Relativistically corrected hyperfine structure constants calculated with the regular approximation applied to correlation corrected \textit{ab initio} theory

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The infinite-order regular approximation (IORA) and IORA with modified metric (IORA/mm) 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\textsuperscript{2+} radical ion, and the mercury containing radicals HgH, HgCH\textsubscript{2}, HgCN, and HgF. By stepwise improvement of the level of theory from Hartree–Fock to second-order Möller–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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{1,2}

Although the theory underlying the hyperfine structure is well understood and was developed already in the early days of quantum mechanics,\textsuperscript{1–3} the first principles calculation of the HFS parameters proved to be a challenging task for wave function \textit{ab initio} methods.\textsuperscript{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.\textsuperscript{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,\textsuperscript{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\textsuperscript{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 (IORA/mm) (Ref. 14) enables one to apply the new procedure efficiently within the context of wave function \textit{ab initio} theory. Analytic energy derivatives have been developed for the IORA/IORA/mm 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,\textsuperscript{16} and analytic calculation of indirect nuclear spin–spin coupling constants.\textsuperscript{17}

In the theory of nuclear spin–spin coupling, one distinguishes, according to Ramsey,\textsuperscript{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 constants\textsuperscript{1,17} 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).\textsuperscript{2,7}

\[
A_{iso}^N = - g_e g_N \mu_B \mu_N \langle S_z \rangle^{-1} \text{tr}(H_{FC,D}^N),
\]

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

$$\hat{h}_{\mathbf{F}}(r_\gamma) = \frac{8\pi}{3} \delta(r_\gamma) \tilde{\mathbf{S}},$$

(2)

where $\delta(r)$ is the Dirac delta function, $r_\gamma$ the electron position with respect to the magnetic nucleus $N$, and $\tilde{\mathbf{S}}$ 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) is used.

In the scalar relativistic IORA/IORAmm formalism, the FC operator is replaced by the quasirelativistic operator $\hat{h}_{\mathbf{F}}^{N,rel}$ in matrix representation as

$$\hat{h}_{\mathbf{F}}^{N,rel} = G^{\dagger} \left[ \hat{h}_{\mathbf{F}}^N - W_{1}^{-1} \hat{h}_{\mathbf{F}}^N T^{-1} W + \frac{1}{2} \left( W_{1}^{-1} \hat{h}_{\mathbf{F}}^N W_{1}^{-2} - W_{1}^{-1} \hat{h}_{\mathbf{F}}^N W_{1}^{-1} W + W_{1}^{-1} \hat{h}_{\mathbf{F}}^N W_{1}^{-1} W \right) \right] G,$$

(3)

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

$$\left( W_{1} \right)_{\mu\nu} = \frac{1}{4e^2} \left( \chi_\mu |p V_n - p| \chi_\nu \right).$$

(4)

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

$$W = W_{0} + W_{2} T^{-1} W$$

(5)

and the matrix $G$ is determined by Eq. (6).

$$G = \left[ S + \frac{1}{2c^2} \left( T + aW + bWT^{-1}W \right) \right]^{-1/2} S^{1/2},$$

(6)

where $S$ is the overlap matrix. The parameters $a$ and $b$ are in Eq. (6) are, for IORA, $a = 2$, $b = 1$, and, for IORAmm, $a = 3/2$ and $b = 1/2$. 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 isoropic 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 theory and coupled cluster theory in the quadratic configuration interaction approximation with all single and double excitations (QCISD). All calculations are performed with the help of the COLOGNE2004D suite of quantum-chemical programs, 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 or in solid matrices 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 Gropp34 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 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 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 relativistic effects 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...
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 $\sim 16\%–19\%$, quadruple excitations, etc. Hence, QCISD accounts for all important correlation effects typical of an atom with a spherical charge distribution. It has been reported in the literature\textsuperscript{7,37} that the perturbational inclusion of the triple excitations in QCISD \textsuperscript{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,\textsuperscript{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,\textsuperscript{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 \textsuperscript{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.

\textbf{TABLE I.} Hyperfine splitting constants (MHz) of alkali and coinage metal atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Expt.</th>
<th>QCISD/IORAmm</th>
<th>QCISD/NR</th>
<th>MP2/IORAmm</th>
<th>MP2/NR</th>
<th>HF/IORAmm</th>
<th>HF/NR</th>
<th>Other investigations</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textsuperscript{7}Li</td>
<td>401.752 \textsuperscript{a} &amp; 401.643</td>
<td>401.058</td>
<td>397.497</td>
<td>396.918</td>
<td>390.673</td>
<td>390.099</td>
<td>384.804 \textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>\textsuperscript{23}Na</td>
<td>885.816 \textsuperscript{b} &amp; 866.984</td>
<td>849.331</td>
<td>859.567</td>
<td>842.033</td>
<td>781.566</td>
<td>765.572</td>
<td>816.406 \textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>\textsuperscript{39}K</td>
<td>230.860 \textsuperscript{c} &amp; 226.127</td>
<td>211.871</td>
<td>225.028</td>
<td>210.762</td>
<td>189.727</td>
<td>177.600</td>
<td>198.216 \textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>\textsuperscript{87}Rb</td>
<td>3417.342 \textsuperscript{e} &amp; 3455.291</td>
<td>2696.144</td>
<td>3519.249</td>
<td>2741.029</td>
<td>2926.352</td>
<td>2268.093</td>
<td>2967.993 \textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>\textsuperscript{133}Cs</td>
<td>2298.158 \textsuperscript{b} &amp; 2409.961</td>
<td>1426.990</td>
<td>2475.747</td>
<td>1456.928</td>
<td>2052.398</td>
<td>1186.676</td>
<td>1952.187 \textsuperscript{e}</td>
<td></td>
</tr>
<tr>
<td>\textsuperscript{211}Fr</td>
<td>8692.2 \textsuperscript{e} &amp; 8436.7</td>
<td>2945.5</td>
<td>8785.0</td>
<td>3005.9</td>
<td>7733.7</td>
<td>2441.6</td>
<td>7900.8 \textsuperscript{e,f}</td>
<td></td>
</tr>
<tr>
<td>\textsuperscript{63}Cu</td>
<td>5867 \textsuperscript{f} &amp; 5411</td>
<td>4608</td>
<td>5792</td>
<td>4916</td>
<td>4338</td>
<td>3821</td>
<td>4075 \textsuperscript{g}</td>
<td></td>
</tr>
<tr>
<td>\textsuperscript{107}Ag</td>
<td>\textsuperscript{–}1713 \textsuperscript{f} &amp; \textsuperscript{–}1698</td>
<td>\textsuperscript{–}1108</td>
<td>\textsuperscript{–}1760</td>
<td>\textsuperscript{–}1143</td>
<td>\textsuperscript{–}1473</td>
<td>\textsuperscript{–}985</td>
<td>\textsuperscript{–}1305 \textsuperscript{b}</td>
<td></td>
</tr>
<tr>
<td>\textsuperscript{197}Au</td>
<td>41300 \textsuperscript{g} &amp; 44327</td>
<td>14634</td>
<td>45448</td>
<td>15098</td>
<td>42946</td>
<td>13594</td>
<td>42366 \textsuperscript{b}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}NR stands for nonrelativistic.
\textsuperscript{b}Taken from Ref. 24.
\textsuperscript{c}Quantum electrodynamics result taken from Ref. 13.
\textsuperscript{d}Taken from Ref. 11.
\textsuperscript{e}Taken from Ref. 25.
\textsuperscript{f}Obtained from the value reported for \textsuperscript{212}Fr using gyromagnetic ratios of the two isotopes (0.924 for \textsuperscript{212}Fr and 0.888 for \textsuperscript{211}Fr).
\textsuperscript{g}Taken from Ref. 26.
\textsuperscript{h}Numerical Dirac–Fock (Kramers-restricted) results from Ref. 35.
\textsuperscript{i}Numerical Hartree–Fock (spin-restricted) results from Ref. 35.
\textsuperscript{j}Value measured in neon matrix in Ref. 27.
\textsuperscript{k}Multiconfiguration Dirac–Fock result from Ref. 46.
\textsuperscript{l}Value measured in argon matrix in Ref. 27.

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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Parameter</th>
<th>Expt.</th>
<th>IORAmm/QCISD</th>
<th>IORAmm/MP2</th>
<th>IORAmm/HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgH</td>
<td>Hg-H</td>
<td>1.735 \textsuperscript{a, b}</td>
<td>1.723</td>
<td>1.691</td>
<td>1.759</td>
</tr>
<tr>
<td>HgCH\textsubscript{3}</td>
<td>q\textsubscript{Hg} \textsuperscript{d}</td>
<td>Hg-C</td>
<td>0.391</td>
<td>0.359</td>
<td>0.456</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>2.319</td>
<td>2.206</td>
<td>na \textsuperscript{e}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HgCH</td>
<td>1.099</td>
<td>1.098</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td></td>
<td>q\textsubscript{Hg}</td>
<td>105.3</td>
<td>106.5</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>HgCN</td>
<td>Hg-C</td>
<td>2.114</td>
<td>2.064</td>
<td>2.150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-N</td>
<td>1.179</td>
<td>1.155</td>
<td>1.145</td>
<td></td>
</tr>
<tr>
<td></td>
<td>q\textsubscript{Hg}</td>
<td>0.678</td>
<td>0.735</td>
<td>0.773</td>
<td></td>
</tr>
<tr>
<td>HgF</td>
<td>Hg-F</td>
<td>2.025</td>
<td>2.009</td>
<td>2.027</td>
<td></td>
</tr>
<tr>
<td></td>
<td>q\textsubscript{Hg}</td>
<td>0.736</td>
<td>0.733</td>
<td>0.835</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}From Ref. 41.
\textsuperscript{b}From Ref. 42.
\textsuperscript{c}Reported in Ref. 43 as corresponding to zero vibrational level.
\textsuperscript{d}NBO charge on the mercury atom.
\textsuperscript{e}Not 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.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis set and geometry</th>
<th>HgH</th>
<th>HgCH₃</th>
<th>HgCN</th>
<th>HgF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt.</td>
<td></td>
<td>6859⁺ 7198ᵇ</td>
<td>492¹ᶜ</td>
<td>1596ᵈ</td>
<td>2216ᵉ</td>
</tr>
<tr>
<td>IORAmm/QCISD</td>
<td>DZ, opt⁸</td>
<td>7919(0.35069)</td>
<td>5194(0.26648)</td>
<td>1662(0.53902)</td>
<td>21564(0.64577)</td>
</tr>
<tr>
<td></td>
<td>TZ, opt¹</td>
<td>7961(0.35253)</td>
<td>na</td>
<td>na</td>
<td>21625(0.64616)</td>
</tr>
<tr>
<td>IORAmm/MP2</td>
<td>DZ, qci¹</td>
<td>6932(0.31580)</td>
<td>5893(0.26892)</td>
<td>22740(0.63647)</td>
<td>21983(0.64397)</td>
</tr>
<tr>
<td></td>
<td>TZ, qci</td>
<td>7036(0.31763)</td>
<td>6327(0.27771)</td>
<td>23204(0.63687)</td>
<td>22283(0.64752)</td>
</tr>
<tr>
<td></td>
<td>DZ, opt</td>
<td>6847(0.32393)</td>
<td>6229(0.31779)</td>
<td>19921(0.59425)</td>
<td>21746(0.64328)</td>
</tr>
<tr>
<td></td>
<td>TZ, opt</td>
<td>6935(0.32540)</td>
<td>6614(0.32382)</td>
<td>20319(0.59368)</td>
<td>22025(0.64637)</td>
</tr>
<tr>
<td>IORAmm/HF</td>
<td>DZ, qci</td>
<td>8060(0.42050)</td>
<td>3010(0.27078)</td>
<td>17821(0.63390)</td>
<td>23110(0.73190)</td>
</tr>
<tr>
<td></td>
<td>TZ, qci</td>
<td>8031(0.42247)</td>
<td>2941(0.26664)</td>
<td>17723(0.62711)</td>
<td>23002(0.72058)</td>
</tr>
<tr>
<td></td>
<td>DZ, opt</td>
<td>8113(0.41054)</td>
<td>na</td>
<td>18803(0.64223)</td>
<td>23140(0.73208)</td>
</tr>
<tr>
<td></td>
<td>TZ, opt</td>
<td>8092(0.41257)</td>
<td>na</td>
<td>18731(0.63582)</td>
<td>23033(0.72976)</td>
</tr>
</tbody>
</table>

*Obtained 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.  
⁸Aug-cc-pVdz basis employed on light elements.  
¹Optimized geometry with respective method (see Table II).  
¹ᶜAug-cc-pVTZ basis employed on light elements.  
⁸Geometry optimized with IORAmm/QCISD (see Table II).

The mercury isotropic HFS constants A₁²ᴴg are collected in Table II along with the results of the natural bond orbital (NBO) analysis. In the geometry optimizations, Dunning’s aug-cc-pVdz basis set was employed for the light atoms. The only experimental gas phase bond length available is that for the mercury hydride radical. The IORAmm/QCISD length of Hg-H (1.723 Å, Table II) is in fair agreement with the experimental value 22740 MHz, 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 A₁²ᴴg 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. 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 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 A₁²ᴴg of methylmercury, even higher-order correlation effects are needed to obtain reliable results.
The measured atomic $^{199}$Hg$^+$, for $^{199}$Hg$^+$, the result of the IORAmm/HF calculation (42946 MHz, Table III) is in good agreement with the value obtained in a multiconfiguration Dirac–Fock calculation (42366 MHz). This indicates that the IORAmm methodology reproduces the results of the exact four-component calculations with sufficient accuracy. Consequently, the IORAmm/QCISD value (including the effects of dynamic electron correlation) of $A_{\text{iso}}^{199}$ for $^{199}$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 $A_{\text{iso}}^{199}$ values (cited in Table I) by 6%–10%. Having this in mind, the observed difference between the calculated and measured values of $A_{\text{iso}}^{199}$ 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 \textit{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 IORAmm/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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