Calculation of Response Properties with the Normalized Elimination of the Small Component Method

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The normalized elimination of the small component method is a first principles two-component relativistic approach that leads to the Dirac-exact description of one-electron systems. Therefore, it is an ideal starting point for developing procedures, by which first- and second-order response properties can be routinely calculated. We present algorithms and methods for the calculation of molecular response properties such as geometries, dipole moments, hyperfine structure constants, vibrational frequencies and force constants, electric polarizabilities, infrared intensities and so forth. The described formalisms are applied to molecules containing mercury and other heavy elements, which require a relativistic treatment. Perspectives for the future development and application of Dirac-exact methods are outlined. © 2013 Wiley Periodicals, Inc.

DOI: 10.1002/qua.24578

Introduction

The influence of relativistic effects[1] on the electronic structure and the chemical properties of heavy elements was recognized more than four decades ago.[2–13] At the quantum mechanical level, the Dirac equation[14,15] provides the basis for an exact description of a single electron in an external field, and the Dirac Hamiltonian is a cornerstone of relativistic quantum chemistry. The Dirac equation considers the electron spin as a dynamic variable and treats the charge-conjugate particle (positron) on the same footing as the electron itself. This leads to a four-component wavefunction, which, in the standard representation, comprises the large-component and the small-component spinors, and imposes a special requirement on the basis sets used in relativistic quantum chemical schemes.[16,17] To guarantee the correct kinetic energy of electrons, the basis functions χ_μ^L and χ_μ^S for the large-component and the small-component spinors, respectively, should satisfy the kinetic balance condition[16] given by Eq. (1)

$$\chi_\mu^S \propto (\sigma \cdot \mathbf{p})\chi_\mu^L \tag{1}$$

in which σ is the vector of Pauli matrices and $\mathbf{p}=-i\nabla$ is the linear momentum operator. The necessity to impose the kinetic balance condition leads to a rapid increase of the number of basis functions and respective molecular integrals required in the relativistic quantum chemical calculation and makes these calculations considerably more time consuming than the corresponding nonrelativistic ones.[7]

The complexity of the four-component relativistic formalism can be bypassed by switching to the two-component (quasi-)relativistic approach, which is achieved by decoupling the electronic and positronic states and by keeping the explicit description for electrons only.[18] However, with the exception of a free electron, the exact algebraic form of such a transformation, the so-called Foldy–Wouthuysen (FW) transformation,[18] is not known. Several approaches were developed to tackle the problem of transforming the four-component

relativistic formalism to a two-component one.[19,20] From the very beginning in the midseventies, the field of (quasi-) relativistic two-component computational schemes was dominated by an operator-driven approach where the (exact or approximate) two-component relativistic Hamiltonian is first expressed in operator form and then transformed to matrix form suitable for quantum chemical calculations. A widely used formalism developed by Douglas and Kroll[19] and later extended by Hess (DKH-method)[21–24] uses a factorization of the unknown FW transformation operator into a free-particle part, which is known exactly, and a field-dependent part, which is approximated to a certain order in the interaction strength. This leads to a convergent series of approximations which, however, uses a large number of auxiliary equations for the intermediate transformation operators and, when converted to matrix form, results in a huge number of matrix operations.[25,26] Therefore, it is not surprising that DKH analytic energy derivatives have been developed only recently and then, only for the low-order approximation of order 2 (DKH2).[27,28]

An alternative to the operator-driven formulation of the two-component relativistic methodology was proposed by Dyall[29] who was probably the first to carry out all the pertinent transformations in matrix form starting from the matrix Dirac equation.[29–32] The resulting normalized elimination of the small component (NESC) formalism is computationally simple and transparent and enables one to obtain the exact electronic (positive-energy) solutions of the Dirac equation.[29,33,34] The initial success of the NESC methodology has led to a subsequent development of alternative matrix-driven two-component methods,[35–38] which have been shown to be equivalent to NESC.[39] It is also noteworthy that approximate relativistic

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methods based on the so-called regular approximation[20,40–43] can be easily derived from NESC, which leads to a simple matrix formulation of these methods.[44,45]

An important advantage of the NESC methodology is the availability of analytic energy derivatives,[46–49] which enable one to obtain relativistically corrected atomic and molecular properties via the response formalism.[50–54] The primary purpose of this article is to provide a succinct overview of the NESC analytic derivatives formalism and its application to the calculation of various relativistically corrected molecular properties. We start by recapitulating the salient features of the NESC methodology and continue by introducing the first-order NESC energy derivatives formalism and its application to the calculation of properties such as the analytic gradient for the accurate and routine optimization of molecular geometries, the determination of contact electron densities and electric field gradients (EFGs) at nuclear positions, or the calculation of magnetic hyperfine structure (HFS) constants. In the subsequent section, the second-order NESC energy derivatives formalism and its application to the calculation of vibrational frequencies, infrared (IR) intensities, and molecular polarizabilities will be described. In the last section, conclusions will be drawn and some thoughts about the future prospects of the NESC methodology will be outlined.

The NESC Method

The derivation of the NESC equations starts from the one-electron Dirac equation represented in matrix form and modified in such a way that the so-called restricted kinetic balance condition is folded into the equation.[29–32] The latter is achieved by introducing[29] a pseudo-large component Φ^L of the relativistic wavefunction via Eq. (2),

$$2mc\Psi^S = (\sigma \cdot \mathbf{p})\Phi^L \qquad (2)$$

which connects it to the small component Ψ^S used in the traditional formulation of the Dirac equation. Although not unique, the definition of the pseudo-large component enables one to eliminate the dependence of the relativistic metric on the spin and to partition the modified Dirac equation into spin-free and spin-dependent (spin-orbit) parts in a simple and transparent way as was first discussed by Kutzelnigg[31,32] and later used by Dyall.[30] In matrix form, the modified Dirac equation is given in Eq. (3),

$$\begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \mathbf{W}-\mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{A}_- & \mathbf{A}_+ \\ \mathbf{B}_- & \mathbf{B}_+ \end{pmatrix} = \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & (2mc^2)^{-1}\mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{A}_- & \mathbf{A}_+ \\ \mathbf{B}_- & \mathbf{B}_+ \end{pmatrix} \begin{pmatrix} \varepsilon^- & \mathbf{0} \\ \mathbf{0} & \varepsilon^+ \end{pmatrix} \qquad (3)$$

where $\mathbf{A}$ and $\mathbf{B}$ are the matrices collecting the expansion coefficients of the large and pseudo-large components of the relativistic wavefuction in terms of the basis functions χ_μ^L (or χ_μ for brevity) and the diagonal matrix ε contains the energy

eigenvalues. The superscripts or subscripts $+$ and $-$ denote the positive (electronic) and negative (positronic) eigenvalue and eigenvector solutions of the equation. Symbols $\mathbf{S}$, $\mathbf{T}$, and $\mathbf{V}$ represent the nonrelativistic overlap, kinetic energy, and potential energy matrices, respectively, and $\mathbf{W}$ is the matrix of the operator $(1/4m^2c^2)(\sigma \cdot \hat{\mathbf{p}})V(\mathbf{r})(\sigma \cdot \hat{\mathbf{p}})$. With the use of the Dirac identity $(\sigma \cdot \mathbf{A})(\sigma \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i\sigma \cdot \mathbf{A} \times \mathbf{B}$, the spin-free and spin-orbit parts of the $\mathbf{W}$ matrix can be separated as in Eq. (4),

$$\mathbf{W} = \mathbf{W}^{sf} + i\sigma \cdot \mathbf{W}^{SO} \qquad (4)$$

which leads to the commonly used spin-scalar approximation resulting from the neglect of the spin-dependent part $\mathbf{W}^{SO}$. In the following, the spin-scalar approximation will be used (unless noted otherwise) and superscript sf of matrix $\mathbf{W}^{sf}$ will be dropped in cases without ambiguity.

By introducing a matrix $\mathbf{U}$ that connects the large and the pseudo-large components via Eq. (5),

$$\mathbf{B}_+ = \mathbf{U}\mathbf{A}_+ \qquad (5)$$

Dyall was able to eliminate the small (pseudo-large) component from the modified Dirac equation and to simultaneously project eigenvalues onto the positive energy (electronic) states.[29] In passing, it should be noted that a similar projection onto the positronic states can also be achieved,[29] however, the latter are not of relevance for chemistry. Focusing on the electronic states only and dropping the $+$ superscript, the working equations of the NESC method are given by Eq. (6),

$$\tilde{\mathbf{L}}\mathbf{A} = \tilde{\mathbf{S}}\mathbf{A}\varepsilon \qquad (6a)$$

$$\tilde{\mathbf{L}} = \mathbf{U}^\dagger\mathbf{T} + \mathbf{T}\mathbf{U} - \mathbf{U}^\dagger(\mathbf{T}-\mathbf{W})\mathbf{U} + \mathbf{V} \qquad (6b)$$

$$\tilde{\mathbf{S}} = \mathbf{S} + \frac{1}{2mc^2}\mathbf{U}^\dagger\mathbf{T}\mathbf{U} \qquad (6c)$$

where the NESC Hamiltonian $\tilde{\mathbf{L}}$ and the NESC large component metric $\tilde{\mathbf{S}}$ are introduced. The elimination of the small component (ESC) matrix $\mathbf{U}$ is to be obtained simultaneously with the NESC Hamiltonian $\tilde{\mathbf{L}}$. This can be achieved either iteratively[29,34] by using the relationships in Eq. (7)

$$\mathbf{U} = \mathbf{T}^{-1}(\mathbf{S}\tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}} - \mathbf{V}) \qquad (7a)$$

$$\mathbf{U} = \mathbf{U}^{IORA} - \frac{1}{2mc^2}\mathbf{U}^{IORA}\mathbf{U}\tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}} \qquad (7b)$$

$$\mathbf{U} = \mathbf{U}^{IORA} - \frac{1}{2mc^2}\mathbf{U}^{IORA}\mathbf{U}\mathbf{S}^{-1}(\mathbf{T}\mathbf{U} + \mathbf{V}) \qquad (7c)$$

or in a one-step method[29,34] that exploits solutions of the modified Dirac equation (3).

$$\mathbf{U} = \mathbf{B}_+\mathbf{A}_+^\dagger(\mathbf{A}_+\mathbf{A}_+^\dagger)^{-1} = \mathbf{B}_+\mathbf{A}_+^\dagger\tilde{\mathbf{S}} \qquad (8)$$

In Eqs. (7b) and (7c), $\mathbf{U}^{IORA} = (\mathbf{T}-\mathbf{W})^{-1}\mathbf{T}$ is the ESC matrix in the infinite-order regular approximation.[45] The iterative solution can be achieved by using a damped fixed point iteration technique,[34] which, if started from an appropriate guess,

requires fewer number of floating point operations than the one-step method. The latter method, however, offers a better stability, especially in cases where a large number of very tight basis functions are used.

The eigenfunctions and eigenvalues of the NESC method are fully equivalent to the electronic solutions of the one-electron Dirac equation.[29,34] For many-electron systems, it is possible to derive, when starting from the modified Dirac–Coulomb equation,[55,56] a similar set of equations to obtain electronic states only.[29] However, this leads to the necessity of calculating a large number of two-electron integrals in addition to those required by a nonrelativistic Hartree–Fock (HF) calculation. A simpler alternative is to consider relativistic effects in the one-electron part of the many-electron Hamiltonian only and treat the electron–electron interactions nonrelativistically.[57] As has been shown by Dyall,[57] the one-electron approximation defined in this way is a sufficiently accurate approximation to the many-electron relativistic self-consistent field (SCF) approach in the FW representation. Within the one-electron (1e) approximation, the atomic or molecular Fock operator is given by Eq. (9),

$$\mathbf{F}_{1e}^{\text{NESC}} = \mathbf{G}^{\dagger}\tilde{\mathbf{L}}\mathbf{G} + (\mathbf{J} - \mathbf{K}) = \mathbf{H}_{1e} + (\mathbf{J} - \mathbf{K}) \qquad (9)$$

where $\mathbf{J}$ and $\mathbf{K}$ correspond to the Coulomb and exchange contributions to the two-electron part of the nonrelativistic Fock operator. The total energy of a many-electron system in the 1e-approximation is then given by Eq. (10),

$$E_{1e}^{\text{NESC}} = tr\mathbf{P}\mathbf{H}_{1e} + \frac{1}{2}tr\mathbf{P}(\mathbf{J} - \mathbf{K}) \qquad (10)$$

where $\mathbf{P} = \mathbf{C}\mathbf{n}\mathbf{C}^{\dagger}$ is the density matrix constructed using the eigenvectors $\mathbf{C}$ of the Fock operator (9) and the diagonal matrix of the orbital occupation numbers $\mathbf{n}$.

The renormalization matrix $\mathbf{G}$ takes care of the transformation of the one-electron NESC Hamiltonian from the relativistic normalization of the electronic wavefunction to the nonrelativistic normalization. The $\mathbf{G}$ matrix possesses correct transformation properties under linear transformations of the basis set. It is calculated as the square root of $\tilde{\mathbf{S}}^{-1}\mathbf{S}$ as given in Eq. (11)

$$\mathbf{G} = \mathbf{S}^{-1/2}(\mathbf{S}^{1/2}\tilde{\mathbf{S}}^{-1}\mathbf{S}^{1/2})^{1/2}\mathbf{S}^{1/2} \qquad (11)$$

which was derived by Peng and Liu.[58] The NESC formalism described can be easily implemented in the existing nonrelativistic quantum chemical codes as it does not require the calculation of new molecular integrals over basis functions. Investigations based on NESC require essentially the same elapsed central processing unit (CPU) time as the corresponding nonrelativistic calculations. The NESC method provides the exact quantum mechanical description of any one-electron system and by this it is fully equivalent to the Dirac four-component method. Hence, NESC is termed a Dirac-exact method. Further details on the implementation of the NESC method can be found in the original publication.[34]

NESC Analytic Energy Derivatives

When differentiating the NESC total energy (10) with respect to an arbitrary external perturbation parameter λ, one obtains Eq. (12)

$$\frac{\partial E}{\partial \lambda} = tr\mathbf{P}\left(\frac{\partial \mathbf{H}_{1e}}{\partial \lambda}\right) + \frac{1}{2}tr\mathbf{P}\frac{\partial'}{\partial \lambda}(\mathbf{J} - \mathbf{K}) + tr\Omega\left(\frac{\partial \mathbf{S}}{\partial \lambda}\right) \qquad (12)$$

where $\Omega = -\mathbf{C}\mathbf{n}\varepsilon\mathbf{C}^{\dagger}$ is the energy-weighted density matrix (Lagrangian) and the prime at $\frac{\partial'}{\partial \lambda}$ implies that only the two-electron integrals have to be differentiated.[46]

The first term in Eq. (12) can be explicitly written as

$$tr\mathbf{P}\left(\frac{\partial \mathbf{H}_{1e}}{\partial \lambda}\right) = tr\mathbf{P}\mathbf{G}^{\dagger}\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda}\mathbf{G} + tr\mathbf{P}\frac{\partial \mathbf{G}^{\dagger}}{\partial \lambda}\tilde{\mathbf{L}}\mathbf{G} + tr\mathbf{P}\mathbf{G}^{\dagger}\tilde{\mathbf{L}}\frac{\partial \mathbf{G}}{\partial \lambda} \qquad (13a)$$

$$= tr\tilde{\mathbf{P}}\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda} + tr\mathbf{D}\frac{\partial \mathbf{G}^{\dagger}}{\partial \lambda} + tr\mathbf{D}^{\dagger}\frac{\partial \mathbf{G}}{\partial \lambda} \qquad (13b)$$

where new matrices $\tilde{\mathbf{P}} = \mathbf{G}\mathbf{P}\mathbf{G}^{\dagger}$ and $\mathbf{D} = \tilde{\mathbf{L}}\mathbf{G}\mathbf{P}$ are introduced. Differentiating Eq. (6b) with respect to λ and inserting the derivative into the first term of Eq. (13b) yields

$$tr\tilde{\mathbf{P}}\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda} = tr\left(\mathbf{U}\tilde{\mathbf{P}} + \tilde{\mathbf{P}}\mathbf{U}^{\dagger} - \mathbf{U}\tilde{\mathbf{P}}\mathbf{U}^{\dagger}\right)\frac{\partial \mathbf{T}}{\partial \lambda} + tr\left(\mathbf{U}\tilde{\mathbf{P}}\mathbf{U}^{\dagger}\right)\frac{\partial \mathbf{W}}{\partial \lambda} + tr\tilde{\mathbf{P}}\frac{\partial \mathbf{V}}{\partial \lambda} \qquad (14a)$$

$$+ tr(\mathbf{T} - (\mathbf{T} - \mathbf{W})\mathbf{U})\tilde{\mathbf{P}}\frac{\partial \mathbf{U}^{\dagger}}{\partial \lambda} + tr\tilde{\mathbf{P}}\left(\mathbf{T} - \mathbf{U}^{\dagger}(\mathbf{T} - \mathbf{W})\right)\frac{\partial \mathbf{U}}{\partial \lambda} \qquad (14b)$$

Equations (13) and (14) depend on the molecular integral derivatives already available in most of the nonrelativistic quantum chemical codes. The only new terms for which derivatives need to be developed are the last two terms in Eq. (13b) and the terms in Eq. (14b), which depend on the derivatives $\partial \mathbf{G}/\partial \lambda$ of the renormalization matrix and $\partial \mathbf{U}/\partial \lambda$ of the ESC matrix, respectively.[46]

When calculating the derivatives $\partial \mathbf{G}/\partial \lambda$, square roots of matrices [in short: matrix square root, see Eq. (11)] have to be differentiated. A commonly adopted algorithm[27,48,59] for obtaining these derivatives is based on the definition of a positive (semi-)definite matrix in terms of its eigenvalues and the eigenvectors according to $\mathbf{M}^{1/2} = \mathbf{C}\mathbf{m}^{1/2}\mathbf{C}^{\dagger}$, where the diagonal matrix $\mathbf{m}^{1/2}$ has the square roots of the eigenvalues of matrix $\mathbf{M}$ on its diagonal. Differentiation of this definition leads to Eq. (11).[27,48,59]

$$\left(\mathbf{C}^{\dagger}\frac{\partial \mathbf{M}^{1/2}}{\partial \lambda}\mathbf{C}\right)_{ij} = \frac{1}{m_{jj}^{1/2} + m_{ii}^{1/2}}\left(\mathbf{C}^{\dagger}\frac{\partial \mathbf{M}}{\partial \lambda}\mathbf{C}\right)_{ij} \qquad (15)$$

Using Eq. (15), the derivatives of the square root of a matrix are calculated element by element and stored to external memory for later use in the gradient calculation.[27,48] Such an approach is computationally inefficient and may represent a bottleneck in the gradient computation. A more efficient computational strategy[46] is based on the fact that the derivatives of $\mathbf{M}^{1/2}$ contribute to the final gradient in the form of traces of matrix products [see Eq. (13b)]. Exploiting the cyclic

property of the trace, that is, $tr\mathbf{ABC}=tr\mathbf{CAB}$, these contributions can be transformed according to Eq. (16),

$$tr\mathbf{X}\frac{\partial \mathbf{M}^{1/2}}{\partial \lambda}=tr\mathbf{Z}\frac{\partial \mathbf{M}}{\partial \lambda} \qquad (16)$$

where two new matrices are introduced: $\mathbf{Z}$ with elements $Z_{ij}=\sum_{k,l}C_{ik}Y_{kl}C_{lj}^{\dagger}(m_{kk}^{1/2}+m_{ll}^{1/2})^{-1}$ and $\mathbf{Y}=\mathbf{C}^{\dagger}\mathbf{XC}$. With the use of Eq. (12), the contributions of the renormalization matrix derivatives $\partial \mathbf{G}/\partial \lambda$ to the final gradient, that is, the last two terms in Eq. (13b), are given by Eq. (17)

$$tr\left(\mathbf{D}\frac{\partial \mathbf{G}^{\dagger}}{\partial \lambda}\right)+tr\left(\mathbf{D}^{\dagger}\frac{\partial \mathbf{G}}{\partial \lambda}\right)=tr(\mathbf{D}_{0Z}+\mathbf{D}_{2Z}-\mathbf{D}_3)\frac{\partial \mathbf{S}}{\partial \lambda} \qquad (17a)$$

$$-\frac{1}{2mc^2}tr(\mathbf{UD}_3\mathbf{U}^{\dagger})\frac{\partial \mathbf{T}}{\partial \lambda}$$

$$-\frac{1}{2mc^2}tr\left(\mathbf{TUD}_3\frac{\partial \mathbf{U}^{\dagger}}{\partial \lambda}+\mathbf{D}_3\mathbf{U}^{\dagger}\mathbf{T}\frac{\partial \mathbf{U}}{\partial \lambda}\right) \qquad (17b)$$

where the matrices $\mathbf{D}_{0Z}$, $\mathbf{D}_{2Z}$, and $\mathbf{D}_3$ do not depend on the perturbation λ and their calculation requires only a few matrix multiplications (see the original publication[46] for further detail). Thus, the algorithm for obtaining the contributions of the derivatives of the renormalization matrix is formulated entirely in terms of traces of matrix products, which makes it convenient for the implementation in existing nonrelativistic quantum chemical codes.[46]

The calculation of the contributions of the ESC matrix derivatives $\partial \mathbf{U}/\partial \lambda$ into the energy gradient [see Eqs. (14b) and (17b)] represent another potential bottleneck for the calculation, as the ESC matrix $\mathbf{U}$ does not have an explicit algebraic expression in terms of the molecular integrals. The most accurate and computationally efficient way of calculating $\partial \mathbf{U}/\partial \lambda$ is based on the use of the response of the modified matrix Dirac equation (3) with respect to an external perturbation λ.[47,48,50] Differentiating Eqs. (3) and (5) with respect to λ and introducing the orbital response matrix $\mathbf{O}^{\lambda}$ according to Eq. (18),

$$\begin{pmatrix} \partial \mathbf{A}_-/\partial \lambda & \partial \mathbf{A}_+/\partial \lambda \\ \partial \mathbf{B}_-/\partial \lambda & \partial \mathbf{B}_+/\partial \lambda \end{pmatrix}=\begin{pmatrix} \mathbf{A}_- & \mathbf{A}_+ \\ \mathbf{B}_- & \mathbf{B}_+ \end{pmatrix}\begin{pmatrix} \mathbf{O}^{\lambda}_{--} & \mathbf{O}^{\lambda}_{-+} \\ \mathbf{O}^{\lambda}_{+-} & \mathbf{O}^{\lambda}_{++} \end{pmatrix} \qquad (18)$$

one obtains Eq. (19),

$$\frac{\partial \mathbf{U}}{\partial \lambda}=(\mathbf{B}_- -\mathbf{UA}_-)\mathbf{O}^{\lambda}_{-+}\mathbf{A}_+^{\dagger}\tilde{\mathbf{S}} \qquad (19)$$

which shows that the ESC matrix derivative $\partial \mathbf{U}/\partial \lambda$ depends on the coupling between the electronic and positronic solutions of the Dirac equation as given by the $\mathbf{O}^{\lambda}_{-+}$ block of the orbital response matrix.[47,50]

The ESC matrix derivatives $\partial \mathbf{U}/\partial \lambda$ make contributions to the final energy gradient in the form of traces of products $tr\mathbf{P}_0^{\dagger}\ \partial \mathbf{U}/\partial \lambda+tr\mathbf{P}_0\ \partial \mathbf{U}^{\dagger}/\partial \lambda$, where the $\mathbf{P}_0=\left(\mathbf{T}-(\mathbf{T}-\mathbf{W})\mathbf{U}\right)$ $\tilde{\mathbf{P}}-(1/2mc^2)\mathbf{TUD}_3$ combine contributions from Eqs. (14b) and (17b). Exploiting the cyclic property of the trace and the expression for the orbital response operator (see the original

publications,[47,50] for further detail) after some algebra one arrives at Eq. (20),

$$tr\mathbf{P}_0^{\dagger}\frac{\partial \mathbf{U}}{\partial \lambda}=tr\mathbf{Z}'^{\dagger}\mathbf{O}^{\lambda}_{-+}=tr\mathbf{P}_{0V}^{\dagger}\frac{\partial \mathbf{V}}{\partial \lambda}+tr\mathbf{P}_{0W}^{\dagger}\frac{\partial \mathbf{W}}{\partial \lambda}+tr\mathbf{P}_{0T}^{\dagger}\frac{\partial \mathbf{T}}{\partial \lambda}+tr\mathbf{P}_{0S}^{\dagger}\frac{\partial \mathbf{S}}{\partial \lambda}$$

$$(20)$$

where the new matrices $\mathbf{P}_{0X}$, $X=V,W,T,S$ do not depend on the perturbation λ and are calculated using the eigenvectors and eigenvalues of the matrix Dirac equation as described in the original publications.[50,52]

The NESC analytic derivatives formalism[46,50] requires only a modest computational effort and can be easily implemented in the nonrelativistic quantum chemical codes. The formalism was tested by comparing analytically and numerically obtained energy gradients for a number of molecules containing heavy elements. As demonstrated in Table 1, the formalism developed leads to exact energy derivatives and requires only a fraction of the CPU time elapsed for a single SCF iteration. In the following subsections, the NESC analytic derivatives formalism is applied to obtain molecular geometries and other first-order response properties.

Geometry optimizations using the NESC analytic gradient

The NESC analytic energy gradient was applied to determine molecular geometries of molecules containing heavy atoms such as Hg, Tl, I, or Au.[46,60] Zou, Filatov, and Cremer (ZFC)[46] used the analytic NESC energy gradient in connection with the NESC/CCSD (coupled cluster with single and double substitutions) method for geometry optimizations and the NESC/CCSD(T) (CCSD with perturbational treatment of triple substitutions) to obtain bond dissociation energies (BDE) at the NESC/CCSD geometries. A selection of the calculated geometries and BDEs is given in Table 2.

It was found[46] that the NESC/CCSD geometries are close to the experimental geometries (see HgCl and HgBr in Table 2) with deviations of the order of 0.1 Å or less. The agreement between NESC/CCSD(T) and experimental bond dissociation enthalpies D_0 for mercury halides was excellent in view of a mean deviation of just 0.3 kcal/mol.[46]

A number of studies have been published since then, which confirm the reliability of molecular geometries optimized using NESC in connection with either density functional theory (DFT) or coupled cluster theory.[47,50–53,60,71]

Table 1. Comparison of numeric and analytic NESC/HF energy gradients (in a.u./bohr) for a number of diatomic molecules.[a]

	Au$_2$	Hg$_2$	HgF
R, bohr	4.000	4.000	3.000
Analytic $\partial E/\partial R$	0.285936	0.340823	0.478037
Numeric $\partial E/\partial R$	0.285925	0.340837	0.478034
N_{basis}	254	612	364
Time/SCF iteration, sec.[b]	3	24	23
Time/NESC grad, sec.	1	6	2

[a] Uncontracted SARC basis set used on Au and uncontracted TZ basis set of Dyall used on Hg. [b] Calculations use eight cores on a 2×E5-2687W workstation.

Table 2. NESC/CCSD geometries and NESC/CCSD(T) bond dissociation energies D_e (enthalpies D_0) of mercury molecules.[a]

Molecule	Sym	State	Method	Geometry parameters	D_e (D_0)	Reference
HgF	$C_{\infty v}$	$^2\Sigma^+$	NESC/CCSD(T)//NESC/CCSD	2.024	33.0 (32.3)	[46]
			Expt.		32.9	[61]
HgCl	$C_{\infty v}$	$^2\Sigma^+$	NESC/CCSD(T)//NESC/CCSD	2.402	23.8 (23.4)	[46]
			SOC/ECP/CCSD(T)	2.354	22.9	[62]
			Expt.	2.395, 2.42	23.4, 24.6	[63–65]
HgBr	$C_{\infty v}$	$^2\Sigma^+$	NESC/CCSD(T)//NESC/CCSD	2.546	20.0 (17.5)	[46]
			SOC/ECP/CCSD(T)	2.498	16.3	[62]
			Expt.	2.62	17.2, 18.4	[66–68]
HgI	$C_{\infty v}$	$^2\Sigma^+$	NESC/CCSD(T)//NESC/CCSD	2.709	12.9 (7.6)	[46]
			SOC/ECP/CCSD(T)	2.708	8.6	[62]
			Expt.	2.81	7.8, 8.1, 8.9	[64,65,69]
HgCN	$C_{\infty v}$	$^2\Sigma^+$	NESC/CCSD(T)//NESC/CCSD	Hg-C: 2.118, C-N: 1.161	36.1	[46]
			IORA/QCISD	Hg-C: 2.114, C-N: 1.179		[70]
HgNC	$C_{\infty v}$	$^2\Sigma^+$	NESC/CCSD(T)//NESC/CCSD	Hg-N: 2.077, N-C: 1.176	22.4	[46]
HgCH₃	C_{3v}	$^2A_1$	NESC/CCSD(T)//NESC/CCSD	Hg-C: 2.344, H-C: 1.084, Hg-C-H: 104.3	3.2	[46]

[a] From Ref. [46], NESC/CCSD(T)//NESC/CCSD denotes NESC/CCSD(T) energies calculated at NESC/CCSD geometries. For HgX (X = F, Cl, Br, I), BDE values D_e include SOC corrections and are corrected by ZPE (zero-point energies) to yield D_0 values. In the calculation of HgCH₃, 14 4f-electrons of Hg were frozen. D values in kcal/mol, bond lengths in Å, angles in degree.

NESC contact density and Mösbauer isomer shift

The contact density, which in nonrelativistic quantum theory is defined as the electron density at the nuclear position, is used for the interpretation[72–74] of the shift of the resonance absorption line in nuclear γ-resonance spectroscopies, such as the Mössbauer spectroscopy[75] or synchrotron nuclear forward scattering.[76] During the nuclear γ-transition, the charge radius of the nucleus changes and this leads to a slight variation of the electron-nuclear interaction that can be sensed by experimental measurements.[73,74] The key electronic structure parameter that defines the magnitude of the resonance line shift (the so-called isomer shift) is the contact density that, at a fully relativistic level of description, can be calculated as a derivative of the total electronic energy with respect to the nuclear charge radius.[77] According to linear response approach proposed by Filatov,[77,78] the isomer shift δ (and contact density , see below) is given by Eq. (21)

$$\delta = \frac{c}{E_\gamma}\left(\frac{\partial E^a(R)}{\partial R}\bigg|_{R=R_a} - \frac{\partial E^s(R)}{\partial R}\bigg|_{R=R_a}\right)\Delta R_a \quad (21)$$

where E^a and E^s denote the electronic energy of the absorbing and source systems, respectively.

A fully analytic approach to obtaining effective contact densities within the linear response formalism based on the NESC method was presented by Filatov, Zou, and Cremer (FZC).[50] For this purpose, the point nucleus (pn) model was extended to a finite nucleus (fn) model. Based on the assumption of a Gaussian nuclear charge distribution in Eq. (22a),

$$\rho_K(r) = Z_K\left(\frac{1}{\pi\zeta'^2}\right)^{3/2} e^{-r^2/\zeta_K'^2} \quad (22a)$$

$$V(\mathbf{r}-\mathbf{R}_K) = -\frac{1}{|\mathbf{r}-\mathbf{R}_K|}\ erf\left(\frac{|\mathbf{r}-\mathbf{R}_K|}{\zeta_K}\right) \quad (22b)$$

$$\zeta_K = \sqrt{\frac{2}{3}}\langle R_K^2\rangle^{1/2} \quad (22c)$$

the nucleus-electron attraction potential V adopts the form of Eq. (22b) where the exponential parameter ζ related to the nuclear charge radius R_K of K-th nucleus is given by Eq. (22c). Then, the effective contact density is given by[77,78]

$$\overline{\rho}_a = \frac{1}{2\pi}\frac{1}{Z_a\zeta}\frac{\partial E(\zeta)}{\partial\zeta}\bigg|_{\zeta=\zeta_0} \quad (23)$$

in which ζ_0 is the value of the parameter obtained from the experimentally measured root-mean-square charge radius of the resonating nucleus a. The effective contact density a can be directly compared to the contact density calculated within a traditional approach as the expectation value of the electron density operator at the nuclear position.[50,77,78] In the context of the NESC method, the energy derivative in Eq. (23) is given by Eq. (24),

$$\frac{\partial E^{NESC}(\zeta)}{\partial\zeta} = tr\left(\tilde{\mathbf{P}} + \mathbf{P}_{0V} + (\mathbf{P}_{0V})^\dagger\right)\frac{\partial\mathbf{V}}{\partial\zeta} + tr\left(\mathbf{U}\tilde{\mathbf{P}}\mathbf{U}^\dagger + \mathbf{P}_{0W} + (\mathbf{P}_{0W})^\dagger\right)\frac{\partial\mathbf{W}}{\partial\zeta} \quad (24)$$

where matrices $\tilde{\mathbf{P}}$, $\mathbf{P}_{0V}$, and $\mathbf{P}_{0W}$ are defined in Eqs. (13) and (20).[46,50]

Using the equations given above, ZFC[50] investigated the contact densities (in e/bohr^{-3}) of the Hg nucleus in free mercury and in a series of mercury compounds, where in the latter case the contact density differences $\bar{\rho}_{Hg} - \bar{\rho}_{mol}$ were determined (see Table 3).[50] Trends in the calculated contact density differences were reasonably reproduced already at the NESC/HF and NESC/MP2 (second-order Møller–Plesset perturbation) levels of theory although the NESC/CCSD represented the most reliable values.[50]

The values of the contact density differences are large when the electronic environment strongly differs from that of the

Table 3. Effective contact densities (e/bohr^{-3}) of the Hg atom obtained at the NESC level of theory.			
Atom/molecule	NESC/HF	NESC/MP2	NESC/CCSD
Hg	2104944.971	2105047.821	2105035.382
Hg$^+$	112.876	127.943	121.136
Hg^{2+}	278.394	305.695	293.217
HgF	98.086	81.294	76.872
HgF$_2$	121.352	108.368	104.387
HgF$_4$	96.586	109.453	96.264
HgCl$_2$	108.118	94.572	91.592
Hg(CH$_3$)$_2$	49.001	43.610	42.184
Hg(H$_2$O)$_6^{2+}$	240.820	245.550	237.066

The absolute contact density is given for Hg($^1S_{1/2}$) whereas contact density differences $\bar{\rho}_{Hg} - \bar{\rho}_{mol}$ are listed for ions and molecules.[50]

free Hg atom. The differences stretch from about 40 e/bohr^{-3} in dimethyl mercury to 293 e/bohr^{-3} in the mercury dication. With increasing electronegativity of the Hg-substituents, the difference contact density increases to 104 e/bohr^{-3}, which confirms that the contact densities and Mössbauer isomer shifts δ are sensitive probes of the electronic environment and coordination sphere of the Hg nucleus.[50]

As the proportionality constant between the contact density and the isomer shift depends on the fractional nuclear charge radius $\langle \Delta r^2 \rangle = R^2 (\Delta R/R)$, the latter can be determined by comparing the experimentally measured isomer shifts with the theoretically calculated contact densities in a series of compounds of the same element. Although measured ^{199}Hg isomer shifts are scarce, one can attempt to derive the fractional charge radius of mercury from the isomer shifts of Hg$_2$F$_2$ and HgF$_2$ measured by Wurtinger and Kankeleit.[79] Using simple cluster models of the Hg$_2$F$_2$ and HgF$_2$ crystals, which were modeled by an Hg$_2$F$_2$ linear fragment and an HgF$_4^{2-}$ tetrahedral fragment with the geometries taken from the crystallographic data, the NESC/CCSD calculations yielded for $\Delta \bar{\rho}$ with respect to mercury atom 86.432 e/bohr^{-3} (Hg$_2$F$_2$) and 220.839 e/bohr^{-3} (HgF$_2$), respectively. Using these densities and the experimental Mössbauer isomer shift difference of -1.77 mm/s, a value $\langle \Delta r^2 \rangle = 2.4 \cdot 10^{-3}$ fm^2 was obtained[80] that is in good agreement with $\langle \Delta r^2 \rangle = 2.9 \cdot 10^{-3}$ fm^2 for the ^{199}Hg 158.4 keV E2 γ-transition obtained from experimental data on muonic atoms.[81] This demonstrates the usefulness of the approach based on the high-level *ab initio* calculations in connection with the NESC formalism for refining the nuclear structure data.

Nuclear quadrupole interaction and EFG

Magnetic nuclei with the spin $I > 1/2$ possess an electric quadrupole moment Q, which can interact with an inhomogeneous electric field caused by electrons and other nuclei in a molecule.[82] The magnitude of the nuclear quadrupole interaction (NQI), which is associated with the Hamiltonian in Eq. (25),

$$\hat{H}^{int} = \sum_{\alpha,\beta} Q_{\alpha\beta} \mathcal{V}_{\alpha\beta}, \; \alpha, \beta = x, y, z \quad (25)$$

is characterized by the nuclear quadrupole coupling constant (NQCC) ν_Q given by Eq. (26),

$$\nu_Q = \frac{eQ \langle \mathcal{V}_{cc} \rangle}{h} \quad (26)$$

The NQCC can be measured utilizing experimental techniques such as Mössbauer spectroscopy,[83] nuclear quadrupole resonance spectroscopy,[84,85] or perturbed angular correlations (PAC) of γ-rays spectroscopy.[86] In Eq. (18), the nuclear quadrupole tensor $Q_{\alpha\beta}$ is defined by Eq. (27),

$$Q_{\alpha\beta} = \frac{eQ}{2I(2I-1)} \left(\frac{1}{2} (\hat{I}_\alpha \hat{I}_\beta + \hat{I}_\beta \hat{I}_\alpha) - \frac{1}{3} \delta_{\alpha\beta} I(I+1) \right) \quad (27)$$

where Q is the nuclear quadrupole moment (NQM). The EFG tensor $\mathcal{V}_{\alpha\beta}$ is defined by Eq. (28),

$$\mathcal{V}_{\alpha\beta} = \left(\frac{\partial}{\partial x_\alpha} \frac{\partial}{\partial x_\beta} - \frac{1}{3} \delta_{\alpha\beta} \nabla^2 \right) V \quad (28)$$

Using the NESC analytic derivatives formalism, FZC[51] expressed the expectation values of the components of the EFG tensor $\langle \mathcal{V} \rangle_{\alpha\beta}$ as derivatives of the NESC total energy with respect to the quadrupole tensor components of the K-th nucleus:

$$\langle \mathcal{V}_{\alpha\beta}^K \rangle = \frac{\partial E^{NESC}(Q_{\alpha\beta}^K)}{\partial Q_{\alpha\beta}^K} \bigg|_{Q_{\alpha\beta}^K \to 0} + \sum_{L \neq K} Z_L \frac{3X_{\alpha,KL} X_{\beta,KL} - \delta_{\alpha\beta} R_{KL}^2}{R_{KL}^5} \quad (29)$$

Here, the second term on the right side represents the nuclear-nuclear part of the EFG and $X_{\alpha,KL}$ are the Cartesian components of the internuclear distance vector $\mathbf{R}_{KL} = \mathbf{R}_K - \mathbf{R}_L$. The first term on the right side of Eq. (29) is given by Eq. (30),

$$\frac{\partial E^{NESC}(Q_{\alpha\beta})}{\partial Q_{\alpha\beta}^K} = tr\left(\tilde{\mathbf{P}} + \mathbf{P}_{0V} + (\mathbf{P}_{0V})^\dagger \right) \frac{\partial \mathbf{V}}{\partial Q_{\alpha\beta}^K} + tr\left(\mathbf{U}\tilde{\mathbf{P}}\mathbf{U}^\dagger + \mathbf{P}_{0W} + (\mathbf{P}_{0W})^\dagger \right) \frac{\partial \mathbf{W}}{\partial Q_{\alpha\beta}^K}$$

(30)

where $\partial \mathbf{V}/\partial Q_{\alpha\beta}^K$ and $\partial \mathbf{W}/\partial Q_{\alpha\beta}^K$ are the derivatives of the electron-nuclear potential energy V and the relativistic correction to V obtained by differentiating the respective molecular integrals after adding the NQI Hamiltonian (25).[51,87] The NESC EFG formalism developed by FZC[51] uses a finite-size nucleus model given in Eq. (22), which makes it possible to study the dependence of the EFG on the parameters of the nuclear charge distribution. Normally, the EFG tensor is diagonalized to determine its principal axes a, b, and c, which are ordered in the way that the eigenvalue relation $|\mathcal{V}_{aa}| \leq |\mathcal{V}_{bb}| \leq |\mathcal{V}_{cc}|$ is fulfilled. Then, the EFG tensor can be characterized by the principal value $\mathcal{V}_{cc}$ and the asymmetry parameter $\eta = (\mathcal{V}_{aa} - \mathcal{V}_{bb})/\mathcal{V}_{cc}$.

Using the NESC EFG formalism in connection with correlation corrected *ab initio* methods, FZC[51] investigated a series of molecules and found that the EFG values obtained are in good agreement with measured values as well as the results as the four-component relativistic calculations, especially. Table 4 compares the EFG principal values obtained at the NESC/HF and the NESC/MP2 level of theory with four-component Dirac–Coulomb HF and CCSD-T results.[88] The NESC/MP2 EFG values

Table 4. NESC electric field gradients $\langle \mathcal{V}_{cc} \rangle$ (a.u.) on Hg nucleus calculated at the HF and MP2 levels in comparison with four-component Dirac–Coulomb values from Ref. [88].

Molecule	4c-DC-HF[a]	NESC(pn)/HF[b]	NESC(fn)/HF[c]	4c-DC-CCSD-T[d]	NESC(fn)/MP2
$HgCl_2$	−12.95	−12.14	−12.12	−9.51	−9.32
$HgBr_2$	−11.82	−11.11	−11.09	−8.63	−8.54
HgI_2	−11.68	−11.04	−11.03	−8.61	−8.64
$Hg(CH_3)_2$	−19.83	−18.77	−18.78	−15.71	−15.22

[a] Four-component Dirac–Coulomb Hartree–Fock results from Ref. [88]. [b] Point-charge nucleus (pn) is used in the calculations. [c] Finite-size nucleus (fn) is used in the calculations. [d] Four-component Dirac–Coulomb CCSD-T results from Ref. [88].

are in an excellent agreement with the state of the art 4c-DC-CCSD-T calculations.[88] Using the ^{199}Hg NQM value of 0.675 ± 0.012 barn,[88] the NESC/MP2 calculation yields 2414 ± 43 MHz for the NQCC of $Hg(CH_3)_2$, which is in good agreement with the NQCC of 2400 MHz obtained by PAC in frozen neat $Hg(CH_3)_2$.[88] The convincing performance of NESC/MP2 is partly a result of the electron correlation corrections, which contribute up to 40% to the final EFG value (see Table 4).

Although the NESC/HF data in Table 4 does not show a pronounced dependence on the nuclear charge distribution (the pn and fn results are nearly the same), the formalism developed offers the possibility of investigating the dependence of the EFG tensor on the nuclear size. It has been suggested by Pyykkö[89] that, in a series of compounds of two different isotopes I_1 and I_2 of the same element Z, the ratio of the NQCCs may vary from compound to compound, thus revealing a nuclear quadrupole anomaly $^{I_1}\Delta^{I_2}_Z$ given by Eq. (31).

$$\frac{v_Q(I_1)}{v_Q(I_2)} = \frac{Q_{I_1}}{Q_{I_2}}\left(1 + {}^{I_1}\Delta^{I_2}_Z\right) \tag{31}$$

Provided that closed shell molecules are considered (the magnetic pseudo-quadrupole interaction is small in this case), the nuclear quadrupole anomaly is caused by the dependence of the EFG on the nuclear charge radius[89] because the charge radii of different isotopes are generally different. Using the NESC EFG formalism, FZC[90] investigated the nuclear quadrupole anomaly by expanding the EFG principal value in Eq. (26) in a Taylor series in terms of the nuclear charge radius R, which upon substitution into Eq. (31) leads to Eq. (32),

$$\frac{v_Q(I_1)}{v_Q(I_2)} = \frac{Q_{I_1}}{Q_{I_2}}\left(1 + \frac{1}{\langle \mathcal{V}_{cc} \rangle}\frac{\partial\langle \mathcal{V}_{cc}\rangle}{\partial R}\bigg|_{R=R_{I_2}}\Delta R_{12}\right) + O(\Delta R_{12}^2) \tag{32}$$

where R_{I_2} is the charge radius of the isotope I_2 and ΔR_{12} is the variation of the charge radius between isotopes I_1 and I_2. Calculating the logarithmic derivative of the principal EFG value in a series of gold compounds, FZC[90] found that the nuclear quadrupole anomaly $^{195}\Delta^{197}_{Au}$ can reach values up to 0.2% according to NESC/CCSD calculations. An anomaly of such a magnitude should be reflected by measured NQCC, as the accuracy of current techniques in microwave spectroscopy is sufficient to detect an anomaly predicted for the $^{195}_{79}$Au, $^{197}_{79}$Au pair of isotopes.[90]

Magnetic hyperfine structure constants

In atoms and molecules with open electronic shells and non-zero net electronic spin, the interaction between the unpaired electrons and the moments of magnetic nuclei results in the HFS of the optical and electron spin resonance (ESR) spectra.[91,92] Nuclei with nonzero magnetic dipole moment μ_K generate a nonuniform magnetic field characterized by the magnetic induction $\mathcal{B}(\mathbf{r})$ and its associated vector potential $\mathcal{A}(\mathbf{r})$ according to $\mathcal{B}(\mathbf{r}) = \nabla\times\mathcal{A}(\mathbf{r})$. The latter is given in Eq. (33),

$$\mathcal{A}(\mathbf{r}) = \frac{1}{c^2}\sum_K \frac{\mu_K\times(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3} \tag{33}$$

where μ_K is the magnetic moment of the nucleus K at position $\mathbf{R}_K$. According to the minimal coupling principle, the electron linear momentum couples to the electromagnetic field vector potential via $\pi = \mathbf{p} + \mathcal{A}$, which leads to alteration of the electron kinetic energy and to hyperfine splitting of the electron energy levels described by the HFS tensor. The latter is commonly characterized by the isotropic HFS constant $\mathcal{A}^{iso}_K$.

Including minimal coupling with the vector potential (33) in the NESC equations and defining the HFS tensor via derivative of the total energy with respect to the nuclear magnetic moment (see Eq. (13.42) in Ref. [7]) FZC[52] derived Eq. (34)

$$\mathcal{A}^{iso}_K = -g_e g_K \mu_B \mu_K \langle S_z\rangle^{-1}\sum_\sigma\left(tr\tilde{\mathbf{P}}^\sigma_T\mathbf{H}^{FC}_{K,z} + \frac{3}{4}\tilde{\mathbf{P}}^\sigma_W(\mathbf{WT}^{-1}\mathbf{H}^{FC}_{K,z} + \mathbf{H}^{FC}_{K,z}\mathbf{T}^{-1}\mathbf{W})\right) \tag{34a}$$

$$= -g_e g_K \mu_B \mu_K \langle S_z\rangle^{-1}\left(tr\tilde{\mathbf{P}}^s_T\mathbf{H}^{FC}_{K,z} + \frac{3}{4}\tilde{\mathbf{P}}^s_W(\mathbf{WT}^{-1}\mathbf{H}^{FC}_{K,z} + \mathbf{H}^{FC}_{K,z}\mathbf{T}^{-1}\mathbf{W})\right) \tag{34b}$$

for the isotropic HFS constant within the NESC formalism. In Eq. (34), $\mathbf{H}^{FC}_{K,\alpha}$ is the matrix of the Fermi-contact operator $\hat{h}^{FC}_K(\mathbf{r}) = (4\pi/3c^2)\delta(\mathbf{r}-\mathbf{R}_K)\sigma$, 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, and the quantity $\langle S_z\rangle$ is the expectation value of the z-component of the electron spin. The matrices $\tilde{\mathbf{P}}^\sigma_T$ and $\tilde{\mathbf{P}}^\sigma_W$ are defined in Ref. [52] and refer to a specific electron spin σ. The matrices $\tilde{\mathbf{P}}^s_T$ and $\tilde{\mathbf{P}}^s_W$ are calculated by substituting the spin-density matrix $\mathbf{P}^s = \mathbf{P}^\alpha - \mathbf{P}^\beta$ into Eq. (34).[52] In ab initio methods with electron correlation, the corresponding response density matrices have to be used. The formalism developed by FZC can utilize the finite distribution of the nuclear magnetic dipole moment similar to Eq. (22a) for the nuclear charge. This enables one to investigate the dependence of the isotropic HFS constants on the nuclear magnetic radius.

Table 5. Comparison of measured isotropic HFS constants (in MHz) of alkali metals with NESC/CCSD or four-component Dirac–Coulomb CISDpT values[93] with experimental data

Atom	Exp.[a]	NESC/CCSD[b]	4c-DC-CISDpT[c]
[7]Li	401.7	402.0	–
[23]Na	885.8	880.2	888.3
[39]K	230.8	232.1	228.6
[85]Rb	1011.9	1019.1	1011.1

[a] Experimental data adopted from Ref. [93]. [b] NESC/CCSD results from Ref. [94]. [c] Four-component Dirac–Coulomb configurational interaction singles and doubles with perturbative treatment of triples from Ref. [93].

The NESC HFS formalism is capable of predicting the $\mathcal{A}_K^{iso}$ values, which are in good agreement with the experiment and the results of high-level four-component relativistic calculations as is reflected by the data in Table 5. In the calculations reported by Hauser et al.,[94] a finite nuclear charge distribution and finite distribution of the nuclear magnetic moment were used in connection with large uncontracted basis sets of pentuple-zeta quality. Although the magnetic and charge nuclear radii are generally different (see e.g., Ref. [95]), the former are not available for most elements and accordingly, one uses the same radius for both electric charge and magnetic dipole distributions.[93]

The accuracy of the NESC HFS calculations makes it possible to estimate the nuclear magnetic radii from a comparison of calculated and measured HFS constants. Table 6 compares $\mathcal{A}_{Hg}^{iso}$ values obtained by NESC[52] and four-component DFT calculations[96] with the corresponding experimental data. The NESC values of Table 6 indicate the importance of electron correlation for obtaining reliable HFS constants. Using a finite nuclear model leads to more accurate NESC values. Relativistic DFT calculations noticeably underestimate the magnitude of $\mathcal{A}_{Hg}^{iso}$ and strongly depend on the nuclear model used. The hyper sensitivity of the DFT calculations to the nuclear model used is due to an incorrect behavior of the exchange-correlation potential in the vicinity of the nucleus.[101] The *ab inito* NESC calculations are free of such drawbacks and yield accurate values, which can be used for refining models of the distribution of the nuclear magnetic moment. To explore this possibility, it is necessary to extend the existing spin-scalar

NESC analytic derivatives formalism by including spin-orbit coupling (SOC) and using a two-component relativistic approach.

Second Analytic Derivatives and Second-Order Response Properties

For the calculation of second-order response properties within the context of Dirac-exact methods, ZFC[47] derived analytic second derivatives of the NESC energy and a similar formalism has been developed by Cheng and Gauss[49] in the context of spin-free X2C method. Differentiating the NESC energy gradient (12) with respect to another external perturbation parameter μ, leads to Eq. (35),

$$\frac{\partial^2 E}{\partial\mu\partial\lambda} = tr\mathbf{P}\frac{\partial^2\mathbf{H}_{1e}}{\partial\mu\partial\lambda} + \frac{1}{2}tr\mathbf{P}\frac{\partial^{2'}}{\partial\mu\partial\lambda}(\mathbf{J}-\mathbf{K}) + tr\Omega\frac{\partial^2\mathbf{S}}{\partial\mu\partial\lambda} \quad (35a)$$

$$+ tr\frac{\partial\mathbf{P}}{\partial\mu}\frac{\partial\mathbf{H}_{1e}}{\partial\lambda} + tr\frac{\partial\mathbf{P}}{\partial\mu}\frac{\partial'}{\partial\lambda}(\mathbf{J}-\mathbf{K}) + tr\frac{\partial\Omega}{\partial\mu}\frac{\partial\mathbf{S}}{\partial\lambda} \quad (35b)$$

in which the majority of the terms are either available in the nonrelativistic quantum chemical codes [terms 2 and 3 in (35a)] or have been already derived in the course of obtaining the first derivatives of the NESC energy [all terms in (35b)]. In the latter case, the derivatives $\partial\mathbf{H}_{1e}/\partial\mu$ are to be used in the context of the coupled-perturbed formalism[102,103] for obtaining the derivatives $\partial\mathbf{P}/\partial\mu$ of the density matrix and $\partial\Omega/\partial\mu$ of the Lagrangian matrix.[47] The remaining term contains second derivatives of the NESC one-electron Hamiltonian and is given in Eq. (36) derived by ZFC.[47]

$$tr\mathbf{P}\frac{\partial^2\mathbf{H}_{1-e}}{\partial\mu\partial\lambda} = tr\tilde{\mathbf{P}}\frac{\partial^2\tilde{\mathbf{L}}}{\partial\mu\partial\lambda} + tr\left(\mathbf{D}\frac{\partial^2\mathbf{G}^\dagger}{\partial\mu\partial\lambda} + \mathbf{D}^\dagger\frac{\partial^2\mathbf{G}}{\partial\mu\partial\lambda}\right) \quad (36a)$$

$$+ tr\mathbf{P}\left(\left(\frac{\partial\mathbf{G}^\dagger}{\partial\mu}\frac{\partial\tilde{\mathbf{L}}}{\partial\lambda} + \frac{\partial\mathbf{G}^\dagger}{\partial\lambda}\frac{\partial\tilde{\mathbf{L}}}{\partial\mu}\right)\mathbf{G} + \mathbf{G}^\dagger\left(\frac{\partial\tilde{\mathbf{L}}}{\partial\lambda}\frac{\partial\mathbf{G}}{\partial\mu} + \frac{\partial\tilde{\mathbf{L}}}{\partial\mu}\frac{\partial\mathbf{G}}{\partial\lambda}\right)\right) \quad (36b)$$

$$+ tr\mathbf{P}\left(\frac{\partial\mathbf{G}^\dagger}{\partial\mu}\tilde{\mathbf{L}}\frac{\partial\mathbf{G}}{\partial\lambda} + \frac{\partial\mathbf{G}^\dagger}{\partial\lambda}\tilde{\mathbf{L}}\frac{\partial\mathbf{G}}{\partial\mu}\right) \quad (36c)$$

All the terms in Eqs. (36b) and (36c) are available from the NESC first analytic derivatives formalism[46,50] and the only new

Table 6. Comparison of calculated isotropic HFS constants (in MHz) of mercury compounds with experimental data

Molecule	Exp.	Nuc. model[a]	NESC/CCSD	NESC/MP2	NESC/HF	4c-DKS/BP86[b]
HgH	6859[c]; 7198[d]	pn	7463	6616	8238	6921
		fn	7332	6500	8093	6244
HgF	22163[e]	pn	20558	21790	23188	18927
		fn	20198	21408	22782	16895
HgCN	15960[f]	pn	16135	19766	17341	15599
		fn	15853	19420	17037	13967
HgAg	2723[g]	pn	2962	2873	2713	3690
		fn	2910	2822	2665	3285

[a] pn: point-like distribution of nuclear charge and magnetic moment; fn: finite-size distribution of nuclear charge and magnetic moment. [b] Four-component Dirac–Kohn–Sham results from Ref. [96]. [c] Ref. [97]; measurement in neon matrix. [d] Ref. [97]; measurement in argon matrix. [e] Ref. [98]; measurement in argon matrix. [f] Ref. [99]; measurement in argon matrix. [g] Ref. [100].

terms are those in Eq. (36a). A careful analysis of Eqs. (35) and (36) carried out by ZFC[47] showed that certain terms make contributions on the order of $O(c^{-4})$ and can be neglected without any noticeable loss of accuracy. The remaining contributions to the first terms in Eqs. (35a) and (35b) are given by Eq. (37),

$$tr\frac{\partial \mathbf{P}}{\partial \mu}\frac{\partial \mathbf{H}_{1e}}{\partial \lambda} + tr\mathbf{P}\frac{\partial^2 \mathbf{H}_{1e}}{\partial \mu \partial \lambda} = tr(U\tilde{\mathbf{P}} + \tilde{\mathbf{P}}U^\dagger - U\tilde{\mathbf{P}}U^\dagger)\frac{\partial^2 \mathbf{T}}{\partial \mu \partial \lambda}$$
$$+ tr(\mathbf{U}\tilde{\mathbf{P}}\mathbf{U}^\dagger)\frac{\partial^2 \mathbf{W}}{\partial \mu \partial \lambda} + tr\tilde{\mathbf{P}}\frac{\partial^2 \mathbf{V}}{\partial \mu \partial \lambda} \qquad (37a)$$

$$+ tr\frac{\partial \mathbf{P}}{\partial \mu}\left(\frac{\partial \mathbf{G}^\dagger}{\partial \lambda}\tilde{\mathbf{L}}\mathbf{G} + \mathbf{G}^\dagger\tilde{\mathbf{L}}\frac{\partial \mathbf{G}}{\partial \lambda} + \mathbf{G}^\dagger\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda}\mathbf{G}\right) \qquad (37b)$$

$$+ tr\left(\mathbf{D}\frac{\partial^2 \mathbf{G}^\dagger}{\partial \mu \partial \lambda} + \mathbf{D}^\dagger\frac{\partial^2 \mathbf{G}}{\partial \mu \partial \lambda}\right) \qquad (37c)$$

$$+ tr\mathbf{P}\left(\left(\frac{\partial \mathbf{G}^\dagger}{\partial \mu}\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda} + \frac{\partial \mathbf{G}^\dagger}{\partial \lambda}\frac{\partial \tilde{\mathbf{L}}}{\partial \mu}\right)\mathbf{G} + \mathbf{G}^\dagger\left(\frac{\partial \tilde{\mathbf{L}}}{\partial \lambda}\frac{\partial \mathbf{G}}{\partial \mu} + \frac{\partial \tilde{\mathbf{L}}}{\partial \mu}\frac{\partial \mathbf{G}}{\partial \lambda}\right)\right) \qquad (37d)$$

where the contributions in Eqs. (37a) and (37b) are most important.[47] Whenever an accurate calculation of second derivatives is not required, such as in the case of vibrational frequencies, the terms of Eqs. (37c) and (37d) can be neglected.[47]

A complete application of Eq. (37) requires an accurate calculation of the second derivatives of the ESC matrix $\mathbf{U}$ and the renormalization matrix $\mathbf{G}$, for which ZFC developed computationally efficient algorithms.[47] When calculating the second derivatives $\partial^2\mathbf{G}/\partial\mu\lambda$, ZFC proposed to utilize the relationship $\mathbf{GG}=\tilde{\mathbf{S}}^{-1}\mathbf{S}$, which upon differentiation with respect to perturbations λ and μ leads to Eq. (38).

$$\mathbf{G}\frac{\partial^2 \mathbf{G}}{\partial \lambda \partial \mu} + \frac{\partial^2 \mathbf{G}}{\partial \lambda \partial \mu}\mathbf{G} = \frac{\partial^2(\tilde{\mathbf{S}}^{-1}\mathbf{S})}{\partial \lambda \partial \mu} - \frac{\partial \mathbf{G}}{\partial \lambda}\frac{\partial \mathbf{G}}{\partial \mu} - \frac{\partial \mathbf{G}}{\partial \mu}\frac{\partial \mathbf{G}}{\partial \lambda} \qquad (38)$$

The latter equation can be represented in the form of a Sylvester equation $\mathbf{GX}+\mathbf{XG}=\mathbf{Q}$, where $\mathbf{X}=\partial^2\mathbf{G}/\partial\lambda\partial\mu$ and $\mathbf{Q}$ is given by the right side of Eq. (38). The Sylvester equation can be efficiently solved by using the r-Smith iterative method or by using a one-step method based on eigenvalue decomposition technique applied to positive-semidefinite non-Hermitian matrices.[47] The second derivatives $\partial^2\mathbf{U}/\partial\mu\partial\lambda$, which are necessary for obtaining the derivatives of the $\tilde{\mathbf{S}}^{-1}$ matrix, are calculated by utilizing the second-order response of the modified matrix Dirac equation (3) as described in Refs. [47] and [49]. The NESC analytic second-derivatives formalism developed by ZFC[47] was tested by comparing the analytically calculated vibrational frequencies with the numerically obtained ones and it was found that the deviations from the numeric frequencies are of the order of 0.1 cm^{-1} or less.[47] In the case of molecular Hessian calculation, the simplifications introduced in Eqs. (35) and (37) lead to considerable savings of computer resources and make the NESC vibrational frequencies calculation as efficient as the corresponding nonrelativistic calculation.[47]

IR spectra: Vibrational frequencies and intensities

A reliable prediction of IR spectra is needed in connection with the identification and structure description of unknown compounds. This task becomes especially challenging for compounds containing heavy elements for which the effect of relativity on the vibrational frequencies and IR intensities must be included. Often, accurate quantum chemical calculations represent a sole source of absolute IR intensities for large molecules as, most commonly, only relative intensities are measured[104] and experimental data on the absolute intensities are scarce.

The IR intensity of a normal mode $\mathbf{d}_i$ is a response property that can be calculated from the second derivative of the total energy of a molecule with respect to the normal coordinates $\mathcal{Q}_i$ and to the electric field $\mathcal{F}$ of the IR radiation[104] as given in Eq. (39),

$$\Gamma_i = \frac{8\pi^3 N_A g}{3hc}\left|\frac{\partial^2 E}{\partial \mathcal{F}_\alpha \partial \mathcal{Q}_i}\right|^2 \qquad (39)$$

where N_A is the Avogadro number, h the Planck constant, g the degeneracy of normal mode $\mathbf{d}_i$, and $\mathcal{F}_\alpha$ is a Cartesian component of the electric field. It is convenient to transform Eq. (39) from normal coordinates $\mathcal{Q}_i$ to Cartesian coordinates X_n of the nuclei of a molecule by using relationship (40):

$$(\Delta^Q)^\dagger\Delta^Q = \mathbf{l}_i^\dagger\left((\Delta^X)^\dagger\Delta^X\right)\mathbf{l}_i \qquad (40)$$

Here, $\mathbf{l}_i$ is a mass-weighted normal vibrational mode given in terms of Cartesian coordinates.[105] Hence, the IR intensities can be calculated by Eq. (41),

$$\Gamma_i = \delta_i^\dagger \ \delta_i = \mathbf{l}_i^\dagger(\Delta^\dagger\Delta)\mathbf{l}_i \qquad (41a)$$

$$\delta_i = \Delta \ \mathbf{l}_i \qquad (41b)$$

where Δ is a rectangular matrix of dimension $3\times3N$ of energy derivatives with regard to nuclear Cartesian coordinates and electric field components. Utilizing the NESC analytic second-derivatives formalism, ZFC[53] derived Eq. (42),

$$\Delta_{\alpha,n} = tr\left(\tilde{\mathbf{P}}\frac{\partial^2 \tilde{\mathbf{L}}}{\partial X_n \partial \mathcal{F}_\alpha}\right) + tr\frac{\partial \mathbf{P}}{\partial X_n}\left(\mathbf{G}^\dagger\frac{\partial \tilde{\mathbf{L}}}{\partial \mathcal{F}_\alpha}\mathbf{G}\right) \qquad (42a)$$

$$= tr\left(\tilde{\mathbf{P}}\frac{\partial^2 \mathbf{V}}{\partial X_n \partial \mathcal{F}_\alpha}\right) + tr\frac{\partial \mathbf{P}}{\partial X_n}\left(\mathbf{G}^\dagger\frac{\partial \mathbf{V}}{\partial \mathcal{F}_\alpha}\mathbf{G}\right) \qquad (42b)$$

in which the terms containing derivatives of the matrices $\mathbf{G}$ and $\mathbf{U}$ were neglected because they make very small contributions to the IR intensity.

Using NESC in connection with DFT calculations utilizing the PBE0 hybrid density functional,[106] ZFC[53] calculated IR spectra for a series of compounds of heavy elements. Table 7 compares the calculated geometries, vibrational frequencies, and IR intensities with the available experimental data, some of which have been measured in solid state samples. The vibrational frequencies calculated are in good agreement with the experimental data considering that the calculated harmonic frequencies were not scaled to approximately include

Table 7. Comparison of NESC/PBE0 geometries (distances in Å), harmonic vibrational frequencies (cm^{-1}), and IR intensities (km/mol) with the corresponding experimental values measured in the gas or the solid phase (the latter are indicated by the word *solid*).[a]

Mol. (sym.)	Method	Geometry	Frequency (infrared intensity, mode symmetry)
AuH ($C_{\infty v}$)	NESC/PBE0	Au-H: 1.530	2283.7 (14.7; σ^+)
	Expt.[61]	Au-H: 1.524	2305.0 (σ^+)
AuH$_2^-$ ($D_{\infty h}$)	NESC/PBE0	Au-H: 1.652	773.8 (115.7; π_u), 1685.2 (1035.8; σ_u^+), 1994.9 (0; σ_g^+)
	Expt.[107]		1636.0 (σ_u^+)
AuH$_4^-$ (D_{4h})	NESC/PBE0	Au-H: 1.631	776.4 (0; b_{2g}), 793.9 (66.6; e_u), 828.7 (42.3; a_{2u}), 843.1 (0; b_{2u})
			1780.6 (2318.0; e_u), 2113.7 (0; b_{1g}), 2118.1 (0; a_{1g})
	Expt.[107]		1676.4 (e_u)
AuF ($C_{\infty v}$)	NESC/PBE0	Au-F: 1.923	556.7 (52.3; σ^+)
	Expt.[108]	Au-F: 1.918	563.7 (σ^+)
AuF$_2^-$ ($D_{\infty h}$)	NESC/PBE0	Au-F: 1.963	184.4 (25.0; π_u), 516.3 (0; σ_g^+), 548.1 (182.7; σ_u^+)
AuF$_4^-$ (D_{4h})	NESC/PBE0	Au-F: 1.916	184.0 (0; b_{2u}), 217.7 (0; b_{2g}), 233.1 (25.8; a_{2u}), 253.8 (8.7; e_u)
			572.0 (0; b_{1g}), 597.1 (0; a_{1g}), 613.4 (383.9; e_u)
	Expt. (solid)[109]		230 (b_{2g}), 561 (b_{1g}), 588 (a_{1g})
ThO ($C_{\infty v}$)	NESC/PBE0	Th-O: 1.826	926.1 (245.7; σ^+)
	Expt.[110]	Th-O: 1.840	895.8 (σ^+)
Th$_2$O$_2$ (D_{2h})	NESC/PBE0	Th-O: 2.089	155.7 (4.8; b_{3u}), 192.7 (0; a_g), 373.1 (0; b_{3g}), 527.2 (35.2; b_{2u}),
		O-Th-O: 74.4	623.8 (297.9; b_{1u}), 633.9 (0; a_g)
	Expt.[111]		619.7 (b_{1u})
UF$_6$ (O_h)	NESC/PBE0	U-F: 1.994	139.1 (0; t_{2u}), 184.0 (51.7; t_{1u}), 199.3 (0; t_{2g}), 539.1 (0; e_g)
			629.4 (810.3; t_{1u}), 681.4 (0; a_{1g})
	Expt.[112,113]	U-F: 1.996	142 (t_{2u}), 186.2 (~38; t_{1u}), 202 (t_{2g}), 532.5 (e_g), 624 (750; t_{1u})
			667.1 (a_{1g})
OsO$_4$ (T_d)	NESC/PBE0	Os-O: 1.686	352.6 (22.4; t_2), 356.5 (0; e), 1031.9 (465.8; t_2), 1063.9 (0; a_1)
	Expt.[114,115]	Os-O: 1.711	322.7 (t_2), 333.1 (e), 960.1 (t_2), 965.2 (a_1)
^{265}HsO$_4$ (T_d)	NESC/PBE0	Hs-O: 1.757	316.1 (32.9; t_2), 335.2 (0; e), 1010.4 (463.2; t_2), 1056.2 (0; a_1)

[a] For details, see Refs. [47] and [53].

anharmonicity effects. In the case of UF$_6$, measured absolute IR intensities are available.[112] The t_{1u}-symmetrical vibrational modes at 184 (exp.: 186) and 629 (exp.: 624) cm^{-1} with intensities of 52 (exp.: 38) and 810 (exp.: 750) km/mol are in a good agreement with the experimental values (see Table 7). It is noteworthy that apart from being essential for identifying unknown compounds via their IR spectra, the IR intensities are also useful for deriving effective atomic charges.[116]

Static electric dipole polarizabilities

Another second-order response property important for the characterization of the electronic structure of molecules and intermolecular interactions is the static electric dipole polarizability, henceforth just called polarizability. The polarizability provides a measure of the distortion of the electric charge distribution in an atom or a molecule exposed to an external electric field.[117] Knowledge of atomic and molecular polarizabilities is important in many areas of chemistry ranging from electron and vibrational spectroscopy to molecular modeling, drug design, and nanotechnology. Especially, for molecules containing relativistic atoms, measured values of polarizabilities are sparse and, therefore, their reliable prediction with the help of relativistic quantum chemical methods is desirable.

Polarizability tensor α is defined as a second derivative of the electronic energy with respect to external electric field $\mathcal{F}$ as in Eq. (43).

$$\alpha = -\frac{\partial^2 E(\mathcal{F})}{\partial \mathcal{F} \partial \mathcal{F}}\bigg|_{\mathcal{F}=0} \qquad (43)$$

As a result of rotational averaging, the scalar isotropic polarizability $= (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ is typically obtained by measurements is the gas phase.

Utilizing the NESC analytic second-derivatives formalism, ZFC[53] derived Eq. (44) for the individual components of the polarizability tensor,

$$\alpha_{\alpha\beta} = -tr\tilde{\mathbf{P}}\frac{\partial^2 \tilde{\mathbf{L}}}{\partial \mathcal{F}_\alpha \partial \mathcal{F}_\beta} - tr\frac{\partial \mathbf{P}}{\partial \mathcal{F}_\alpha}\left(\mathbf{G}^\dagger \frac{\partial \tilde{\mathbf{L}}}{\partial \mathcal{F}_\beta}\mathbf{G}\right) \qquad (44a)$$

$$= -tr\tilde{\mathbf{P}}\frac{\partial^2 \mathbf{V}}{\partial \mathcal{F}_\alpha \partial \mathcal{F}_\beta} - tr\frac{\partial \mathbf{P}}{\partial \mathcal{F}_\alpha}\left(\mathbf{G}^\dagger \frac{\partial \mathbf{V}}{\partial \mathcal{F}_\beta}\mathbf{G}\right) \qquad (44b)$$

which takes a simple form after removing small contributions involving the derivatives of $\mathbf{W}$, $\mathbf{U}$, and $\mathbf{G}$ matrices. As $\mathbf{V}$ is a linear function of the external electric field, $V(\mathbf{r}) = V_{nuc}(\mathbf{r}) + \mathcal{F} \cdot \mathbf{r}$ ($V_{nuc}(\mathbf{r})$, the electron-nuclear attraction potential), the second derivative of $\mathbf{V}$ in Eq. (44b) vanishes and one is left with Eq. (45),

$$\alpha_{\alpha\beta} = -tr\frac{\partial \mathbf{P}}{\partial \mathcal{F}_\alpha}\left(\mathbf{G}^\dagger \frac{\partial \mathbf{V}}{\partial \mathcal{F}_\beta}\mathbf{G}\right) \qquad (45)$$

which differs from the nonrelativistic expression only by the fact that the derivative $\partial \mathbf{V}/\partial \mathcal{F}_\beta$ has to be renormalized by matrix $\mathbf{G}$.

Polarizabilities are affected by the relativistic contraction of the atomic s- and p-orbitals and, to a lesser extent, expansion of the d- and f-orbitals. In molecules, the interplay of relativistic and correlation effects necessitates the use of accurate theoretical calculations to analyze the trends in series of

Table 8. Polarizabilities (in $Å^3$) at optimized geometries obtained using NESC/MP2, NESC/PBE0, or nonrelativistic (NR) calculations

Molecule	Method	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$
AuH	NESC/MP2	5.05	5.05	6.01	5.37
AuH_2^-	NESC/MP2	7.01	7.01	9.34	7.79
AuH_4^-	NESC/MP2	9.85	9.85	6.38	8.69
AuF	NESC/MP2	4.12	4.12	4.91	4.38
AuF_2^-	NESC/MP2	5.34	5.34	6.30	5.66
AuF_4^-	NESC/MP2	7.52	7.52	4.34	6.46
UF_6	NESC/MP2	8.03	8.03	8.03	8.03
OsO_4	NESC/MP2	8.23	8.23	8.23	8.23 (8.17)[118]
HsO_4	NESC/MP2	8.30	8.30	8.30	8.30
HgH	NESC/MP2	4.56	4.56	7.27	5.46
	NESC/PBE0	5.05	5.05	7.38	5.83
	NR/PBE0	7.50	7.50	8.57	7.86
HgF	NESC/MP2	3.87	3.87	6.85	4.86
	NESC/PBE0	4.37	4.37	6.53	5.09
	NR/PBE0	6.35	6.35	6.65	6.45
HgCl	NESC/MP2	5.28	5.28	11.48	7.34 (7.4)[118]
	NESC/PBE0	5.72	5.72	10.65	7.36
	NR/PBE0	7.63	7.63	10.91	8.73
$HgCl_2$	NESC/MP2	5.99	5.99	13.82	8.60
	NESC/PBE0	6.04	6.04	13.62	8.57
	NR/PBE0	6.39	6.39	13.16	8.65

Experimental values are given in parentheses when available.[53]

homologous compounds. Trends in the isotropic polarizability $\bar{\alpha}$ in molecules containing heavy atoms such as Au, Hg, Os, and Hs (hassium, element 108) were studied by ZFC[53] by utilizing the NESC analytic derivatives formalism (see Table 8 for some of the results). Typically, inclusion of relativistic effects leads to a decrease in the polarizability as a result of s-orbitals contraction that outweighs the indirect relativistic effect of an expansion of the d- and f-orbitals. The relativistic corrections for the isotropic polarizabilities lie between -0.2 and -2.0 $Å^3$ where the largest effect is found for HgH ($\bar{\alpha}$: 5.83–7.86 = -2.03 $Å^3$, see Table 8). Isotropic polarizabilities $\bar{\alpha}$ are larger for anionic species than for neutral molecules and larger for radicals as opposed to closed-shell molecules. Also, molecules with more electropositive atoms have larger polarizabilities than molecules with more electronegative atoms.

The polarizability of osmium tetroxide calculated with the NESC/MP2 method (8.23 $Å^{-3}$) deviates only slightly from the experimental value of 8.17 $Å^{-3}$.[118] The NESC/MP2 value is in better agreement with experiment than the NESC/PBE0 polarizability of 6.89 $Å^{-3}$,[53] which is too small by more than 1 $Å^{-3}$. In general, the NESC/MP2 method is more reliable when calculating polarizability values, whereas DFT polarizabilities can be only used when discussing general trends. NESC/MP2 polarizability calculations can be used to correct unreliable experimental values. For example, the measured isotropic polarizability of UF_6 was reported to be 12.5 $Å^3$,[119] which is far too large in view of a NESC/MP2 value of 8.03 $Å^3$ (Table 8). The value of $\bar{\alpha}$ ($HgCl_2$) was given in the literature as 11.6 $Å^3$,[119] whereas the calculated NESC/MP2 value is 8.60 $Å^3$.[53]

Conclusions and Outlook

The derivation of the NESC equations published by Dyall almost two decades ago[29] delineated a new direction of development in the domain of relativistic quantum chemistry. For the first time, the matrix-driven approach to the development of exact and approximate two-component relativistic theories was formulated in a concise way and this demarcated a paradigm shift away from operator-driven approaches, which were dominating the field at that time. It took about a decade to realize the full extent of advantages offered by the matrix-driven approach and the NESC method of Dyall triggered article by other researchers[35–38,58,120,121] in an attempt to extend or reformulate the method. Currently, the development of matrix-driven quasirelativistic computational methods is an active field of research that holds a considerable promise for the computational modeling of molecules and chemical reactions involving heavy and super-heavy elements.

In this review, we have surveyed the most recent developments in the framework of the NESC methodology, which was extended by adding extra functionality in form of analytic energy derivatives,[46,47] the availability of which lays down the basis for calculating first- and second-order response properties of molecules containing heavy atoms.[50–53] The major advantage of the formalism presented is in its computational efficiency, which enables one to calculate relativistically corrected properties of large and very large molecular systems. Although the analytic derivatives formalism presented was formulated within the scalar-relativistic approximation, recent article by FZC[122] lays the basis for its extension to a genuine two-component form and the calculation of SOC effects on molecular properties.

Apart from the extension of the response property formalism by taking SOC effects into account, the development of higher order derivatives and higher order response properties can be foreseen for the future. Especially, the extension of the existing NESC first- and second-analytic derivatives formalism to the calculation of magnetic properties measured NMR or ESR spectroscopy such as the magnetic shielding tensor, nuclear spin–spin coupling constants, or the electronic g-tensor are within reach. A routine calculation of Raman activities and curvature coupling coefficients (derivatives of the normal vibrational modes) will become feasible for the compounds of heavy elements after the development and implementation of a NESC third-order analytic derivatives formalism. Already in its current form, the NESC method can serve as a solid basis for the computational investigation of the properties of molecules containing relativistic elements. Any future extension of the algorithms currently available will strengthen the position of NESC as a generally applicable Dirac-exact relativistic method.

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