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Relativistic Calculation of Hyperfine Parameters of Mercury Compounds

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Abstract: The normalized elimination of the small component (NESC) method is a Dirac-exact relativistic method that leads to reliable first order response properties such as contact densities, Mössbauer shifts, electric field gradients, quadrupole coupling constants, or hyperfine structure constants for heavy atoms. In this review, the calculation of these hyperfine parameters with a NESC analytical derivatives formalism is discussed and demonstrated for mercury containing molecules. There is a distinct need for accurate calculated hyperfine parameters because the possibilities of experiment are limited in a case such as mercury. This need can be fulfilled if, beside scalar relativistic effects, the influence of spin-orbit coupling, electron correlation and the finite dimension of the nucleus are accounted for.

Keywords: Contact density, dirac-exact relativistic methods, electric field gradient, hyperfine structure constant, Mössbauer shift, normalized elimination of the small component, quadrupole coupling constant.

1. HYPERFINE FIELDS IN ATOMS AND MOLECULES

The measurement of electron-nuclear hyperfine interactions in molecules and solids yields valuable information on the local electronic structure and bonding, which is obtained on an atomic scale [1, 2]. Experimental spectroscopic techniques such as Mössbauer spectroscopy [3], nuclear forward scattering (NFS) [4], perturbed angular correlation of γ-rays (PAC) [5], nuclear quadrupole resonance (NQR) [1, 6] or electron spin resonance (ESR) [7, 8] are capable of providing information on the oxidation and spin state of the resonating atom. In addition, information on its local chemical environment is gained, which makes these spectroscopic methods valuable tools to probe chemical bonding.

The combination of electronic structure theory and the measured spectroscopic data leads to the desirable hyperfine parameters, which are specified within given molecular models [2, 9, 10]. Following this approach, reasonable models of the local environment of the resonating atom can be established. The knowledge of the local hyperfine fields enables one to refine parameters of the electron-nuclear hyperfine interactions such as the nuclear electric quadrupole moment Q, the fractional nuclear charge radius $\delta R / R$, or the nuclear magnetic dipole moment ì, where the results of quantum chemical calculations for the resonating systems play an important role [9-11]. The accurate calculation of these nuclear properties strongly depends on an accurate account of relativity and electron correlation, which requires the use of the most advanced quantum chemical methods. In this connection, the application of the Dirac-exact computational methods, which provide an accurate account of relativistic effects and are applicable to large molecular systems, is most awarding as they offer an opportunity of studying realistic molecular models. At the all-electron level of description, these methods provide a first principles account of the effects of relativity for the inner core electrons without resorting to the use of an *a posteriori* restoration of the core electron wavefunctions sometimes proposed in the context of relativistic effective core potential techniques (see Ref. 12 and references cited therein).

When describing hyperfine fields in atoms, molecules, and solids, one conventionally uses perturbation theory to obtain the parameters of these fields in form of expectation values of the corresponding quantum mechanical operators [13-16]. Alternatively, the hyperfine parameters can be expressed as derivatives of the electronic energy with respect to suitable perturbing fields [9, 17]. The derivatives based formalism is well suited for use in the context of Dirac-exact computational methods, as in this way the drawbacks of separately transforming the electronic states and the interaction operators from the Dirac 4-component representation to the Foldy-Wouthuysen 2-component representation are avoided [18]. However, the crucial requirement in this case is the availability of analytic energy derivatives for the respective computational method. This requirement is fulfilled for the NESC method [19, 20]. In this review, the salient features of the derivatives formalism for the hyperfine parameters will be briefly reviewed and the application of this formalism in the context of the NESC method will be outlined.

2. CONTACT DENSITY AND MÖSSBAUER ISOMER SHIFT

The contact electron density is a property that is required in Mössbauer [3] and nuclear forward scattering spectroscopy [4] to interpret the shift of the absorption line of the γ-transition in a nucleus where its embedment in a specific local chemical environment relative to that a sample source nucleus plays an important role. The physical origin of this shift, known as the isomer shift, lays in the variation

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of the nuclear electric charge radius during the γ-transition because this variation leads to a slight alteration of the electron-nuclear interaction [14, 15]. It is a sensitive probe for the local electronic structure and bonding features of the target compound [2]. The isomer shift δ is expressed in terms of the Doppler velocity (in mm/s) needed to achieve a resonant absorption of the γ-quantum (having the energy E_γ) between the source (s) and absorber (a) nucleus according to eq. (1):

$$\delta = \frac{c}{E_\gamma}\left(\Delta E_\gamma^a - \Delta E_\gamma^s\right) \tag{1}$$

where $\Delta E_\gamma^{a(s)}$ is the shift of the energy of the γ-quantum caused by the electron-nuclear interaction in the absorber (source) system. The quantity $\Delta E_\gamma^{a(s)}$ is usually expressed with the help of the contact electron density at the absorber (source) nucleus:

$$\delta(K) = \frac{4\pi}{5}\frac{cZ_K R_K^2}{E_\gamma}\frac{\Delta R_K}{R_K}\left(\bar{\rho}^a - \bar{\rho}^s\right) = \alpha(K)\left(\bar{\rho}^a - \bar{\rho}^s\right) \tag{2}$$

where Z_K gives the proton number and $\Delta R_K / R_K$ is the nuclear fractional charge radius that reflects the variation of the root-mean-square (RMS) nuclear electric charge radius R_K during the γ-transition. As the quantity $\Delta R_K / R_K$ can not be accurately determined by experiment, the use of calculated contact electron densities $\bar{\rho}$ in connection with the experimentally measured isomer shifts remains the most reliable method of its determination [2, 16]. The knowledge of the fractional charge radius or the calibration constant $\alpha(K)$ is a prerequisite for a reliable interpretation of the Mössbauer and NFS spectra of chemical compounds.

At a fully relativistic level of description, the isomer shift and the contact electron density can be expressed with the help of the derivatives of the total electronic energy with respect to the nuclear electric charge radius [9, 17]. When a finite size nucleus model is employed in the quantum chemical calculations, the isomer shift is given by eq. (3):

$$\delta(K) = \frac{c}{E_\gamma}\left(\frac{\partial E^a(R)}{\partial R}\bigg|_{R=R_K} - \frac{\partial E^s(R)}{\partial R}\bigg|_{R=R_K}\right)\Delta R_K \tag{3}$$

where $E^{a(s)}(R)$ is the electronic energy of the absorbing (source) system and R_K is the experimentally measured RMS nuclear charge radius [17]. From eq. (3), it follows that the contact density can be also expressed via the derivatives of the total electronic energy with respect to the RMS nuclear charge radius as given in eq. (4):

$$\bar{\rho} = \frac{5}{4\pi Z_K R_K}\frac{\partial E(R)}{\partial R}\bigg|_{R=R_K} \tag{4}$$

It is the major advantage of derivatives based formalism of the isomer shift and the contact density that the effects of relativity and electron correlation can be routinely included into the calculation in a convenient way thus guaranteeing the accuracy of the quantum chemical results [9, 17, 21]. As the detailed expressions for the energy derivatives involved in eq. (4) and the formulae in the following Sections are rather lengthy, they are not reproduced here and reader is referred to the original publications [19, 21-23].

3. ELECTRIC FIELD GRADIENT AND QUADRUPOLE COUPLING CONSTANT

A non-spherically symmetric nucleus (i.e. a nucleus with spin $I_k > 1/2$) possesses a quadrupole moment Q^K, which leads to a splitting of the nuclear energy levels when the nucleus K is embedded into an electronic environment without cubic symmetry [2, 11, 24]. The nuclear quadrupole splitting can be accessed by a number of experimental techniques including Mössbauer, NFS, PAC, NQR, and microwave spectroscopy. The interaction of the nuclear quadrupole moment with the electric field of the electrons (nuclear quadrupole interaction, NQI) can be described by the Hamiltonian [2, 24]:

$$\hat{H}^{NQI} = \sum_{i,j} Q_{ij}^K V_{ij}^K \tag{5}$$

where the summation runs over the Cartesian (*i,j* = *x,y,z*) components of the nuclear quadrupole moment (NQM) tensor Q_{ij}^K and the electric field gradient V_{ij}^K at the site of the nucleus *K*. The electric field gradient operator V_{ij}^K is defined as a second derivative of the potential *V*(*r*) due to the electrons and other nuclei as given in eq. (6):

$$V_{ij}^K = \left(\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} - \frac{1}{3}\delta_{ij}\nabla^2\right)V(r) \tag{6}$$

The expectation value of the EFG operator over the electronic ground state wavefunction is used to characterize the magnitude of the NQI. The nuclear quadrupole coupling constant (NQCC):

$$\nu_Q = \frac{eQ\langle V_{cc}\rangle}{h} \qquad (MHz) \tag{7}$$

characterizes the magnitude of quadrupole splitting in Mössbauer and NQR spectra. [16, 27] The nuclear quadrupole splitting is also characterized by the asymmetry parameter $\eta = (\langle V_{aa}\rangle - \langle V_{bb}\rangle) / \langle V_{cc}\rangle$ where the EFG expectation values are presented in a principal axes system and ordered to satisfy $|\langle V_{aa}\rangle| \le |\langle V_{bb}\rangle| \le |\langle V_{cc}\rangle|$.

Using the energy derivatives formalism, the expectation value of the EFG operator (6) is obtained as a derivative of the total electronic energy with respect to the components of the NQM tensor Q_{ij}^K given by eq. (8) [22]:

$$\langle V_{ij}^K\rangle = \frac{\partial E(Q_{ij}^K)}{\partial Q_{ij}^K}\bigg|_{Q_{ij}^K \to 0} \tag{8}$$

When applying eq. (8), the NQI Hamiltonian should be included into the calculation of the total electronic energy $E(Q_{ij}^K)$. With the use of eq. (8) the effects of relativity and electron correlation can be conveniently taken into account. Although the derivatives in eq. (8) can be calculated by numeric differentiation [25], the most accurate and numerically stable results are obtained with the use of analytic energy derivatives provided that they are available for the selected method of calculation. This condition is fulfilled by the NESC method that facilitates to study the effects of relativity and electron correlation. If the NESC method is carried out with a finite size nuclear model, one can study the influence of a finite nuclear charge distribution on the calculated EFG via eq. (8) [22, 26].

4. MAGNETIC DIPOLE INTERACTION AND HYPERFINE STRUCTURE

A nucleus with a non-zero spin I_k has a dipole magnetic moment $\grave{\imath}_k = g_K \mu_N \mathbf{I}_K$, which interacts with local magnetic field **B** as described by the spin Hamiltonian given by eq. (9):

$$\hat{H}_B = -g_K \mu_N \mathbf{I}_K \cdot \mathbf{B} \tag{9}$$

This leads to a splitting of the nuclear energy levels (Zeeman splitting) [7,8]. In eq. (9), g_K is the Landé factor of the nucleus K, μ_N is the nuclear magneton, and the magnetic field **B** comprises the external field $\mathbf{B}_{ext}$ and the local field generated by electrons in the molecule or solid. The Zeeman splitting of the nuclear energy levels is a sensitive measure of the local electronic structure that can be accessed by a variety of experimental techniques such as ESR, Mössbauer, paramagnetic NMR, or optical spectroscopy.

The strength of the nuclear magnetic dipole interaction is characterized by the hyperfine structure (HFS) tensor, which can be split into the isotropic and anisotropic parts. When the spin Hamiltonian (9) is included into the calculation of the electronic energy, the HFS tensor A_K can be obtained as a derivative of the electronic energy with respect to the nuclear magnetic moment [27] as in eq. (10):

$$\mathbf{A}_K = \frac{\partial E(\mathbf{B}_{ext}, \mu_K)}{\partial \mu_K}\bigg|_{\mathbf{B}_{ext}\to 0, \mu_K \to 0} = A_K^{iso} + \mathbf{A}_K^{aniso} \tag{10}$$

where the dominant part of A_K^{iso} originates from the Fermi-contact (FC) magnetic interaction (with non-vanishing isotropic contributions from the spin-orbit (SO) coupling) and the anisotropic part comprises the spin-dipolar (SD) and anisotropic SO contributions [25]. Within the widely employed scalar-relativistic approximation that is neglecting the SO contributions, only FC and SD parts of the HFS tensor remain in eq. (10).

In most cases, the FC part of the HFS constant A_K^{iso} is dominating the absolute magnitude of the HFS tensor. It is this part that experiences the greatest influence of relativity as it depends on the electron spin-density in the immediate vicinity and inside the nucleus. Traditionally, the isotropic HFS constant is calculated using the value of the electron spin-density at the position of the nucleus [10] which may lead to divergent results when the effect of relativity is included in connection with a point like nuclear model. Utilizing the analytic derivatives formalism in connection with a Dirac-exact computational scheme such as NESC, one can avoid these difficulties and incorporate the effects of relativity and electron correlation into the calculated isotropic HFS constant in a seamless way [23]. Since a finite size nuclear model can be employed in these calculations, the effects of the finite nuclear electric charge distribution and the effects of the finite distribution of the nuclear magnetic moment can be taken into account. Generally speaking, the nuclear magnetic moment distribution is different from its electric charge distribution, however the parameters of the former are not known for most elements. In this regard, the accurate quantum chemical calculations of magnetic hyperfine interactions can provide valuable information needed for refining models of the nuclear magnetic moment distribution.

5. HYPERFINE PARAMETERS OF MERCURY COMPOUNDS

The hyperfine parameters of mercury have been studied by a variety of techniques primarily in connection with its biological activity and its role as environmental pollutant [28]. Especially, PAC spectroscopy has been employed to study the NQI parameters of mercury compounds [25, 29-33] whereas its hyperfine parameters are accessible via ESR measurements [34-37]. So far, Mössbauer spectroscopy has only sporadically been used to study mercury. In the literature, only the Mössbauer spectra of crystalline Hg_2F_2 and HgF_2 have been reported [41]. Although a statistically significant parametrization of its fractional nuclear charge radius does not seem to be possible with the available data, it is worth studying its contact density and other hyperfine parameters as they experience a strong dependence on relativity. Apart from this, knowledge of the hyperfine parameters provides a detailed insight into the electronic structure of mercury compounds and helps to discriminate between structural motifs and the oxidation states of the mercury atom.

5.1. Mercury Contact Density and Quadrupole Splitting

The contact densities of a series of mercury molecules, which represent the most commonly occurring mercury oxidation states (including the experimentally detected +4 oxidation state [39]) and structural motifs, have been investigated by Filatov and co-workers [21] using the recently developed scalar-relativistic NESC analytic derivatives formalism [19, 21] employed to calculate contact density and isomer shift in the context of formalism outlined in Section 2 [17]. The results of their calculations are listed in Table **1** where the NESC contact densities on mercury nucleus and NESC contact density differences are compared with the corresponding densities obtained with a standard non-relativistic method. The non-relativistic density differences are scaled by the ratio $\bar{\rho}_{rel}(Hg)/\bar{\rho}_{non-rel}(Hg)$ to approximately take into account the effect of relativity in a traditional manner [2, 16].

The data in Table **1** clearly demonstrate that relativity plays the dominant role not only for the total contact densities (the relativistic densities are enhanced by a factor of ca. 6), but also for the density differences. The trends in the density variation within the compounds in Table **1** are not followed by the non-relativistic calculations, even qualitatively, thus demonstrating that a simple scaling of the non-relativistic densities is not sufficient to take relativistic effects on the density into account. It can be seen from a comparison of the results of the NESC/HF calculations with the results of the electron correlated NESC/CCSD method that electron correlation plays an important role for the contact densities and density differences (see Table **1**). The effect of electron correlation is non-uniform across the compounds studied and leads to a noticeable, up to *ca.* 20 % decrease in the contact density (HgF).

Table 1. Effective contact densities (e/bohr^3) of the Hg atom calculated using Dirac-exact and non-relativistic computational methods. The absolute contact density is given for Hg($^1S_0$) whereas contact density differences $\bar{\rho}_{Hg} - \bar{\rho}_{mol}$ are listed for ions and molecules [21].

Atom /Molecule	NESC/CCSD	NESC/MP2	NESC/HF	non-rel MP2	non-rel HF
Hg	2105035.382	2105047.821	2104944.971	360636.823	360632.831
Hg^+	121.136	127.943	112.876	69.951[a]	60.797
Hg^{2+}	293.217	305.695	278.394	179.244	158.352
HgF	76.872	81.294	98.086	71.842	72.394
HgF_2	104.387	108.368	121.352	83.115	84.7931
HgF_4	96.264	109.453	96.586	69.485	46.800
$Hg(SH)_4$	81.143	84.369	88.214	55.855	49.654
$Hg(SH)_4^{2-}$	144.369	146.332	161.635	97.438	96.375
$HgCl_2$	91.592	94.572	108.118	71.630	72.207
$HgCl_4^{2-}$	174.841	180.683	190.637	117.167	112.863
$Hg(CH_3)_2$	42.184	43.610	49.001	26.240	25.705
$Hg(H_2O)_6^{2+}$	237.066	245.550	240.820	148.196	138.266

[a] The non-relativistic density differences are scaled by the ratio $\bar{\rho}_{rel}(Hg)/\bar{\rho}_{non-rel}(Hg)$ of total contact densities for mercury atom.

The values of the contact density differences in Table **1** vary in a broad range of values stretching from about 40 e/bohr^3 in dimethyl mercury to 293 e/bohr^3 in the mercury dication. With the increasing electronegativity of the ligands, the mercury nucleus is deshielded as evidenced by the trends in molecules HgX_2 with X = F, Cl, and CH_3. There is also a noticeable dependence of the contact density differences on the coordination number of the mercury atom, *e. g.* in $HgCl_2$ (linear) and $HgCl_4^{2-}$ (tetrahedral). These observations confirm that the contact densities $\bar{\rho}$ and Mössbauer isomer shifts δ are sensitive descriptors of the electronic environment and coordination sphere of Hg nucleus [21].

The importance of including the effects of electron correlation and relativity into the calculation of EFG values has been demonstrated previously by means of full four-component relativistic calculations, where it was shown that relativity is noticeable even for elements as light as ^{27}Al and ^{69}Ga [22]. Recently, Arcisauskaite *et al.* [25] have investigated the NQI and EFG in a series of HgX_2 (X = Cl, Br, I, CH_3) compounds where it was found that relativity and electron correlation make non-additive and opposite sign contributions to the final EFG value, thus underlining the importance of an accurate treatment of these effects in practical calculations. Their conclusions have been fully confirmed in a study of NQI and EFG values in a series of mercury compounds reported in Table **2**, which was carried out by Filatov and co-workers [14] using the recently developed NESC analytic derivatives formalism.

Generally, the relativistic effects on the EFG are treated accurately within the NESC analytic derivatives formalism which is illustrated by comparing the NESC EFGs against the reference values taken from the full relativistic 4-component calculations in Ref. 3. At the computational level that includes electron correlation into account, the NESC/MP2 EFGs in Table **2** are in excellent agreement with the values obtained by Arcisauskaite *et al.* [25] using the 4-component coupled cluster (CCSD-T) formalism. This is especially gratifying in view of the fact that NESC/MP2 can be used to study large molecular species whereas the fully relativistic correlated methods are restricted in their applicability to molecules with a few atoms only. The accuracy of the NESC/MP2 calculations can be further demonstrated by comparing the calculated NQCC of 2414 MHz in $Hg(CH_3)_2$ (^{199}Hg NQM of 0.675 ± 0.012 barn was used) with the experimentally measured value of 2400 MHz [25]. This demonstrates that NESC/MP2 is capable of providing accurate EFG values for compounds of realistic size.

The data in Tables **1** and **2** demonstrate that the contact density shift and the EFG enable one to reliably discriminate not only between different oxidation states of the mercury atom, but also between different types of ligands. The EFG reveals sufficiently high sensitivity to the local chemical environment and, even in the cases where the contact density shifts are nearly the same, helps to discriminate between different types of coordination spheres, *e. g.* linear *vs.* square in HgF_2 and HgF_4 and in HgI_2 and $Hg(SH)_4$. For the same oxidation state and the same local geometry the EFG value may vary by almost a factor of two in dependence on the electronegativity of the ligands, as seen in a series of HgX_2 (X = F, Cl, Br, I, CH_3) compounds with the Hg atom in the +2 formal oxidation state and linear arrangement of ligands. However, there is no simple correlation between the total electron charge on the central atom and the EFG value. For the same local geometry (*e.g.* linear molecules of Hg(II)), a weakly

Table 2. NESC electric field gradients $\langle V_{cc} \rangle$ (a.u.) on the Hg nucleus calculated at the HF and MP2 levels in comparison with the reference 4-component Dirac-Coulomb data from Ref. 25.

Molecule	NESC/HF	NESC/MP2	4c-DC-CCSD-T[a]	4c-DC-HF[b]
HgF	-8.68	-5.78		
HgF_2	-12.85	-9.18		
HgF_4	+4.40	+3.74		
$HgCl_2$	-12.40	-9.32	-9.51	-12.95
$HgBr_2$	-11.31	-8.54	-8.63	-11.82
HgI_2	-11.17	-8.64	-8.61	-11.68
$Hg(CH_3)_2$	-19.30	-15.22	-15.71	-19.83
$Hg(SH)_4$	+8.00	+4.99		
$Hg(SH)_4^{2-}$	+0.84	+0.82		
$Hg(cys)_2$	-13.23	-9.38		

[a] 4-component Dirac-Coulomb CCSD-T results from Ref. 3; [b] 4-component Dirac-Coulomb Hartree-Fock results from Ref. [25].

pronounced dependence of the EFG on the deformation population of the valence p- and d-orbitals (i. e., the sum of the number of electrons in 6p-orbitals and the number of holes in 5d-orbitals) of Hg was observed by Filatov and co-workers. Indeed, the deformation density contains a significant quadrupole component which is important for the nuclear quadrupole interaction. Furthermore, due to a combined effect of depletion of the electron density from the 6s- and 5d-orbitals of Hg and population of the 6p-orbitals, screening of the Hg nucleus by electrons alters as seen in the variation of the contact density in the HgX_2 series in Table **1**. Qualitatively similar conclusions have been also drawn by Arcisauskaite *et al.*[41] on the basis of 4-component density functional calculations.

5.2. Magnetic Hyperfine Interaction

The calculation of HFS parameters is a challenging task that often requires the use of high level *ab initio* calculations to reliably estimate the spin-density in the vicinity of the nucleus [42]. As there is a demand for accurate theoretical estimates of these parameters in large molecules and models of defects in crystalline solids, the performance of density functional theory (DFT) has been evaluated by Sinnecker and co-workers [43], who showed that DFT systematically underestimates the isotropic HFS constant A_K^{iso} and that the inclusion of relativity noticeably improves the agreement with experiment even for element as light as iron.

The necessity to include the effects of relativity and electron correlation becomes even more pronounced for a heavier element such as mercury. Table **3** lists the isotropic HFS constants A_{Hg}^{iso} for a series of open-shell mercury molecules calculated by Filatov and co-workers [23] using the NESC analytic derivatives formalism in connection with the MP2 and CCSD level of electron correlation. As shown by Filatov and co-workers, relativity accounts for up to 50 % or more (HgF and HgCN) of the overall A_{Hg}^{iso} value thus underlying its importance. However, even with the exact treatment of relativistic effects, the 4-component DFT calculations can not reach the same level of accuracy as shown by the NESC/CCSD results in Table **3**. Inclusion of electron correlation leads to a contraction of the atomic inner shell electrons toward the nucleus, thus increasing the A_{Hg}^{iso} value. This increase is counterbalanced by the increasing bond ionicity, which depletes the unpaired electron density from the valence 6s-orbital of Hg, thus reducing the A_{Hg}^{iso} value. A delicate balance in the description of the effects of relativity and correlation can only be achieved with the use of highly correlated methods and may require to go beyond the CCSD level for obtaining accurate theoretical estimates of the HFS parameters.

CONCLUSION

With the availability of Dirac-exact relativistic methods such as NESC [46], which can be routinely applied to relatively large molecules, the properties of molecules containing relativistic atoms can be investigated in a systematic way. Essential for these studies is an energy derivatives formalism as it has been developed for the NESC method [19, 20]. In this way, first order and second order response properties are accessible at the NESC level [19, 20, 21-23] where especially the calculation of hyperfine parameters is challenging. This article has shown that properties such as the contact densities, Mössbauer shifts, electric field gradients, quadrupole coupling constants, or hyperfine structure constants of heavy atoms strongly depend on scalar relativistic effects and electron correlation. Finite size of the nucleus, though not extensively reviewed here, does also play an important role for obtaining accurate hyperfine parameters [22, 26] and is crucial for the contact densities and isomer shifts [21]. It is also shown that experiment has its limits with the techniques presently available. For example, the Mössbauer spectroscopy of mercury compounds is still at its infancy. In this situation,

Table 3. Comparison of calculated isotropic HFS constants (in MHz) of mercury compounds with experimental data.

Molecule	Exp.	NESC/CCSD	NESC/MP2	NESC/HF	4c-DKS/BP86[a]
HgH	6859[b]; 7198[c]	7332	6500	8093	6244
HgF	22163[d]	20198	21408	22782	16895
HgCN	15960[e]	15853	19420	17037	13967
$HgCH_3$	4921[f]	5332	6257	3989	--
$HgCH_2CH_3$	--	3559	4760	1333	--
HgAg	2723[g]	2910	2822	2665	3285

[a] 4-component Dirac-Kohn-Sham results from Ref. [44]; [b] Ref. [37]; measurement in neon matrix. [c] Ref. [37]; measurement in argon matrix. [d] Ref. [36]; measurement in argon matrix. [e] Ref. [35]; measurement in argon matrix. [f] Ref. [45]; measurement in neon matrix. [g] Ref. [34].

reliably calculated hyperfine parameters are highly desirable for a two-pronged approach based on both experiment and relativistic quantum chemistry.

Future work has to focus on a response property formalism that also takes spin-orbit coupling (SOC) effects into account. For the NESC method, the first step has been made with the development of an efficient two-component NESC formalism [15], which makes the routine calculation of SOC-corrected energies possible and which can be extended to SOC-corrected properties by introducing analytical energy derivatives.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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