

Relativistically corrected hyperfine structure constants calculated with the regular approximation applied to correlation corrected *ab initio* theory

Michael Filatov^{a)} and Dieter Cremer

Department of Chemistry, Göteborg University, Kemigården 3, S-41296 Göteborg, Sweden

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The infinite-order regular approximation (IORA) and IORA with modified metric (IORAmm) is used to develop an algorithm for calculating relativistically corrected isotropic hyperfine structure (HFS) constants. The new method is applied to the calculation of alkali atoms Li–Fr, coinage metal atoms Cu, Ag, and Au, the Hg^+ radical ion, and the mercury containing radicals HgH , HgCH_3 , HgCN , and HgF . By stepwise improvement of the level of theory from Hartree–Fock to second-order Møller–Plesset theory and to quadratic configuration interaction theory with single and double excitations, isotropic HFS constants of high accuracy were obtained for atoms and for molecular radicals. The importance of relativistic corrections is demonstrated. © 2004 American Institute of Physics. [DOI: 10.1063/1.1785772]

I. INTRODUCTION

Atomic and molecular species with unpaired electrons often exhibit features known as the hyperfine structure (HFS) in their electron spin resonance (ESR) and optical spectra.^{1,2} The hyperfine structure arises from the interaction between the unpaired electrons and the magnetic field generated by the nuclear magnetic moments (nuclei with nonzero spin). HFS carries valuable information on the electronic structure and the molecular geometry.^{1,2} The HFS tensor, which determines the magnitude of the splitting, can be written as the sum of an isotropic Fermi-contact (FC) and an anisotropic spin-dipolar (SD) contribution. As a result of molecular motion, anisotropic contributions average to zero and only isotropic (or FC) contribution can be observed in gas or liquid phase spectra. These isotropic HFS constants are commonly used as a measure of the spin density at the various nuclei in a molecule.^{1,2}

Although the theory underlying the hyperfine structure is well understood and was developed already in the early days of quantum mechanics,^{1–3} the first principles calculation of the HFS parameters proved to be a challenging task for wave function *ab initio* methods.^{4–7} Besides the well known problems arising from the necessity of considering all electrons within the system and the effects of electron correlation, relativity has to be taken into account in accurate calculations.^{8–10} Indeed, the Fermi-contact interaction depends on the electron distribution in the closest vicinity of the nuclei, where relativistic effects, originating from the finite velocity of light, are non-negligible. Although the use of the four-component relativistic Hamiltonian together with many-body techniques for electron correlation leads to very accurate results for atomic HFS constants,^{11–13} application of this rigorous approach to molecules is prohibitively costly. Hence, there is the necessity to develop simple yet accurate

two- or one-component quasirelativistic techniques for the calculation of molecular HFS parameters.

Recently, we have developed^{14–17} a quasirelativistic computational procedure based on the regular approximation for relativistic effects. A fully analytic algorithm for the calculation of the Hamiltonian matrix elements within the infinite-order regular approximation (IORA) (Ref. 18) and IORA with modified metric (IORAmm) (Ref. 14) enables one to apply the new procedure efficiently within the context of wave function *ab initio* theory. Analytic energy derivatives have been developed for the IORA/IORAmm procedures thus guaranteeing the fast calculation of the analytic gradient (derivative of the total energy with respect to nuclear coordinates) (Ref. 15) for geometry optimizations, analytic calculation of static electric properties,¹⁶ and analytic calculation of indirect nuclear spin–spin coupling constants.¹⁷

In the theory of nuclear spin–spin coupling, one distinguishes, according to Ramsey,¹⁹ four different types of perturbations due to the presence of magnetic nuclei. Two of the four Ramsey terms, the FC and SD terms, are identical (apart from a constant factor) to the FC and SD contributions of the hyperfine Hamiltonian. Hence, the formalism developed for the determination of nuclear spin–spin coupling constants¹⁷ can be straightforwardly reformulated for the calculation of HFS constants.

II. THEORY OF HFS CONSTANTS

Within the spin-unrestricted formalism, the isotropic HFS constant A_{iso}^N for the magnetic nucleus N can be calculated according to Eq. (1):^{2,7}

$$A_{\text{iso}}^N = -g_e g_N \mu_B \mu_N \langle S_z \rangle^{-1} \text{tr}(\mathbf{H}_{\text{FC},z}^N \mathbf{D}), \quad (1)$$

where g_e , g_N , μ_B , and μ_N are the electron and nuclear g factors, and the Bohr and nuclear magnetons, respectively. $\langle S_z \rangle$ is the expectation value of the z component of the elec-

^{a)}Electronic mail: filatov@theoc.gu.se

tron spin operator, \mathbf{D} the one-particle density matrix expanded in terms of basis set functions, and $\mathbf{H}_{\text{FC},z}^N$ the matrix of the z component of the Fermi coupling operator $\hat{\mathbf{h}}_{\text{FC}}$. The nonrelativistic Fermi coupling operator is given in Eq. (2):

$$\hat{\mathbf{h}}_{\text{FC}}(\mathbf{r}_N) = \frac{8\pi}{3} \delta(\mathbf{r}_N) \hat{\mathbf{S}}, \quad (2)$$

where $\delta(r)$ is the Dirac delta function, \mathbf{r}_N the electron position with respect to the magnetic nucleus N , and $\hat{\mathbf{S}}$ the electron spin operator. Note that Eq. (1) is applicable within the self-consistent field spin-unrestricted Hartree–Fock (HF) formalism as well as within the correlated formalism, provided that the so-called relaxed density matrix (i.e., the density matrix which incorporates the first-order response)^{7,20} is used.

In the scalar relativistic IORA/IORamm formalism,^{14,17} the FC operator is replaced by the quasirelativistic operator $\hat{\mathbf{H}}_{\text{FC},z}^{N,\text{rel}}$ given in matrix representation as

$$\begin{aligned} \mathbf{H}_{\text{FC},z}^{N,\text{rel}} = & \mathbf{G}^\dagger [\mathbf{H}_{\text{FC},z}^N - \mathbf{W}\mathbf{T}^{-1}\mathbf{H}_{\text{FC},z}^N\mathbf{T}^{-1}\mathbf{W} \\ & + \frac{3}{4}(\mathbf{W}\mathbf{T}^{-1}\mathbf{H}_{\text{FC},z}^N\mathbf{W}_0^{-1}\mathbf{W} \\ & + \mathbf{W}\mathbf{W}_0^{-1}\mathbf{H}_{\text{FC},z}^N\mathbf{T}^{-1}\mathbf{W})\mathbf{G}, \end{aligned} \quad (3)$$

which is correct up to terms of the order of c^{-6} (see Ref. 17 for more detail). In Eq. (3), \mathbf{T} is the matrix of the nonrelativistic kinetic energy operator $-1/2\nabla^2$ and the matrix \mathbf{W}_0 has the following elements:

$$(\mathbf{W}_0)_{\mu\nu} = \frac{1}{4c^2} \langle \chi_\mu | \mathbf{p}V_n \cdot \mathbf{p} | \chi_\nu \rangle, \quad (4)$$

where χ_μ denotes the basis set functions, V_n the electron-nuclear attraction potential, $\mathbf{p} = -i\nabla$ the linear momentum operator, and c the velocity of light. The matrix \mathbf{W} is the solution of the following equation:

$$\mathbf{W} = \mathbf{W}_0 + \mathbf{W}_0\mathbf{T}^{-1}\mathbf{W} \quad (5)$$

and the matrix \mathbf{G} is determined by Eq. (6),

$$\mathbf{G} = \left[\mathbf{S} + \frac{1}{2c^2} (\mathbf{T} + a\mathbf{W} + b\mathbf{W}\mathbf{T}^{-1}\mathbf{W}) \right]^{-1/2} \mathbf{S}^{1/2}, \quad (6)$$

where \mathbf{S} is the overlap matrix. The parameters a and b in Eq. (6) are, for IORA, $a=2$, $b=1$, and, for IORamm, $a=3/2$ and $b=1/2$.¹⁴ The IORamm method has much weaker gauge dependence than IORA (Refs. 14 and 15) and is the method of choice in all subsequent calculations.^{14–17}

III. DETAILS OF CALCULATIONS

In the present communication, we report the results of the IORamm calculations of atomic and molecular isotropic HFS constants carried out at the HF and correlation corrected level of *ab initio* wave function theory, using in the latter case second-order Møller–Plesset (MP2) many-body perturbation theory²¹ and coupled cluster theory in the quadratic configuration interaction approximation with all single and double excitations (QCISD).²² All calculations are performed with the help of the COLOGNE2004 suite of quantum-chemical programs,²³ which contains the IORA/IORamm formalism.

The calculations have been done for atomic and molecular systems with one unpaired electron: alkali metal atoms Li to Fr, coinage metal atoms Cu, Ag, Au, the mercury cation, and four mercury containing radicals HgH, HgCH₃, HgCN, and HgF. Accurate experimental data obtained either in the gas phase^{24–26} or in solid matrices^{27–30} are available for these species. Because all these species possess nondegenerate ground states, the application of the theory is straightforward.

The basis sets employed in this study were constructed from standard basis sets in the following way. For lithium, the aug-cc-pVTZ set of Dunning was used.³¹ For sodium through francium, the aug-cc-pVTZ basis sets of Sadlej were employed.³² For all alkali metal atoms, the s -type basis functions were completely decontracted, with the exception of francium where complete decontraction leads to serious linear dependencies in the basis set (due to the use of the Cartesian basis functions) and only partial decontraction of (the most tight) s -type basis functions was done. Five tight primitive s -type functions obtained in geometric sequence were added for Li to K, four tight functions were added for Rb, one for Cs, and none for Fr. This resulted in a [16s3p2d1f] set for Li, a [18s5p2d] set for Na, a [20s7p2d] set for K, a [22s9p4d] set for Rb, a [24s11p6d] set for Cs, and a [16s12p8d2f] set for Fr. The [16s4p3d1f] basis set for copper was constructed from the TZVpp basis set of Ahlrichs³³ by decontraction of the s -type basis functions and augmentation with three tight s -type primitives. The [14s10p7d] basis set for silver and the [14s10p9d3f] basis sets for gold and mercury were constructed from the corresponding basis sets of Gropen³⁴ as described in our previous publications.^{14,15}

In the molecular calculations, Dunning's standard aug-cc-pVDZ and aug-cc-pVTZ basis sets were used for the light elements H, C, N, and F.³¹ The geometries of the mercury containing radicals were optimized with the quasirelativistic IORamm/HF, IORamm/MP2, and IORamm/QCISD methods. All electrons were correlated when calculating the isotropic HFS constants. In the geometry optimizations, however the $1s$ to $4d$ electrons on mercury and $1s$ electrons on carbon, nitrogen, and fluorine were frozen.

IV. RESULTS AND DISCUSSION

The results of the atomic calculations are collected in Table I along with the experimental data^{24–26,29} and a selection of results from other quantum chemical investigations.^{11,13,35} The isotropic HFS constant is determined by the atomic s -electron density, which experiences the largest relativistic contraction, thus making a proper description of relativistic effects absolutely important. This is apparent from a comparison of the IORamm and nonrelativistic results listed in Table I. Even for elements as light as sodium ($Z=11$) and potassium ($Z=19$), the relativistic contraction results in a noticeable shift in the HFS constants. For the elements with $Z \approx 30$ and larger, the inclusion of relativity is mandatory to obtain useful results by the quantum-chemical calculations.

The IORamm/QCISD results in Table I compare fairly well with the experimental figures. This is not surprising

TABLE I. Hyperfine splitting constants (MHz) of alkali and coinage metal atoms.

Atom	Expt.	QCISD/ IORAmm	QCISD/ NR ^a	MP2/ IORAmm	MP2/ NR	HF/ IORAmm	HF/ NR	Other investigations
⁷ Li	401.752 ^b	401.643	401.058	397.497	396.918	390.673	390.099	384.804 ^c
²³ Na	885.816 ^b	866.984	849.331	859.567	842.033	781.566	765.572	816.406 ^c
³⁹ K	230.860 ^b	226.127	211.871	225.028	210.762	189.727	177.600	198.216 ^c
⁸⁷ Rb	3417.342 ^b	3455.291	2696.144	3519.249	2741.029	2926.352	2268.093	2967.993 ^c
¹³³ Cs	2298.158 ^b	2409.961	1426.990	2475.747	1456.927	2052.398	1186.676	1952.187 ^c 2346.5 ^d
²¹¹ Fr	8692.2 ^e	8436.7	2945.5	8785.0	3005.9	7733.7	2441.6	7900.8; ^{e,f} 9017.8 ^d
⁶³ Cu	5867 ^g	5411	4608	5792	4916	4338	3821	4075; ^h 3536 ⁱ
¹⁰⁷ Ag	-1713 ^g	-1698	-1108	-1760	-1143	-1473	-985	-1305; ^h -874 ⁱ
¹⁹⁷ Au	3053 ^g	3029	907	3189	959	2826	783	2584; ^h 685 ⁱ
¹⁹⁹ Hg ⁺	41300 ^j 39600 ^l	44327	14634	45448	15098	42946	13594	42366 ^k

^aNR stands for nonrelativistic.^bTaken from Ref. 24.^cQuantum electrodynamics result taken from Ref. 13.^dTaken from Ref. 11.^eTaken from Ref. 25.^fObtained from the value reported for ²¹²Fr using gyromagnetic ratios of the two isotopes (0.924 for ²¹²Fr and 0.888 for ²¹¹Fr).^gTaken from Ref. 26.^hNumerical Dirac-Fock (Kramers-restricted) results from Ref. 35.ⁱNumerical Hartree-Fock (spin-restricted) results from Ref. 35.^jValue measured in neon matrix in Ref. 27.^kMulticonfiguration Dirac-Fock result from Ref. 46.^lValue measured in argon matrix in Ref. 27.

because QCISD corresponds to full configuration interaction in the space of all single and double excitations. In addition, it includes higher correlation effects in the form of disconnected triple excitations (16%–19%), quadruple excitations, etc.³⁶ Hence, QCISD accounts for all important correlation effects typical of an atom with a spherical charge distribution. It has been reported in the literature^{7,37} that the perturbational inclusion of the triple excitations in QCISD(T) does not lead to a noticeable change in the calculated QCISD HFS constants of radicals.

Although the spin-unrestricted HF formalism provides a fair account of the exchange spin polarization of the core

electrons,³⁸ dynamic electron correlation accounted for by QCISD or MP2 makes a sizable contribution to the HFS constants. MP2 has a tendency to exaggerate the pair correlation effects,^{21,39} which leads to somewhat larger HFS constants for the MP2 calculations. For atoms, this exaggeration is not significant and, accordingly, MP2 and QCISD results are fairly close to each other (Table I). This however, may not be true in molecules, where the proper description of correlation effects, achieved by infinite-order methods such as QCISD, is necessary to obtain realistic spin densities and HFS constants.

The optimized molecular geometries of the mercury con-

TABLE II. Molecular geometries (in Å, deg) and NBO charges of mercury containing radicals.

Molecule	Parameter	Expt.	IORAmm/QCISD	IORAmm/MP2	IORAmm/HF
HgH	Hg-H	1.735 ^a	1.723	1.691	1.759
		1.741 ^b (1.766) ^c			
HgCH ₃	<i>q</i> _{Hg} ^d		0.391	0.359	0.456
	Hg-C		2.319	2.206	na ^e
	C-H		1.099	1.098	na
	HgCH		105.3	106.5	na
HgCN	<i>q</i> _{Hg}		0.321	0.375	na
	Hg-C		2.114	2.064	2.150
	C-N		1.179	1.155	1.145
HgF	<i>q</i> _{Hg}		0.678	0.735	0.773
	Hg-F		2.025	2.009	2.027
	<i>q</i> _{Hg}		0.736	0.733	0.835

^aFrom Ref. 41.^bFrom Ref. 42.^cReported in Ref. 43 as corresponding to zero vibrational level.^dNBO charge on the mercury atom.^eNot available. Molecule not bound at this level.

TABLE III. Hyperfine splitting constants (MHz) and NAO spin populations of the metal 6s orbital (in parentheses) of mercury containing radicals.

Method	Basis set and geometry	HgH	HgCH ₃	HgCN	HgF
Expt.		6859; ^a 7198 ^b	4921 ^c	15960 ^d	22163 ^e
IORAmm/QCISD	DZ, ^f <i>opt</i> ^g	7919(0.35069)	5194(0.26648)	16624(0.53902)	21564(0.64577)
	TZ, ^h <i>opt</i>	7961(0.35253)	na	na	21625(0.64616)
IORAmm/MP2	DZ, <i>qci</i> ⁱ	6932(0.31580)	5893(0.26892)	22740(0.63647)	21983(0.64397)
	TZ, <i>qci</i>	7036(0.31763)	6327(0.27771)	23204(0.63687)	22283(0.64752)
	DZ, <i>opt</i>	6847(0.32393)	6229(0.31779)	19921(0.59425)	21746(0.64328)
	TZ, <i>opt</i>	6935(0.32540)	6614(0.32382)	20319(0.59368)	22025(0.64637)
IORAmm/HF	DZ, <i>qci</i>	8060(0.42050)	3010(0.27078)	17821(0.63390)	23110(0.73190)
	TZ, <i>qci</i>	8031(0.42247)	2941(0.26663)	17723(0.62711)	23002(0.72958)
	DZ, <i>opt</i>	8113(0.41054)	na	18803(0.64223)	23140(0.73208)
	TZ, <i>opt</i>	8092(0.41257)	na	18731(0.63582)	23033(0.72976)

^aObtained in Ref. 27 from measurement in neon matrix.

^bObtained in Ref. 27 from measurement in argon matrix.

^cObtained in Ref. 30 from measurement in neon matrix.

^dObtained in Ref. 29 from measurement in argon matrix.

^eObtained in Ref. 28 from measurement in argon matrix.

^faug-cc-pVDZ basis employed on light elements.

^gGeometry optimized with respective method (see Table II).

^haug-cc-pVTZ basis employed on light elements.

ⁱGeometry optimized with IORAmm/QCISD (see Table II).

taining radicals are collected in Table II along with the results of the natural bond orbital (NBO) analysis.⁴⁰ In the geometry optimizations, Dunning's aug-cc-pVDZ basis set³¹ was employed for the light atoms. The only experimental gas phase bond length available is that for the mercury hydride radical.^{41–43} The IORAmm/QCISD length of Hg-H (1.723 Å, Table II) is in fair agreement with the experimental value⁴² of 1.741 Å and with the results of other theoretical calculations^{44,45} (not reported in Table II). For example, the GRECP/MRD-CI calculations of Mosyagin *et al.*⁴⁴ produced exactly the same Hg-H distance of 1.723 Å as the IORAmm/QCISD calculation (Table II).

The mercury isotropic HFS constants $A_{\text{iso}}^{\text{Hg}}$ are collected in Table III along with the available experimental data obtained in noble gas matrices.^{27–30} Two types of molecular geometries were used in the MP2 and HF calculations: the IORAmm/QCISD geometry as the most reliable one and the geometry optimized with the method used for the HFS calculations. Comparison of the HFS constants calculated with and without correlation corrections at the same geometry should elucidate the role of electron correlation.

With the only exception of mercury hydride, the IORAmm/QCISD HFS constants are in excellent agreement with the experimental data (Table III). Even in an extreme case as that of mercury fluoride, which possesses probably the largest observed HFS constant (22163 MHz, Table III),²⁸ the error in the calculated HFS constant is only 2%. The extension of the basis sets for the light atoms from aug-cc-pVDZ to aug-cc-pVTZ quality leads to an insignificant variation in the calculated HFS constants. Due to program limitations, the QCISD calculations for mercury cyanide and methylmercury radicals could not be carried out with the triple-zeta basis set.

Electron correlation leads to noticeable differences in the spin-density distribution of a radical. This is indicated by the spin populations of the 6s natural atomic orbital (NAO) of

mercury as reported in Table III. However, the difference in the spin populations does not always translate to the difference in the isotropic HFS constants. Thus, for HgH, the HFS constants from QCISD and HF calculations are close to each other, whereas the 6s orbital spin populations are quite different. Similar situations are found for the radicals mercury cyanide and mercury fluoride. In contrast, the 6s orbital spin populations of methylmercury calculated at the QCISD, MP2, and HF level of theory are similar, whereas the HFS constants differ noticeably (Table III).

In general, the inclusion of correlation leads to a contraction of core electron density toward the nucleus, which causes an increase of the calculated HFS constant. This is reflected by the results of Table I and, for the case of methylmercury, of Table III. However, a positive increment in HFS constant due to electron correlation is compensated by a negative increment due to a decrease in the orbital spin population, which occurs for HgH, HgCN, and HgF when improving the method from HF to QCISD. Thus, the two effects cancel each other and the results of HF and QCISD calculations for these radicals are close. However, this similarity of the HFS constants should not be interpreted in the way that electron correlation plays only a minor role. A proper account of correlation effects does play a role and, as it is seen from the MP2 and QCISD HFS constant $A_{\text{iso}}^{\text{Hg}}$ of methylmercury, even higher-order correlation effects are needed to obtain reliable results.

The experimental HFS constants cited in Table III were obtained in matrix isolation experiments.^{27–30} Although, noble gases such as neon and argon are chemically inert, the measured HFS values of the molecular radicals are shifted relative to the gas phase values due to nonbonded interactions between radical atoms and the inert matrix. The IORAmm/QCISD values of atomic HFS constants reported in Table I are in a fairly good agreement with the experimental data from the gas phase (all entries besides that of

$^{199}\text{Hg}^+$). For $^{199}\text{Hg}^+$, the result of the IORAm/HF calculation (42946 MHz, Table III) is in good agreement with the value obtained in a multiconfiguration Dirac–Fock calculation (42366 MHz).⁴⁶ This indicates that the IORAm methodology reproduces the results of the exact four-component calculations with sufficient accuracy. Consequently, the IORAm/QCISD value (including the effects of dynamic electron correlation) of $A_{\text{iso}}^{\text{Hg}}$ for $^{199}\text{Hg}^+$ should be also in good agreement with the gas phase HFS constant (not available in the literature). The seemingly inert matrices can shift the measured atomic $A_{\text{iso}}^{\text{Hg}}$ values (cited in Table I) by 6%–10%. Having this in mind, the observed difference between the calculated and measured values of $A_{\text{iso}}^{\text{Hg}}$ in the HgH radical does not seem unreasonable.

V. CONCLUSIONS

In summary, a new algorithm for an efficient calculation of relativistically corrected molecular hyperfine structure constants has been developed and implemented within the context of wave function *ab initio* theory. The new approach can be used with both HF and correlated (Møller–Plesset, coupled-cluster, quadratic CI) wave functions. Benchmark calculations for atoms demonstrated that HFS constants of high accuracy can be obtained provided that electron correlation is accounted for at a sufficiently high level of theory (e.g., as in QCISD). For the first time, relativistically corrected isotropic HFS constants for molecules containing a heavy element such as mercury were calculated with the inclusion of electron correlation. In view of the accurate atomic HFS constants obtained with the same method, the results of the IORAm/QCISD calculations represent a reasonable estimate of the gas phase molecular HFS constants, which may deviate from the constants measured in matrix isolation experiments up to 10%.

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