.0
cc-pVTZ	−10.166	0.5545	0.7564	553.6
aug-cc-pVTZ	−10.412	0.5240	0.7627	599.0
daug-cc-pVTZ	−10.415	0.5255	0.7643	577.7
cc-pVQZ	−10.292	0.5534	0.7611	635.2
aug-cc-pVQZ	−10.399	0.5229	0.7624	644.4
daug-cc-pVQZ	−10.399	0.5251	0.7627	n.c. ^b
cc-pV5Z	−10.367	0.5432	0.7627	638.8
aug-cc-pV5Z	−10.393	0.5254	0.7625	652.0

^aThe corresponding pCV n Z basis set has been used for the spin–spin coupling constant.

^bNot calculated.

are closely related to each other.^{13,38} In accordance with previous observations for the magnetizability,³⁹ the Hartree–Fock magnetizabilities (at the experimental geometry) are almost all within 2% of the experimental number. However, the problems faced in converging the magnetizability anisotropy $\Delta\xi$ indicate that the errors in the individual tensor components are larger than that of the isotropic part, also in line with previous observations.⁴⁰ For the correlation-consistent basis sets, the aug-cc-pVQZ basis gives results that are virtually identical to the estimated basis-set limit.

To explore the saturation of the outer valence region of the ANO set, diffuse functions (with exponents forming a geometric series) were added to the uncontracted ANO basis. However, these diffuse functions have only a marginal effect on the calculated properties. The only significant change is for the anisotropy of the magnetizability (−0.002 ppm cgs), caused by the addition of one extra d -function to the fluorine basis, explaining the difference between the uncontracted ANO basis and the aug-cc-pV5Z basis. We conclude that the larger basis sets give results for ξ and g close to the basis-set limit. For the isotropic and anisotropic magnetizabilities, our estimated Hartree–Fock limits (−10.393 and 0.5254 ppm-cgs, respectively) are in excellent agreement with the SCF results of Cybulski and Bishop (−10.392 and 0.5256 ppm cgs).⁴¹

We now turn our attention to the indirect nuclear spin–spin coupling constant. According to the theory of Ramsey,⁴² there are four contributions to the indirect spin–spin coupling constant,

$$J = J_{\text{DSO}} + J_{\text{PSO}} + J_{\text{FC}} + J_{\text{SD}}. \quad (2)$$

Here J_{DSO} and J_{PSO} are the diamagnetic and paramagnetic spin–orbit contributions, J_{FC} is the Fermi-contact contribution, and J_{SD} the spin-dipole contribution. For the spin–spin coupling, the basis set convergence is particularly slow. Still, the uncontracted ANO basis and the aug-cc-pV5Z basis

TABLE II. $^{1000}\text{CAS}^{4220}$ Fermi-contact contributions to the spin–spin coupling term.^a

	$^1J_{\text{FC}}^{\text{HF}}/\text{Hz}$
cc-pCVQZ	385.3
cc-pCV5Z	385.9
aug-cc-pCVQZ	393.6
aug-cc-pCV5Z	398.6
ANO[6s5p4d3f/5s4p3d]	402.5
ANO uncontracted	397.3
ANO+F:3s;H:4s	421.0
ANO+F:4s;H:4s	421.3
ANO+F:3s;H:5s	419.9
ANO+F:3s;H:6s	419.9

^as-functions with large exponents are added according to a geometric series.

give the same result to within a few Hz. However, the addition of diffuse functions to the ANO basis changes the coupling by several Hz. Indirect spin–spin coupling constants are usually not even qualitatively correct at the restricted Hartree–Fock level,^{43,44} but a basis set convergence similar to that of the RHF convergence in Table I is found for a $^{1000}\text{CAS}^{4220}$ wave function.

As expected, the largest basis-set effects are found for the FC term, although substantial changes are also observed for the PSO and SD contributions. The contraction of the ANO basis leads to dramatic changes in the FC term, which is related to the sensitivity of the FC term to the description of the charge distribution at the nucleus.^{43,44} The contraction of the ANO sets thus appears to significantly affect the electron distribution at the nuclei.

To investigate the FC term in more detail, basis functions with large exponents were added to the primitive ANO basis, forming a geometric series (see Table II). To converge the coupling constant to within a few tenths of a Hz (at the $^{1000}\text{CAS}^{4220}$ level), an extension of the primitive ANO basis with three *s* functions at the fluorine atom and five *s* functions at the hydrogen atom (ANO+F:3s;H:5s) is required. The effect of these extra *s*-functions is, however, as large as 22.6 Hz. Both the uncontracted ANO basis and the aug-cc-pCV5Z basis are therefore more than 20 Hz off our estimated basis-set limit, a change which is about as large as the experimental error bars.^{45,46} Note also that the ANO+F:3s;H:5s basis set consists of 125 basis functions, substantially smaller than the aug-cc-pCV5Z basis set (256 primitive functions contracted to 236 basis functions). Since the experimental error bars are 20 Hz,^{45,46} we believe that this extended basis set gives results with smaller residual errors than the uncertainty in the experimental number. Since our results indicate that the ANO basis converges faster to the basis-set limit than does the correlation-consistent basis sets, only ANO sets have been used in the remaining calculations.

B. Electron-correlation treatment

The effects of electron correlation at the CASSCF and RASSCF level have been investigated using the ANO[6s5p4d3f/5s4p3d] basis set (see Table III). The correlation contribution to the magnetizability is about -0.25

TABLE III. Magnetic properties of the hydrogen fluoride molecule for the ANO[6s5p4d3f/5s4p3d] basis set.

	$\xi/\text{ppm cgs}$	$\Delta\xi/\text{ppm cgs}$	<i>g</i>	$^1J_{\text{FC}}^{\text{HF}}/\text{Hz}$
HF	-10.395	0.5319	0.7626	647.3
$^{1000}\text{CAS}^{4220}$	-10.688	0.5189	0.7621	578.7
$^{1000}\text{CAS}^{6331}$	-10.623	0.5212	0.7584	530.4
$^{1000}\text{RAS}^{4220}_{2111}$	-10.624	0.5210	0.7584	528.4
$^{1000}\text{RAS}^{4220}_{4221}$	-10.642	0.5177	0.7503	522.5
$^{1000}\text{RAS}^{4220}_{6332}$	-10.640	0.5205	0.7518	524.8
$^{1000}\text{RAS}^{4220}_{8553}$	-10.630	0.5204	0.7532	518.3
$^{1000}\text{RAS}^{4220}_{9553}$	-10.631	0.5206	0.7514	516.3
$^{1000}\text{RAS}^{4220}_{10:663}$	-10.644	0.5181	0.7506	n.c. ^a
$^{1000}\text{RAS}^{4220}_{12:884}$	-10.643	0.5198	0.7503	n.c. ^a

^aNot calculated.

ppm cgs, and the smallest CASSCF wave function accounts for almost all the electron correlation effects. The same observation is made for the magnetizability anisotropy, even though the absolute change due to electron correlation is only about 0.01 ppm cgs. The correlation effects on the rotational *g* factor is less than 1% (about 0.002). However, since the experimental error bar is 5×10^{-6} ,⁴⁶ this change is rather large. The error arising from a truncated configuration space is about two orders of magnitude larger than the experimental error bars.

It is of interest to compare our results with the recent MP2/MP3/L-CCD results of Cybulski and Bishop, obtained using large conventional basis sets;⁶ $\xi = -10.74/-10.57/-10.60$ ppm cgs, $\Delta\xi = 0.5270/0.5180/0.5127$ ppm cgs, and $g = 0.7619/0.7527/0.7488$. For the isotropic magnetizability, MP2 overestimates the correlation effect, whereas MP3 and L-CCD slightly underestimates the correlation effect. For the magnetizability anisotropy and the rotational *g* factor, the three methods converge from the same side, although none of methods reproduces the results of our largest MCSCF calculations. In contrast, the modest-sized $^{1000}\text{CAS}^{6331}$ wave function accounts for almost all the correlation effect.

The calculated isotropic spin–spin coupling constants are listed in Table III and the individual contributions are in Table IV. The DSO term is small and is not discussed further. The PSO term has a correlation contribution of about -13 Hz but appears to be converged to within 1 Hz for the

TABLE IV. The correlation dependence of the spin–spin coupling terms calculated with the ANO[6s5p4d3f/5s4p3d] basis set.

	$^1J_{\text{DSO}}^{\text{HF}}/\text{Hz}$	$^1J_{\text{PSO}}^{\text{HF}}/\text{Hz}$	$^1J_{\text{SD}}^{\text{HF}}/\text{Hz}$	$^1J_{\text{FC}}^{\text{HF}}/\text{Hz}^a$
HF	-0.10	199.2	-10.8	487.5
$^{1000}\text{CAS}^{4220}$	-0.10	177.6	-1.30	419.9
$^{1000}\text{CAS}^{6331}$	-0.11	182.0	-1.41	363.2
$^{1000}\text{RAS}^{4220}_{2111}$	-0.11	181.9	-1.44	364.2
$^{1000}\text{RAS}^{4220}_{4221}$	-0.05	186.7	-0.21	352.3
$^{1000}\text{RAS}^{4220}_{6332}$	-0.06	187.3	-5.69	360.3
$^{1000}\text{RAS}^{4220}_{8553}$	-0.05	186.2	-0.29	350.2
$^{1000}\text{RAS}^{4220}_{9553}$	-0.05	186.7	-0.11	348.1
$^{1000}\text{RAS}^{4220}_{10:663}$	n.c. ^b	n.c. ^b	n.c. ^b	344.6
$^{1000}\text{RAS}^{4220}_{12:884}$	n.c. ^b	n.c. ^b	n.c. ^b	341.5
$^{1000}\text{RAS}^{4220}_{14:10:5}$	n.c. ^b	n.c. ^b	n.c. ^b	342.6

^aThe ANO+F:3s;H:5s basis set has been used.

^bNot calculated.

TABLE V. Molecular parameters used in Eq. (1).

		Calculated	Experiment ^a
HF ^{a,c}	r_e/a_0	1.7341	1.7325
	ω_e/cm^{-1}	4138.5	4138.32
	B_e/cm^{-1}	20.917	20.9557
DF ^{b,c}	r_e/a_0	1.7341	1.7328
	ω_e/cm^{-1}	3000.22	2998.19
	B_e/cm^{-1}	10.993	11.0102

^aThe molecular parameters obtained for HF are $r_{\text{eff}}=1.764 a_0$, $\omega_{\text{eff}}=3903.38 \text{ cm}^{-1}$, $B_{\text{eff}}=20.214 \text{ cm}^{-1}$, $(\partial\xi/\partial r)=-1.01 \text{ ppm cgs } a_0^{-1}$, $(\partial^2\xi/\partial r^2)=2.53 \text{ ppm cgs } a_0^{-2}$, $(\partial\Delta\xi/\partial r)=-0.055 \text{ ppm cgs } a_0^{-1}$, $(\partial^2\Delta\xi/\partial r^2)=-3.06 \text{ ppm cgs } a_0^{-2}$, $(\partial g/\partial r)=-0.305 a_0^{-1}$, $(\partial^2 g/\partial r^2)=-0.406 a_0^{-2}$, $(\partial^1 J^{\text{HF}}/\partial r)=-1410 \text{ Hz } a_0^{-1}$, $(\partial^2 J^{\text{HF}}/\partial r^2)=2012 \text{ Hz } a_0^{-2}$.

^bThe molecular parameters obtained for DF are $r_{\text{eff}}=1.756 a_0$, $\omega_{\text{eff}}=2874.59 \text{ cm}^{-1}$, $B_{\text{eff}}=10.721 \text{ cm}^{-1}$, $(\partial\xi/\partial r)=-1.03 \text{ ppm cgs } a_0^{-1}$, $(\partial^2\xi/\partial r^2)=2.53 \text{ ppm cgs } a_0^{-2}$, $(\partial\Delta\xi/\partial r)=-0.031 \text{ ppm cgs } a_0^{-1}$, $(\partial^2\Delta\xi/\partial r^2)=-3.03 \text{ ppm cgs } a_0^{-2}$, $(\partial g/\partial r)=-0.156 a_0^{-1}$, $(\partial^2 g/\partial r^2)=-0.220 a_0^{-2}$.

^cThe geometrical derivatives are calculated in the effective geometries r_{eff} . They are calculated as a finite difference with $\partial r=0.08 a_0$ for HF and $\partial r=0.088 a_0$ for DF.

^dSee Ref. 37.

two largest RAS spaces. In contrast, the SD term increases by 10.5 Hz from HF to ¹⁰⁰⁰CAS⁴²²⁰ (becoming almost zero), but most of the correlation contribution is included already with this smallest CASSCF wave function.

For the FC term, the correlation effects are larger than for the other terms. The total correlation contribution is about -150 Hz . Moreover, the full-valence ¹⁰⁰⁰CAS⁴²²⁰ space recovers only about half of the correlation correction and the FC term appears to be converged only to within 3–5 Hz for the two largest RAS spaces. Our result obtained with the ¹⁰⁰⁰CAS⁶³³¹ wave function (363.2 Hz) is in good agreement with the corresponding number obtained in a recent spin–spin basis-set study (359.84 Hz).⁴⁷ Similar agreement is observed for the other contributions, with a partial cancellation of the errors in the SD and DSO terms with the error in the PSO contribution.

C. Rovibrational averages

The effective geometry for rovibrational corrections was calculated using the ANO[6s5p4d3f/5s4p3d] basis set and the ¹⁰⁰⁰RAS⁴²²⁰₆₃₃₂ orbital space. As seen from Table V, this wave function gives good agreement with the experimental equilibrium geometry and the harmonic frequencies.³⁷ Therefore, it is reasonable to expect that this wave function will give a good description of r_{eff} and ω_{eff} as well. Except for the FC contribution to the spin–spin coupling constant, the same wave function has been used also for the calculation of the rovibrational averages of the magnetic properties (see Table VI). For the FC term, we have used the extended ANO+F:3s;H:5s basis and the ¹⁰⁰⁰RAS⁴²²⁰_{12;884} orbital space. The error bars are estimated from basis-set and electron–correlation studies of the two previous sections.

The isotropic part of the magnetizability $(\xi)_0$ is found to be $-10.65 \pm 0.02 \text{ ppm cgs}$ and the anisotropy is $0.496 \pm 0.02 \text{ ppm cgs}$. These results are rather far away from the (semi-)

TABLE VI. Rovibrational averaging of magnetic properties of the hydrogen fluoride molecule.^a

		$\xi/\text{ppm cgs}$	$\Delta\xi/\text{ppm cgs}$	g	$^1J^{\text{HF}}/\text{Hz}$
HF	Ω_e	-10.642	0.5205	0.7513	526.4
	Expt			(0.75449) ^d	(540) ^d
	Ω_{eff}	-10.673	0.5204	0.7424	483.3
	$\langle\Omega\rangle_0$	-10.653	0.4957	0.7391	499.5
	Expt	(-10.3) ^b	(0.5370) ^c	[0.7392(50)] ^e	(521) ^e
	Expt			[0.74104(15)] ^c	[529(23)] ^h
DF	Ω_e	-10.642	0.5205	0.3744	...
	Ω_{eff}	-10.665	0.5207	0.3710	...
	$\langle\Omega\rangle_0$	-10.650	0.5033	0.3697	...
	Expt			[0.3695(50)] ^f	...
	$\langle\Omega\rangle_{300}$	-10.652	0.5032	0.3694	...
	Expt		[0.168(8)] ^d	[0.741599(5)] ^d	[500(20)] ^d

^aThe data used in Eq. (1) are taken from Table V.

^bQuoted in Ref. 48.

^cSee Ref. 49.

^dSee Ref. 46.

^eSee Ref. 51.

^fSee Refs. 38, 50.

^gSee Ref. 53.

^hSee Ref. 45.

experimental values of -10.3 ppm cgs (Ref. 48) and 0.5370 ppm cgs ,⁴⁹ respectively. We do not expect that an extension of the basis set or a larger orbital space will change these results noticeably. We have investigated also the effects from the fourth derivative of the magnetizability at the Hartree–Fock level, but these effects are at least one order of magnitude smaller than the difference to experiment. We note that the most recent experimental value for $\Delta\xi$ [0.168(8) ppm-cgs] (Ref. 46) is off by about a factor of 3 relative to the previous experimental investigation⁴⁹ and to our theoretical result, although it was noted in this investigation that their experimental setup was prone to systematic errors in the magnetizability anisotropy.

The averaged rotational g factor $\langle g \rangle_0$ has been calculated to be 0.7391 ± 0.0035 for the HF molecule and 0.3697 ± 0.0035 for DF, which should be compared with the most recent experimental values of 0.741 599(5) for HF (Ref. 46) and 0.3695 ± 0.0050 for DF,^{38,50} respectively. Most of our error (0.003) arises from the correlation treatment. The calculated results are within 1% of experiment^{38,49–51} but not within the experimental error bars, which are only of the order of 0.001% for the most recent value.⁴⁶ The values presented here should probably be considered upper limits since the g factor decreases monotonically with increasing orbital space. The calculated value of the HF molecule is therefore not expected to converge towards the experimental value even though the experimental value is within our error bars. It is also noted that the two most recent experimental results^{46,49} do not overlap—that is, at least one of the experimental error bars is too optimistic. Still, our result for DF is in excellent agreement with experiment.

If instead we focus on the rovibrational correction to the g factor itself, we note that our calculated correction of -0.0129 is in excellent agreement with the experimental estimate of -0.0122 .⁴⁶ The difference between our result and

experiment therefore arises from the treatment of the electronic structure rather than from an approximate treatment of the rovibrational correction. At the MP2 level, Cybulski and Bishop recover only about 80% of the rovibrational correction (-0.0095).⁴¹ Correlation thus appears to be more important, relatively speaking, for the rovibrational corrections than for the properties themselves.

The rovibrationally averaged indirect spin–spin coupling constant $\langle {}^1J^{\text{HF}} \rangle_0$ is estimated to be 510 ± 10 Hz, in excellent agreement with the most recent experiment of 500 ± 20 Hz.⁴⁶ Our error bar of 10 Hz is rather large due to the slow convergence with respect to the size of the orbital and correlation spaces of the FC term. The zero-point vibrational contribution is about -25 Hz, that is, about 5% of the total value, and may thus not be neglected in a comparison with experiment, even when the experimental error bars are as large as in this case.

The relative contribution from shifting the expansion point of the total zero-point vibrational contribution $(\Omega_{\text{eff}} - \Omega_e)/(\langle \Omega \rangle_0 - \Omega_e)$ varies considerably from property to property. For ξ and ${}^1J^{\text{HF}}$, the zero- and second-order terms in Eq. (1) have different signs, but the contribution from the shift in the expansion point is the larger of the two. Whereas the zero-order term is negligible for $\Delta\xi$, the second-order term gives a substantial contribution. For g , both terms change in the same direction, with the zero-order term being the dominant one.

We have also reinvestigated the fluorine shielding of HF at 300 K, $\langle \sigma^{\text{F}} \rangle_{300 \text{ K}}$. In a recent study using an ANO[6s5p4d/5p4d] basis and ${}^{1000}\text{RAS}_{4221}^{4220}$ orbital space,¹ $\langle \sigma^{\text{F}} \rangle_{300 \text{ K}}$ was calculated to be 407.4 ± 3.0 ppm, in agreement with the experimental value of 410 ± 6 ppm.⁵² More recently, Sundholm *et al.*⁵ refined this value to 409.2 ppm in an accurate calculation adopting a CCSD(T) wave function and numerical integration of the rovibrational contribution. With the wave function employed here (ANO[6s5p4d3f/6s5p4d] basis set and a ${}^{1000}\text{RAS}_{6332}^{4220}$ orbital space) [$(\partial \sigma^{\text{F}} / \partial r) = -225.1 \text{ ppm } a_0^{-1}$ and $(\partial^2 \sigma^{\text{F}} / \partial r^2) = -424.8 \text{ ppm } a_0^{-2}$], we obtain 409.5 ± 1.5 ppm, in close agreement with Sundholm *et al.*⁵ The error bars are estimated to be 0.5 ppm from the basis-set truncation and 1.0 ppm from the deficiencies of the RAS treatment. The major difference between our present and previous results arises from a small change of the effective geometry— $1.770 a_0$ in the previous study and $1.764 a_0$ here. The main reason for the improvement in our estimate of $\langle \sigma^{\text{F}} \rangle_{300 \text{ K}}$ is thus the improved accuracy of the potential surface rather than the calculation of the properties and their derivatives.

III. CONCLUSIONS

We have calculated accurate values of the magnetizability and rotational g factor of HF and DF and of the indirect nuclear spin–spin coupling of HF. To allow for a critical comparison with experiment, rovibrational effects have been taken into account. Although the rovibrational corrections have been obtained in a simple manner, employing just one Gaussian function for the vibrational wave function, the main source of error in our calculations is the treatment of

the electronic structure. Our rovibrationally averaged results are probably the most accurate ones so far obtained for these properties. For the magnetizability and the spin–spin coupling constant, our precision is higher than that of experiment. For the rotational g factor, our error bars of about 0.5% encompass the experimental results, although we are not within the very narrow experimental error bars.

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- ¹P.-O. Åstrand and K. V. Mikkelsen, *J. Chem. Phys.* **104**, 648 (1996).
- ²K. Ruud, P.-O. Åstrand, T. Helgaker, and K. V. Mikkelsen, *J. Mol. Struct.: THEOCHEM* **388**, 231 (1996).
- ³P.-O. Åstrand, K. Ruud, K. V. Mikkelsen, and T. Helgaker, *Chem. Phys. Lett.* **271**, 163 (1997).
- ⁴D. Sundholm, J. Gauss, and R. Ahlrichs, *Chem. Phys. Lett.* **243**, 264 (1995).
- ⁵D. Sundholm, J. Gauss, and A. Schäfer, *J. Chem. Phys.* **105**, 11051 (1996).
- ⁶S. M. Cybulski and D. M. Bishop, *J. Chem. Phys.* **106**, 4082 (1997).
- ⁷F. London, *J. Phys. Radium* **8**, 397 (1937).
- ⁸H. Hameka, *Mol. Phys.* **1**, 203 (1958).
- ⁹R. Ditchfield and P. D. Ellis, *Theory of 13C Chemical Shifts*, in *Topics in Carbon-13 NMR*, edited by G. C. Levy (Wiley, New York, 1974), Vol. 1, p. 1.
- ¹⁰T. Helgaker and P. Jørgensen, *J. Chem. Phys.* **95**, 2595 (1991).
- ¹¹K. Ruud, T. Helgaker, K. L. Bak, P. Jørgensen, and H. J. Aa. Jensen, *J. Chem. Phys.* **99**, 3847 (1993).
- ¹²K. Ruud, T. Helgaker, R. Kobayashi, P. Jørgensen, K. L. Bak, and H. J. Aa. Jensen, *J. Chem. Phys.* **100**, 8178 (1994).
- ¹³J. Gauss, K. Ruud, and T. Helgaker, *J. Chem. Phys.* **105**, 2804 (1996).
- ¹⁴K. Wolinski, J. F. Hinton, and P. Pulay, *J. Am. Chem. Soc.* **112**, 8251 (1990).
- ¹⁵O. Vahtras, H. Årgensen, P. Jørgensen, H. J. Aa. Jensen, S. B. Padkjær, and T. Helgaker, *J. Chem. Phys.* **96**, 6120 (1992).
- ¹⁶K. Ruud, T. Helgaker, K. L. Bak, P. Jørgensen, and J. Olsen, *Chem. Phys.* **195**, 157 (1995).
- ¹⁷J. Gauss, *Chem. Phys. Lett.* **191**, 614 (1992).
- ¹⁸J. Gauss, *Chem. Phys. Lett.* **229**, 198 (1994).
- ¹⁹J. Gauss and J. F. Stanton, *J. Chem. Phys.* **104**, 2574 (1996).
- ²⁰A. D. Buckingham, *J. Chem. Phys.* **36**, 3096 (1962).
- ²¹D. F. Zetik and F. A. Matsen, *J. Mol. Spectrosc.* **24**, 122 (1967).
- ²²J. W. Cooley, *Math. Comput.* **15**, 363 (1961).
- ²³P.-O. Åstrand, G. Karlström, A. Engdahl, and B. Nelander, *J. Chem. Phys.* **102**, 3534 (1995).
- ²⁴D. M. Bishop and J. Pipin, *J. Chem. Phys.* **98**, 522 (1993).
- ²⁵V. H. Smith, Jr., A. J. Thakkar, W. H. Henneker, J. W. Liu, B. Liu, and R. E. Brown, *J. Chem. Phys.* **67**, 3676 (1977).
- ²⁶P.-O. Åstrand, K. Ruud, and D. Sundholm, "A modified variation-perturbation approach to zero-point vibrational motion" (submitted).
- ²⁷P.-O. Widmark, P.-Å Malmqvist, and B. O. Roos, *Theor. Chim. Acta* **77**, 291 (1990).
- ²⁸T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ²⁹D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993).
- ³⁰D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 2975 (1994).
- ³¹D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **103**, 4572 (1995).
- ³²B. O. Roos, *Adv. Chem. Phys.* **69**, 399 (1987).
- ³³J. Olsen, B. O. Roos, P. Jørgensen, and H. J. Aa. Jensen, *J. Chem. Phys.* **89**, 2185 (1988).
- ³⁴P.-Å. Malmqvist, A. Rendell, and B. O. Roos, *J. Phys. Chem.* **94**, 5477 (1990).
- ³⁵H. J. Aa. Jensen, P. Jørgensen, H. Ågren, and J. Olsen, *J. Chem. Phys.* **88**, 3834 (1987).
- ³⁶T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Ågren, T. Andersen, K. L. Bak, V. Bakken, O. Christiansen, P. Dahle, E. K.

- Dalskov, T. Enevoldsen, B. Fernandez, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. Saue, P. R. Taylor, and O. Vahtras, DALTON, release 1.0, an *ab initio* electronic structure program, 1997.
- ³⁷Huber and G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1979).
- ³⁸W. H. Flygare and R. C. Benson, *Mol. Phys.* **20**, 225 (1971).
- ³⁹K. Ruud, H. Skaane, T. Helgaker, K. L. Bak, and P. Jørgensen, *J. Am. Chem. Soc.* **116**, 10135 (1994).
- ⁴⁰P.-O. Åstrand, K. Ruud, K. V. Mikkelsen, and T. Helgaker, *Mol. Phys.* **92**, 89 (1997).
- ⁴¹S. M. Cybulski and D. M. Bishop, *J. Chem. Phys.* **100**, 2019 (1994).
- ⁴²N. F. Ramsey, *Phys. Rev.* **91**, 303 (1953).
- ⁴³J. Oddershede, P. Jørgensen, and D. L. Yeager, *Comput. Phys. Rep.* **2**, 33 (1984).
- ⁴⁴A. Barszczewicz, M. Jaszuński, K. Kamińska-Trela, T. Helgaker, P. Jørgensen, and O. Vahtras, *Theor. Chim. Acta* **87**, 19 (1993).
- ⁴⁵J. S. Muentzer and W. Klemperer, *J. Chem. Phys.* **52**, 6033 (1970).
- ⁴⁶S. M. Bass, R. L. DeLeon, and J. S. Muentzer, *J. Chem. Phys.* **86**, 4305 (1987).
- ⁴⁷T. Helgaker, M. Jaszuński, K. Ruud, and A. Górska, *Theor. Chem. Acc.* **99**, 175 (1998).
- ⁴⁸B. R. Appleman and B. P. Dailey, *Adv. Magn. Reson.* **7**, 231 (1974).
- ⁴⁹F. H. de Leeuw and A. Dymanus, *J. Mol. Spectrosc.* **48**, 427 (1973).
- ⁵⁰N. F. Ramsey, *Am. Sci.* **49**, 509 (1961).
- ⁵¹M. R. Baker, C. H. Anderson, J. Pinkerton, and N. F. Ramsey, *Bull. Am. Phys. Soc.* **6**, 19 (1961).
- ⁵²D. K. Hindermann and C. D. Cornwell, *J. Chem. Phys.* **48**, 4148 (1968).
- ⁵³W. E. Quinn, J. M. Baker, J. T. LaTourette, and N. F. Ramsey, *Phys. Rev.* **112**, 1929 (1958).