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 (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 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 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 (IORAmm) (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/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,\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} can be straightforwardly reformulated for the calculation of HFS constants.

II. THEORY OF HFS CONSTANTS

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

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

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 elec-
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, HgCH$_3$, 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 [1s6p3d1f] set for Li, a [1s8p5d2f] 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 Ahlrichs$^{33}$ 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 Gropen$^{34}$ 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...
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, quadruple excitations, etc.\textsuperscript{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\textsuperscript{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,\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 (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 containing radicals are given in Table II. The NBO charges of the mercury atom in these molecules are also shown. The NBO charges are obtained by a method that is based on the natural population analysis of the molecular orbitals. They provide useful information about the localization of the electronic density on the individual atoms.
taining radicals 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) is in fair agreement with the experimental value (1.741 Å) and with the results of other theoretical calculations (not reported in Table II). For example, the GRECP/MRD-CI calculations of Mosyagin et al. produced exactly the same Hg-H distance of 1.723 Å as the IORAmm/QCISD calculation (Table II).

The mercury isotropic HFS constants \( A^\text{Hg}_{\text{iso}} \) are collected in Table III along with the available experimental data obtained in noble gas matrices. 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), 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 \( A^\text{Hg}_{\text{iso}} \) 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

### Table II

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis set and geometry</th>
<th>HgH</th>
<th>HgCH₃</th>
<th>HgCN</th>
<th>HgF</th>
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<tr>
<td>Exp.</td>
<td></td>
<td>6859</td>
<td>4921</td>
<td>15960</td>
<td>22163</td>
</tr>
<tr>
<td>IORAmm/QCISD</td>
<td>DZ, opt</td>
<td>7919</td>
<td>5194</td>
<td>16624</td>
<td>21564</td>
</tr>
<tr>
<td></td>
<td>TZ, opt</td>
<td>7961</td>
<td>na</td>
<td>21625</td>
<td></td>
</tr>
<tr>
<td>IORAmm/MP2</td>
<td>DZ, qci</td>
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<td>2274</td>
<td>21983</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TZ, qci</td>
<td>7036</td>
<td>2320</td>
<td>22833</td>
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<td>1992</td>
<td>21746</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TZ, opt</td>
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<td>2031</td>
<td>22025</td>
<td></td>
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<tr>
<td>IORAmm/HF</td>
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<td>8060</td>
<td>1782</td>
<td>23110</td>
<td></td>
</tr>
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<td>1772</td>
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<tr>
<td></td>
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<td>1880</td>
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<tr>
<td></td>
<td>TZ, opt</td>
<td>8092</td>
<td>1873</td>
<td>23033</td>
<td></td>
</tr>
</tbody>
</table>

*Obtained in Ref. 27 from measurement in argon matrix.
*Obtained in Ref. 27 from measurement in argon matrix.
*Obtained in Ref. 30 from measurement in neon matrix.
*Obtained from Ref. 29 from measurement in argon matrix.
*Obtained in Ref. 28 from measurement in neon matrix.
*Obtained in Ref. 29 from measurement in argon matrix.
*Obtained in measurement in argon matrix.
*Obtained in measurement in argon matrix.
*Geometry optimized with respective method (see Table II).
*Geometry optimized with IORAmm/QCISD (see Table II).
The measured atomic HFS constants obtained with the same method, the calculated and measured values of $A_{10}^{199}$Hg is in good agreement with the gas phase HFS constant. This indicates that the IORAmm/QCISD calculations represent a reasonably accurate calculation 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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