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Analytic Calculation of Isotropic Hyperfine Structure Constants Using the Normalized Elimination of the Small Component Formalism

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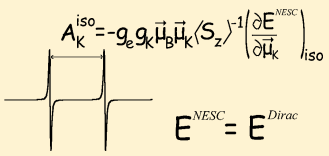
ABSTRACT: Based on the normalized elimination of the small component relativistic formalism, a new approach to the calculation of hyperfine structure parameters of paramagnetic molecules is developed and implemented. The new method is tested in the calculation of the isotropic hyperfine structure constant for a series of open-shell molecules containing mercury. The results of calculations carried out in connection with ab initio methods of increasing complexity demonstrate the high accuracy of the formalism developed. In view of its computational simplicity, the new approach provides the basis for an efficient and accurate calculation of the HFS parameters of large molecules.



1. INTRODUCTION

The hyperfine structure (HFS) of the electron paramagnetic resonance (EPR) spectrum provides valuable information on the electronic structure and molecular geometry of paramagnetic species.[1,2] The HFS of paramagnetic resonance spectra arises from the interaction between the magnetic moment of (the) unpaired electron(s) and the magnetic moment of magnetic nuclei. Commonly, the HFS tensor is split into an isotropic (Fermi-contact) part and an anisotropic (spin-dipolar) part, whereby the latter averages to zero as a result of molecular tumbling in the gas or liquid phase. Although the theory underlying hyperfine structure is well understood,[1−3] the practical calculation of the HFS parameters proves to be a challenging task.[3,4] The isotropic HFS constant is typically associated with the electron spin-density in the vicinity of the magnetic nucleus, an accurate description of which often requires the use of high-level ab initio methods.[5−7]

Apart from the necessity of accurately describing electron correlation, relativity has also to be taken into account when calculating the HFS parameters, especially in the case of molecules containing heavy elements.[3,8−12] Due to the computational complexity of high-level relativistic ab initio methods,[13] density functional theory methods are most often used in connection with the relativistic treatment of HFS constants.[8,10−12] Previously, two of us have developed, with the help of the infinite-order regular approximation,[14,15] a relativistically corrected ab initio approach for the calculation of HFS constants.[9] In the current work, a new formalism based on the use of the exact two-component relativistic theory, the normalized elimination of the small component (NESC) method,[16] will be presented. The new approach utilizes the recently developed methodology for obtaining NESC analytic derivatives,[17,18] which makes it possible to efficiently calculate HFS constants using high-level ab initio computational schemes. In section 2, the theory of the NESC method and its analytic derivatives will be briefly outlined and applied to the calculation of the HFS constants. The new formalism for the determination of HFS constants will be applied to a series of open-shell molecules containing mercury and the results of these calculations will be described in section 4 where the high accuracy of the new approach will be demonstrated.

2. THEORY

When using the NESC method,[16] one solves the following eigenvalue equation,

$$\tilde{\mathbf{L}}\mathbf{A}_+ = \tilde{\mathbf{S}}\mathbf{A}_+\varepsilon^+ \tag{1}$$

which yields the positive-energy (electronic) solutions of the Dirac equation.[19] The positive-energy eigenvectors $\mathbf{A}_+$ are normalized according to $\mathbf{A}_+^\dagger\tilde{\mathbf{S}}\mathbf{A}_+ = \mathbf{I}$ on the metric $\tilde{\mathbf{S}}$ given by eq 2,

$$\tilde{\mathbf{S}} = \mathbf{S} + \frac{1}{2mc^2}\mathbf{U}^\dagger\mathbf{T}\mathbf{U} \tag{2}$$

which corresponds to the exact normalization of the large component of the relativistic 4-component wave function.

In the NESC method, the decoupling between the electronic and the positronic solutions of the Dirac equation is achieved by the elimination of the small-component of the electronic four-component wave function[16] using the operator $\mathbf{U}$, which connects the large $\mathbf{A}_+$ and the pseudolarge $\mathbf{B}_+$ components of the modified Dirac wave function via $\mathbf{B}_+ = \mathbf{U}\mathbf{A}_+$.[16] The operator $\mathbf{U}$ can be obtained, in matrix form, simultaneously with the NESC Hamiltonian $\tilde{\mathbf{L}}$ by iteratively solving the following system of equations.[16,20−23]

$$\mathbf{U} = \mathbf{T}^{-1}(\mathbf{S}\tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}} - \mathbf{V}) \tag{3}$$

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$$\tilde{\mathbf{L}} = \mathbf{TU} + \mathbf{U}^{\dagger}\mathbf{T} - \mathbf{U}^{\dagger}(\mathbf{T} - \mathbf{W})\mathbf{U} + \mathbf{V} \tag{4}$$

Alternatively, a one-step approach based on the modified Dirac equation[16] (5) can be utilized for obtaining $\mathbf{U}$ and $\tilde{\mathbf{L}}$.

$$\begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \mathbf{W} - \mathbf{T} \end{pmatrix}\begin{pmatrix} \mathbf{A}_- & \mathbf{A}_+ \\ \mathbf{B}_- & \mathbf{B}_+ \end{pmatrix} = \begin{pmatrix} \mathbf{S} & 0 \\ 0 & (2mc^2)^{-1}\mathbf{T} \end{pmatrix}\begin{pmatrix} \mathbf{A}_- & \mathbf{A}_+ \\ \mathbf{B}_- & \mathbf{B}_+ \end{pmatrix}\begin{pmatrix} \boldsymbol{\varepsilon}^- & 0 \\ 0 & \boldsymbol{\varepsilon}^+ \end{pmatrix} \tag{5}$$

In the one-step approach, proposed for the first time by Dyall[16] and used later by Iliaš et al.[24] and Zou et al.[23] in practical implementations of the NESC method, the elimination of the small component operator $\mathbf{U}$ is obtained as in eq 6,

$$\mathbf{U} = \mathbf{B}_+\mathbf{A}_+^{\dagger}(\mathbf{A}_+\mathbf{A}_+^{\dagger})^{-1} = \mathbf{B}_+\mathbf{A}_+^{\dagger}\tilde{\mathbf{S}} \tag{6}$$

where $\tilde{\mathbf{S}}^{-1} = \mathbf{A}_+\mathbf{A}_+^{\dagger}$ is used. In eqs 5 and 6, $\mathbf{A}_-$ and $\mathbf{B}_-$ are the large and the pseudolarge components of the negative-energy (positronic) states with the eigenenergies $\boldsymbol{\varepsilon}^-$ whereas matrices $\mathbf{A}_+$, $\mathbf{B}_+$, and $\boldsymbol{\varepsilon}^+$ belong to the positive-energy (electronic) states.[16]

In eqs 1−5, $\mathbf{S}$ and $\mathbf{V}$ are the usual matrices of the overlap and potential energy operators in the basis of the atomic orbitals $\chi_\mu(\mathbf{r})$. Matrices $\mathbf{T}$ and $\mathbf{W}$ are associated with the kinetic energy operator $((\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{\pi})^2/2m)$ and the operator $(1/4m^2c^2)(\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{\pi})V(\mathbf{r})\cdot(\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{\pi})$,[16] in which the external magnetic field $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ caused by the vector-potential $\mathbf{A}(\mathbf{r})$ couples to the electron linear momentum $\mathbf{p} = -\mathrm{i}\nabla$ via eq 7.

$$\boldsymbol{\pi} = \mathbf{p} + \mathbf{A}(\mathbf{r}) \tag{7}$$

In the equations given above, c is the velocity of light (c = 137.035999070(98) au)[25] and $\hat{\boldsymbol{\sigma}}$ is the vector of the Pauli matrices, $\hat{\boldsymbol{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$.[26]

Using the one-electron (1e) approximation of Dyall,[16,27] the NESC Hamiltonian obtained in the potential field of bare nuclei is employed to obtain the energy of an open-shell many-electron system according to eq 8

$$E = \sum_{\sigma} \mathrm{tr}\, \mathbf{P}^{\sigma}\mathbf{H}_{1e} + \frac{1}{2}\sum_{\sigma,\sigma'} \mathrm{tr}\, \mathbf{P}^{\sigma}(\mathbf{J}^{\sigma\sigma'} - \mathbf{K}^{\sigma\sigma'}) \tag{8}$$

for the case of the Hartree−Fock method. In eq 8, σ labels the spin state of electron, α or β, $\mathbf{J}^{\sigma\sigma'}$ and $\mathbf{K}^{\sigma\sigma'}$ are the matrices of the Coulomb and exchange operators, $\mathbf{P}^{\sigma}$ is the density matrix for the spin manifold σ defined as $\mathbf{P}^{\sigma} = \mathbf{C}^{\sigma}\mathbf{n}^{\sigma}(\mathbf{C}^{\sigma})^{\dagger}$, where $\mathbf{C}^{\sigma}$ collects the eigenvectors of the respective Fock operator, $\mathbf{n}^{\sigma}$ is the diagonal matrix of the orbital occupation numbers, and $\mathbf{H}_{1e}$ is a renormalized NESC one-electron Hamiltonian as given by eq 9,

$$\mathbf{H}_{1e} = \mathbf{G}^{\dagger}\tilde{\mathbf{L}}\mathbf{G} \tag{9}$$

with $\mathbf{G}$ being the renormalization matrix according to eq 10.[28]

$$\mathbf{G} = \mathbf{S}^{-1/2}(\mathbf{S}^{1/2}\tilde{\mathbf{S}}^{-1}\mathbf{S}^{1/2})^{1/2}\mathbf{S}^{1/2} \tag{10}$$

The one-electron relativistic Hamiltonian of eq 9 can also be used in connection with the Kohn−Sham energy functional or in the context of post-SCF and multireference correlated ab initio methods. In the following, we will refer to the SCF formalism for simplicity.

Generally, the first derivative of the energy (8) with respect to an external perturbation λ is given by eq 11[17]

$$\frac{\partial E}{\partial \lambda} = \sum_{\sigma} \mathrm{tr}\, \mathbf{P}^{\sigma}\left(\frac{\partial \mathbf{H}_{1e}}{\partial \lambda}\right) + \frac{1}{2}\sum_{\sigma,\sigma'} \mathrm{tr}\, \mathbf{P}^{\sigma}\frac{\partial'}{\partial \lambda}(\mathbf{J}^{\sigma\sigma'} - \mathbf{K}^{\sigma\sigma'}) - \mathrm{tr}\, \sum \boldsymbol{\Omega}^{\sigma}\left(\frac{\partial \mathbf{S}}{\partial \lambda}\right) \tag{11}$$

where $\boldsymbol{\Omega}^{\sigma} = \mathbf{C}^{\sigma}\mathbf{n}^{\sigma}\boldsymbol{\varepsilon}^{\sigma}(\mathbf{C}^{\sigma})^{\dagger}$ is the energy-weighted density matrix and the prime at $(\partial'/\partial\lambda)$ implies that the two-electron integrals rather than the density matrix need to be differentiated. Provided that the two-electron integrals and the overlap matrix are independent of the perturbation, derivative eq 11 is entirely defined by its first term,

$$\mathrm{tr}\, \mathbf{P}^{\sigma}\left(\frac{\partial \mathbf{H}_{1e}}{\partial \lambda}\right) = \mathrm{tr}\, \mathbf{P}^{\sigma}\mathbf{G}^{\dagger}\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda}\mathbf{G} + \mathrm{tr}\, \mathbf{P}^{\sigma}\frac{\partial \mathbf{G}^{\dagger}}{\partial \lambda}\tilde{\mathbf{L}}\mathbf{G} + \mathrm{tr}\, \mathbf{P}^{\sigma}\mathbf{G}^{\dagger}\tilde{\mathbf{L}}\frac{\partial \mathbf{G}}{\partial \lambda} \tag{12}$$

$$= \mathrm{tr}\, \tilde{\mathbf{P}}^{\sigma}\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda} + \mathrm{tr}\, \mathbf{D}^{\sigma}\frac{\partial \mathbf{G}^{\dagger}}{\partial \lambda} + \mathrm{tr}(\mathbf{D}^{\sigma})^{\dagger}\frac{\partial \mathbf{G}}{\partial \lambda} \tag{13}$$

where new matrices $\tilde{\mathbf{P}}^{\sigma} = \mathbf{G}\mathbf{P}^{\sigma}\mathbf{G}^{\dagger}$ and $\mathbf{D}^{\sigma} = \tilde{\mathbf{L}}\mathbf{G}\mathbf{P}^{\sigma}$ are used and the summation with respect to the spin index σ is implied. The formalism for obtaining derivatives in eq 13 has been developed in our previous works[17,18] and, for brevity, only the final formulas will be presented in the following.

The derivative in eq 13 is given by

$$\mathrm{tr}\, \mathbf{P}^{\sigma}\left(\frac{\partial \mathbf{H}_{1e}}{\partial \lambda}\right) = \mathrm{tr}\Bigg(\mathbf{U}\tilde{\mathbf{P}}^{\sigma} + \tilde{\mathbf{P}}^{\sigma}\mathbf{U}^{\dagger} - \mathbf{U}\tilde{\mathbf{P}}^{\sigma}\mathbf{U}^{\dagger} - \frac{1}{2mc^2}(\mathbf{U}\mathbf{D}_3^{\sigma}\mathbf{U}^{\dagger}) + \mathbf{P}_{0T}^{\sigma} + (\mathbf{P}_{0T}^{\sigma})^{\dagger}\Bigg)\frac{\partial \mathbf{T}}{\partial \lambda} \tag{14}$$

$$+ \mathrm{tr}(\mathbf{U}\tilde{\mathbf{P}}^{\sigma}\mathbf{U}^{\dagger} + \mathbf{P}_{0W}^{\sigma} + (\mathbf{P}_{0W}^{\sigma})^{\dagger})\frac{\partial \mathbf{W}}{\partial \lambda} \tag{15}$$

$$+ \mathrm{tr}(\tilde{\mathbf{P}}^{\sigma} + \mathbf{P}_{0V}^{\sigma} + (\mathbf{P}_{0V}^{\sigma})^{\dagger})\frac{\partial \mathbf{V}}{\partial \lambda} \tag{16}$$

$$+ \mathrm{tr}(\mathbf{D}_{0Z}^{\sigma} + \mathbf{D}_{2Z}^{\sigma} - \mathbf{D}_3^{\sigma} + \mathbf{P}_{0S}^{\sigma} + (\mathbf{P}_{0S}^{\sigma})^{\dagger})\frac{\partial \mathbf{S}}{\partial \lambda} \tag{17}$$

where the matrices $\mathbf{D}_q^{\sigma}$ and $\mathbf{D}_{qz}^{\sigma}$ $(q = 0, 1, 2, 3)$ originate from the derivative of the renormalization matrix $\mathbf{G}$ and are given by eqs 18−22,

$$\mathbf{D}_0^{\sigma} = ((\mathbf{D}^{\sigma})^{\dagger}\mathbf{G} - \mathbf{G}(\mathbf{D}^{\sigma})^{\dagger})\mathbf{S}^{-1/2} + \mathbf{S}^{-1/2}(\mathbf{G}^{\dagger}\mathbf{D}^{\sigma} - \mathbf{D}^{\sigma}\mathbf{G}^{\dagger}) \tag{18}$$

$$\mathbf{D}_1^{\sigma} = \mathbf{S}^{1/2}(\mathbf{D}^{\sigma})^{\dagger}\mathbf{S}^{-1/2} + \mathbf{S}^{-1/2}\mathbf{D}^{\sigma}\mathbf{S}^{1/2} \tag{19}$$

$$\mathbf{D}_2^{\sigma} = \mathbf{D}_{1Z}^{\sigma}\mathbf{S}^{1/2}\tilde{\mathbf{S}}^{-1} + \tilde{\mathbf{S}}^{-1}\mathbf{S}^{1/2}\mathbf{D}_{1Z}^{\sigma} \tag{20}$$

$$\mathbf{D}_3^{\sigma} = \tilde{\mathbf{S}}^{-1}\mathbf{S}^{1/2}\mathbf{D}_{1Z}^{\sigma}\mathbf{S}^{1/2}\tilde{\mathbf{S}}^{-1} \tag{21}$$

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$$(\mathbf{D}^{\sigma}_{qZ})_{ij} = \sum_{r,s} (\mathbf{D}^{\sigma}_{q})_{rs} \sum_{k,l} C_{ik} C^{\dagger}_{kr} C_{sl} C^{\dagger}_{lj} (m_k^{1/2} + m_l^{1/2})^{-1} \tag{22}$$

Matrices $\mathbf{C}$ and $\mathbf{m}$ represent the eigenvectors and the eigenvalues of the matrices $\mathbf{S}$ (q = 0, 2) and $\mathbf{S}^{1/2}\tilde{\mathbf{S}}^{-1}\mathbf{S}^{1/2}$ (q = 1) (see ref 17 for detail).

The matrices $\mathbf{P}^{\sigma}_{0x}$ with x = V, W, T, S originate from differentiation of the $\mathbf{U}$ operator with respect to λ and are given by eqs 23−26,

$$(\mathbf{P}^{\sigma}_{0V})_{\nu\mu} = \sum_{i,j} (\mathbf{A}_+)_{\mu j} (\mathbf{A}_-)_{\nu i} \frac{{}^{\sigma}M'_{ji}}{\varepsilon_j^+ - \varepsilon_i^-} \tag{23}$$

$$(\mathbf{P}^{\sigma}_{0W})_{\nu\mu} = \sum_{i,j} (\mathbf{B}_+)_{\mu j} (\mathbf{B}_-)_{\nu i} \frac{{}^{\sigma}M'_{ji}}{\varepsilon_j^+ - \varepsilon_i^-} \tag{24}$$

$$(\mathbf{P}^{\sigma}_{0S})_{\nu\mu} = -\sum_{i,j} (\mathbf{A}_+)_{\mu j} (\mathbf{A}_-)_{\nu i} \frac{\varepsilon_j^{+\sigma} M'_{ji}}{\varepsilon_j^+ - \varepsilon_i^-} \tag{25}$$

$$(\mathbf{P}^{\sigma}_{0T})_{\nu\mu} = \sum_{i,j} \left\{ (\mathbf{B}_+)_{\mu j} (\mathbf{A}_-)_{\nu i} + (\mathbf{A}_+)_{\mu j} (\mathbf{B}_-)_{\nu i} - \left(1 + \frac{\varepsilon_j^+}{2mc^2}\right) (\mathbf{B}_+)_{\mu j} (\mathbf{B}_-)_{\nu i} \right\} \frac{{}^{\sigma}M'_{ji}}{\varepsilon_j^+ - \varepsilon_i^-} \tag{26}$$

which are derived from the first-order response of the modified Dirac equation (5) with respect to λ (see ref 18 for detail). Note that, as was first analyzed by Dyall,[16] the first-order response of the modified Dirac wave function is described entirely in terms of mixing between the electronic and positronic solutions of eq 5.

In eqs 23−26, matrix ${}^{\sigma}\mathbf{M}'$ is defined by eq 27,

$${}^{\sigma}\mathbf{M}'_{ji} = \mathbf{A}_+^{\dagger} \tilde{\mathbf{S}} \mathbf{P}^{\sigma}_0 (\mathbf{B}_- - \mathbf{U}\mathbf{A}_-) \tag{27}$$

where $\mathbf{P}^{\sigma}_0$ takes the form of eq 28.

$$\mathbf{P}^{\sigma}_0 = \tilde{\mathbf{P}}^{\sigma}[\mathbf{T} - \mathbf{U}^{\dagger}(\mathbf{T} - \mathbf{W})] - \frac{1}{2mc^2} \mathbf{D}^{\sigma}_3 \mathbf{U}^{\dagger}\mathbf{T} \tag{28}$$

The equations given above can be used for calculating the analytic gradient of the NESC energy for geometry optimization or for obtaining various molecular properties from the first-order response formalism. Because the final expressions for the NESC energy derivative are given in terms of traces of matrix products, the application of this formalism in practical calculations requires only a fraction of the time needed for a single SCF iteration and computing times scale with the third power of the number N of basis functions used, i.e., N^3.

HFS of paramagnetic resonance spectra originates from the interaction of the electron spin (and/or orbital angular momentum of the electron) with the nonuniform magnetic field $\mathbf{B}(\mathbf{r})$ resulting from the magnetic nucleus. In non-degenerate ground states of molecules, the orbital angular momentum is quenched and the vector-potential, which couples to the electron spin via the kinetic energy operator and the operator $\mathbf{W}$ (for definitions, see the text before eq 7), is given by eq 29,

$$\mathbf{A}(\mathbf{r}) = \frac{1}{c^2} \frac{\boldsymbol{\mu}_K \times (\mathbf{r} - \mathbf{R}_K)}{|\mathbf{r} - \mathbf{R}_K|^3} \tag{29}$$

where $\boldsymbol{\mu}_K$ is the magnetic moment of the nucleus K at position $\mathbf{R}_K$. Provided that the wave function satisfies the Hellmann−Feynman theorem, the hyperfine tensor $\mathbf{A}_K$ is given by the derivative of the total energy with respect to the nuclear magnetic moment $\boldsymbol{\mu}_K$ and can be computed using eqs 14−17. When the kinetic energy operator $((\boldsymbol{\sigma}\cdot(\mathbf{p} + \mathbf{A}_K(\mathbf{r})))^2/2m)$ is differentiated with respect to $\boldsymbol{\mu}_K$, the usual Fermi-contact operator (30) and the spin-dipole operator (31) are obtained,

$$(\hat{h}^{\mathrm{FC}}_K(\mathbf{r}))_{\alpha} = \frac{4\pi}{3c^2} \delta(\mathbf{r} - \mathbf{R}_K) \hat{\sigma}_{\alpha} \tag{30}$$

$$(\hat{h}^{\mathrm{SD}}_K(\mathbf{r}))_{\alpha} = \frac{1}{2c^2} \left(3 \frac{(\hat{\sigma}\cdot(\mathbf{r} - \mathbf{R}_K))(\mathbf{r} - \mathbf{R}_K)_{\alpha}}{|\mathbf{r} - \mathbf{R}_K|^5} - \frac{\hat{\sigma}_{\alpha}}{|\mathbf{r} - \mathbf{R}_K|^3} \right) \tag{31}$$

where α is a Cartesian component (x, y, or z) of a vector. The derivative of the $\mathbf{W}$ matrix with respect to the nuclear magnetic moment was derived in refs 29 and 9. There it was shown that the Fermi-contact part of the derivative can be calculated as in eq 32,

$$\frac{\partial \mathbf{W}^{\mathrm{FC}}}{\partial (\boldsymbol{\mu}_K)_{\alpha}} = \frac{3}{4} (\mathbf{W}\mathbf{T}^{-1}\mathbf{H}^{\mathrm{FC}}_{K,\alpha} + \mathbf{H}^{\mathrm{FC}}_{K,\alpha}\mathbf{T}^{-1}\mathbf{W}) \tag{32}$$

with $\mathbf{H}^{\mathrm{FC}}_{K,\alpha}$ being the matrix of the operator (30). Finally, in the context of the spin-unrestricted formalism, the isotropic HFS constant can be computed according to eq 33.

$$\begin{aligned} A^{\mathrm{iso}}_K &= -g_e g_K \mu_B \mu_K \langle S_z \rangle^{-1} \sum_{\sigma} \left(\mathrm{tr}\, \tilde{\mathbf{P}}^{\sigma}_{\mathrm{T}} \mathbf{H}^{\mathrm{FC}}_{K,z} + \frac{3}{4} \tilde{\mathbf{P}}^{\sigma}_{\mathrm{W}} (\mathbf{W}\mathbf{T}^{-1}\mathbf{H}^{\mathrm{FC}}_{K,z} + \mathbf{H}^{\mathrm{FC}}_{K,z}\mathbf{T}^{-1}\mathbf{W}) \right) \\ &= -g_e g_K \mu_B \mu_K \langle S_z \rangle^{-1} \left(\mathrm{tr}\, \tilde{\mathbf{P}}^{s}_{\mathrm{T}} \mathbf{H}^{\mathrm{FC}}_{K,z} + \frac{3}{4} \tilde{\mathbf{P}}^{s}_{\mathrm{W}} (\mathbf{W}\mathbf{T}^{-1}\mathbf{H}^{\mathrm{FC}}_{K,z} + \mathbf{H}^{\mathrm{FC}}_{K,z}\mathbf{T}^{-1}\mathbf{W}) \right) \end{aligned} \tag{33}$$

The constants g_e, g_K, μ_B, and μ_K are the electron and nuclear g-factors as well as the Bohr and nuclear magnetons, respectively. The quantity $\langle S_z \rangle$ is the expectation value of the z-component of the electron spin, $\tilde{\mathbf{P}}^{\sigma}_T$ and $\tilde{\mathbf{P}}^{\sigma}_W$ are the matrices in parentheses in eqs 14 and 15, respectively, and the matrices $\tilde{\mathbf{P}}^{s}_T$ and $\tilde{\mathbf{P}}^{s}_W$ are obtained by substituting the spin-density matrix $\mathbf{P}^s = \mathbf{P}^{\alpha} - \mathbf{P}^{\beta}$ in the respective expressions. Note that, when using the post-SCF correlated methods, the relaxed density matrices should be used in connection with eqs 14, 15, and 33.

3. DETAILS OF THE HFS CALCULATIONS

The formalism described in section 2 was implemented in the COLOGNE2011 suite of programs[30] and applied in the calculation of isotropic hyperfine structure constants for a series

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of mercury compounds. The calculations were carried out at the NESC/SCF, NESC/MP2, NESC/CCSD, and NESC/QCISD levels of theory. The finite nucleus model with the rms nuclear charge radii taken from the compilation by Visscher and Dyall[31] is used throughout this work. Open-shell species are treated within the spin-unrestricted formalism and the spin−orbit (SO) interaction is neglected in the calculations. According to Alekseyev et al.,[32] the SO plays only a minor role for the ground state of HgH and Hg^+. Because the lowest excitation energy in other mercury compounds, considered in this work, remains sufficiently large, on the order of ca. 30 000 cm^{-1} or more, and the molecules have a nondegenerate ground state, it is unlikely that the SO makes a substantial contribution to the ground state energy and density.

The molecular geometries of HgH, HgF, HgCN, $HgCH_3$, $HgCH_2CH_3$, and HgAg were optimized using the NESC analytic derivatives formalism[17] in connection with the NESC/MP2 method. During the NESC/MP2 geometry optimization, the 4f-, 5s-, 5p-, 5d-, and 6s-electrons of mercury and the valence electrons of all other elements were correlated. The SARC basis set[33] was used for mercury, the 6-311+G(2df,p) basis set[34] for the first-row atoms, and the TZVpp basis set of Ahlrichs and May[35] for silver. When the HFS constants were calculated, the SARC basis set was modified as follows: the two most tight primitive functions from the first s-type basis function were uncontracted and the basis set was augmented by two tight s-type primitive functions obtained in a geometric progression. This modification leads to a sufficient stability of the calculated HFS constants A_{Hg}^{iso} with regard to further basis set extension. For comparison, calculations at the SCF and MP2 level were also carried out for some molecules using the fully uncontracted triple-ζ basis set of Dyall[36] on mercury (augmented by two tight s-type and one p-type primitive functions[18]) combined with the uncontracted aug-cc-pVTZ basis set of Dunning.[37] All electrons were correlated during the calculation of the HFS constants using NESC/MP2, NESC/CCSD, and NESC/QCISD.

4. RESULTS AND DISCUSSION

The mercury compounds selected for this study have an open electronic shell with a single unpaired electron in a predominantly σ-type molecular orbital. Because the mercury atom, in its ground state, has a doubly occupied 6s orbital, formation of the chemical bond in these compounds is possible due to a partial ionization of mercury by the ligand atom or group. Depending on the electronic structure and electronegativity of the ligand, the open-shell orbital varies from covalent to strongly ionic,[38] thus providing a challenging set of molecules, which can be used for benchmarking. The NESC/MP2 optimized molecular geometries of the compounds employed in this study are collected in Table 1, where the available experimental data are also reported. Although the optimized Hg−X bond lengths slightly (ca. 0.01 Å) deviate from the experimental data, we employed only the optimized molecular geometries in the HFS calculations to eliminate geometry effects in the benchmark set of molecules.

The correctness of the implementation of the formalism developed in section 2 was tested by the NESC/SCF calculations reported in Table 2. The nonrelativistic data in the fourth column of Table 2 were obtained by setting the velocity of light to a very large value (10^8 au). The A_{Hg}^{iso} values (in MHz) obtained in this way coincide to the fourth decimal digit with the values calculated using the traditional non-

Table 1. Molecular Geometries (in Å and deg) of Hg-Containing Molecules Optimized Using the NESC/MP2 Method (Details of Basis Sets in Section 3)

molecule	symmetry	geometric calc	parameters exp
HgH	$C_{\infty v}$	r_{Hg-H} = 1.722	1.735;[a] 1.741[b]
HgF	$C_{\infty v}$	r_{Hg-F} = 2.017	2.007[c]
HgCN	$C_{\infty v}$	r_{Hg-C} = 2.069	
		r_{C-N} = 1.146	
$HgCH_3$	C_{3v}	r_{Hg-C} = 2.208	
		r_{C-H} = 1.087	
		α_{HgCH} = 106.1	
$HgCH_2CH_3$	C_s	r_{Hg-C1} = 2.272	
		r_{C1-C2} = 1.509	
		r_{H1-C1} = 1.089	
		r_{H2-C2} = 1.092	
		r_{H3-C2} = 1.096	
		α_{HgC1C2} = 109.1	
HgAg	$C_{\infty v}$	r_{Hg-Ag} = 2.672	

[a]Taken from ref 39. [b]Taken from ref 40. [c]Taken from ref 41.

Table 2. Isotropic Hyperfine Structure Constants A_{Hg}^{iso} (MHz) for the Mercury Atom Obtained in This Work Using the NESC/SCF Method with the Exact Treatment or the Neglect of the $(\partial U/\partial\lambda)$ Term and the Nonrelativistic (nonrel) Formalism[a]

molecule	exact $(\partial U/\partial\lambda)$	no $(\partial U/\partial\lambda)$	nonrel
HgH	8238	8396	4226
HgF	23188	23634	8286
HgCN	17341	17675	6420
$HgCH_3$	4060	4138	2989
$HgCH_2CH_3$	1357	1383	1902
HgAg	2713	2765	1658
Hg^+	43400	44236	13734
Hg^+ [b]	38312	38318	12505

[a]The augmented SARC basis set is used for mercury, TZVpp for silver, and the 6-311+G(2df,p) basis set for all other atoms (see section 3 for more details). [b]Uncontracted SARC basis set is used on mercury atom.

relativistic formalism, within which the HFS constant is calculated as the expectation value of the FC operator (30).

As seen from Table 2, relativity has an enormous effect on the A_{Hg}^{iso} constants. It is therefore worth investigating whether coupling between the electronic and positronic states, as manifested in the terms originating from differentiation of the operator **U** with respect to external perturbation, eq 23−26, makes a sizable contribution to the calculated HFS constants. Inspection of columns 2 and 3 of Table 2 reveals that this contribution is surprisingly small, ca. 1.9%. This finding is consistent with the results of our previous work on the NESC calculation of the contact densities[18] and with the theoretical analysis of Dyall.[16] According to Dyall, the negative-energy states make a contribution of the order $O(c^{-3})$ to the first-order NESC wave function. Such a contribution is sufficiently small and can be neglected in the situations where the calculation of the negative-energy eigenstates of the modified Dirac equation (5) may become tedious as in the case of large molecules.

The relativistic A_{Hg}^{iso} value for Hg^+ reported in the first column of Table 2 is in a good agreement with the value 42366 MHz obtained by the four-component multiconfigurational Dirac−Fock calculation of Brage et al.[42] Note, however, that the SARC basis set was contracted using a Douglas−Kroll

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Table 3. Comparison of the Isotropic Hyperfine Structure Constants A_{Hg}^{iso} (MHz) for the Mercury Atom Obtained in This Work at the NESC/SCF, NESC/MP2, NESC/CCSD, and NESC/QCISD Levels of Theory with the Corresponding Experimental Values[a]

molecule	exp	NESC/QCISD	NESC/CCSD	NESC/MP2	NESC/SCF
HgH	6859;[b] 7198[c]	7446	7463	6616 (6940)	8238 (8873)
HgF	22163[d]	20929	20558	21790 (24189)	23188 (25391)
HgCN	15960[e]	15948	16135	19766 (21720)	17341 (18884)
$HgCH_3$	4921[f]	5299	5428	6369 (6210)	4060 (4260)
$HgCH_2CH_3$		3504	3623	4845	1357
HgAg	2723[g]	2967	2962	2873	2713

[a]The augmented SARC basis set is used for mercury, TZVpp for silver, and the 6-311+G(2df,p) basis set for all other atoms. In parentheses, the values obtained using the uncontracted Dyall's TZ basis set for mercury and uncontracted aug-cc-pVTZ for other atoms (see section 3 for more details). [b]Obtained in ref 43 from measurement in a neon matrix. [c]Obtained in ref 43 from measurement in an argon matrix. [d]Obtained in ref 44 from measurement in an argon matrix. [e]Obtained in ref 45 from measurement in an argon matrix. [f]Obtained in ref 46 from measurement in a neon matrix. [g]Taken from ref 47.

quasirelativistic Hamiltonian in connection with a point-like nucleus model.[33] As the comparison with A_{Hg}^{iso} obtained using a fully uncontracted SARC basis set (the last row of Table 2) reveals, the contraction of the SARC basis set leads to an increase of the magnitude of the HFS constant and therefore we recommend the recontraction of the SARC basis using the NESC method. This, however, exceeds the scope of the present investigation, and in the following, the standard SARC basis set will be augmented by two tight s-type primitive functions as described in section 3. Noteworthy is that adding more tight functions leads to only an insignificant variation of the calculated HFS constants (on the order of 1.7% when four tight s-functions are added).

The results of the correlation corrected A_{Hg}^{iso} calculations are presented in Table 3 where they are compared with the available experimental data. For the purpose of testing the effect of the basis set on the calculated HFS constants, calculations at the NESC/SCF and NESC/MP2 level for HgH, HgF, HgCN, and $HgCH_3$ are also carried out using a large uncontracted basis set as described in section 3. The latter values deviate on the average by ca. 7% from the ones obtained using the SARC basis set, which is comparable with the uncertainty in the experimental values. Although not being specifically designed for the calculation of hyperfine parameters, the SARC basis set yields a reasonable description of this property and, as this basis set is sufficiently compact, it can be used for calculations of large molecules.

Generally, the NESC/QCISD and the NESC/CCSD methods in connection with SARC basis set yield A_{Hg}^{iso} in very good agreement with experiment. With the exception of HgH and HgF molecules, the deviation of the calculated constants from the experimental data lies within a few percent. Inclusion of the electron correlation leads to a contraction of the atomic inner shell electrons toward the nucleus, thus increasing the HFS constant value.[9] This increase is counterbalanced by the increasing bond ionicity, which depletes the unpaired electron density from the 6s orbital of Hg, thus reducing the HFS constant value. A delicate balance between these effects can only be achieved with the use of highly correlated methods and may require to go beyond the CCSD or QCISD level of calculation for obtaining very accurate theoretical HFS constants.

Note that the experimental data reported in Table 3 are obtained from measurement on molecules embedded in inert gas matrices. As has been previously pointed out in ref 9, the effect of the inert gas matrix on the experimentally measured HFS constants may reach to as much as 6−10%. To the best of our knowledge, a systematic study of this effect has not been carried out yet. With the development of an exact yet practically feasible relativistic approach, such as the NESC derivative method presented in this work, this effect can be studied in finer detail, which should strengthen the predictive power of the theoretical calculation of HFS constants of heavy elements.

5. CONCLUSIONS

Based on the analytic derivative formalism of the NESC method, a new approach to the calculation of relativistically corrected hyperfine structure constants has been developed and implemented. The new approach can be used in the context of wave function ab initio theory, both at the correlated and uncorrelated level, as well as in the context of density functional theory. In the present work, the new method for the calculation of HFS constants was tested in ab initio calculations of the isotropic HFS constant A_{Hg}^{iso} for a series of mercury compounds. The results of benchmark calculations show high reliability of the approach developed, which is capable of yielding A_{Hg}^{iso} values within a few percent of measured HFS constants.

In the NESC analytic derivatives formalism, the final formulas for the HFS constants are formulated in terms of traces of products of matrices, thus leading to computational costs that scale with the cubic power of the number of basis functions. This is the why computational requirements are modest compared to those of a single SCF iteration and the formalism developed can be easily applied to study HFS constants for very large molecules. In view of the fact that the formalism presented in this work provides an essentially exact account of relativistic effects on the theoretical HFS constants, it represents a promising tool for testing the performance of various density functional methods. Work on this topic is underway and will be published elsewhere.

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Notes

The authors declare no competing financial interest.

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