

Analytic high-order Douglas-Kroll-Hess electric field gradients

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In this work we present a comprehensive study of analytical electric field gradients in hydrogen halides calculated within the high-order Douglas-Kroll-Hess (DKH) scalar-relativistic approach taking picture-change effects analytically into account. We demonstrate the technical feasibility and reliability of a high-order DKH unitary transformation for the property integrals. The convergence behavior of the DKH property expansion is discussed close to the basis set limit and conditions ensuring picture-change-corrected results are determined. Numerical results are presented, which show that the DKH property expansion converges rapidly toward the reference values provided by four-component methods. This shows that in closed-shell cases, the scalar-relativistic DKH(2,2) approach which is of second order in the external potential for both orbitals and property operator yields a remarkable accuracy. As a parameter-dependence-free high-order DKH model, we recommend DKH(4,3). Moreover, the effect of a finite-nucleus model, different parametrization schemes for the unitary matrices, and the reliability of standard basis sets are investigated. © 2007 American Institute of Physics. [DOI: 10.1063/1.2761880]

I. INTRODUCTION

In recent years much effort has been devoted to the development of efficient and accurate relativistic schemes for the investigation of molecular properties.^{1,2} In particular, the electric field gradient (EFG) has received special attention as a property with $1/r^3$ behavior, which can be calculated within first-order perturbation (i.e., linear response) theory. In the case of molecules containing heavy atoms, a correct calculation of molecular properties requires a consistent treatment of the property operator in the relativistic framework chosen.

A large variety of relativistic all-electron quantum chemical methods is available, ranging from highly accurate, but computationally expensive four-component approaches to elimination and transformation techniques.^{1,2} Among the latter the scalar-relativistic variant of the Douglas-Kroll-Hess (DKH), unitary transformation theory³⁻⁶ has gained increasing attention during the past few years, leading to a rapid development of higher-order and even infinite-order Hamiltonians.^{5,7-10} But a naive calculation of molecular properties within the DKH framework using the *nonrelativ-*

istic expression for the property operator is plagued by an artifact called picture-change effect.¹¹⁻¹⁶

Recent second-order picture-change-affected DKH studies on tin compounds, for instance, revealed that following the estimates of Kellö and Sadlej¹² for the iodine nucleus in HI, one has to expect an overshoot of about 9% when calculating the electric field gradient from nonrelativistic property integrals.¹⁷ Pioneering attempts to cope with that problem gave birth to the development of numerical finite difference schemes.^{18,19} If the role of DKH orders larger than one shall be investigated for the transformed property operator, numerical methods suffer from inaccuracies due to the dependence of the calculated EFG on the displacement of model charges. A first step toward a fully analytical treatment of the property transformation has been taken by Malkin *et al.* by implementing a second-order property transformation.²⁰ A detailed recent EFG study on the hydrogen halides has also been presented by Neese *et al.* instrumentalizing two different transformation schemes denoted as “forward” and “back” transformations.²¹ However, up to now no comprehensive study comprising high-DKH-order orbitals in combination with high-order DKH-transformed EFG operators has been presented in a purely analytical scheme. Hence, the goal of this work is to study the contribution of higher-order terms in the DKH-transformed electric field gradient close to the basis set limit. Then we determine the conditions which guarantee

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picture-change-corrected results in practice, for which we need to consider the balance of basis set size and DKH order of the property operator. Moreover, we discuss finite nuclear size effects in this work and compare the impact of different DKH unitary matrix parametrizations on the EFG. Fully relativistic four-component calculations of the EFG provide a point of reference in order to assess the accuracy of our one-component approach. Linear molecules are ideally suited for such a study, where large decontracted basis sets approaching the basis set limit can be employed. Therefore, we calculate the electric field gradient on the halogen nucleus in the series HX (X=F, Cl, Br, I, At), which has already been discussed in the literature and thus offers an excellent opportunity for comparison. In a subsequent study we will focus on general molecules of extended structure.

This work is organized as follows. In Sec. II a brief account of the underlying theory of the DKH property transformation is presented. The subsequent Secs. III and IV comprise the computational methodology and details concerning the basis set construction, respectively. The following Secs. V and VI contain a discussion of results and concluding remarks, respectively.

II. THEORETICAL BACKGROUND

Starting from the four-component one-electron Dirac picture, an electric-field-like property operator X is added to the original Dirac-Hamiltonian H_D ,

$$H_D(\lambda) = H_D + \lambda X, \quad (1)$$

as a perturbation in linear response theory. H_D denotes the unperturbed one-electron Dirac-Hamiltonian in standard notation,

$$H_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - \mathbf{1}_4)mc^2 + V\mathbf{1}_4, \quad (2)$$

and λ is a formal expansion parameter. The natural constants c and m in Eq. (2) are the speed of light and the rest mass of the electron, respectively. The linear momentum operator \mathbf{p} is given in its well-known differential form, β is a (4×4) diagonal Dirac matrix with $(1, 1, -1, -1)$ as entries, and $\boldsymbol{\alpha}$ denotes a 3-vector, whose elements consist of (4×4) matrices constructed from the Pauli spin matrices.²² The external potential V represents the instantaneous Coulombic electron-nucleus interaction. In accordance with Eq. (1), the relativistic energy E_D of the perturbed system is given by

$$E_D(\lambda) = \langle \Psi_D(\lambda) | H_D(\lambda) | \Psi_D(\lambda) \rangle, \quad (3)$$

with $\Psi_D(\lambda)$ representing the four-component wave function in the presence of the additional potential energy term λX . An electric-field-dependent property is described fully by an even and thus block-diagonal operator,²³

$$X = \begin{pmatrix} X_{LL} & 0 \\ 0 & X_{SS} \end{pmatrix}. \quad (4)$$

In the case of an EFG calculation X features a completely diagonal form. However, a solution of Eq. (3) is not mandatory, and linear response theory may be used instead. Taylor series expansions for energy and wave function usually converge fast in the case of weak perturbations. It is hence suf-

ficient to consider the lowest order correction $E_D^{(1)}$ to the unperturbed energy $E_D(\lambda=0)$,

$$E_D^{(1)} = \left[\frac{dE_D(\lambda)}{d\lambda} \right]_{\lambda=0} = \langle \Psi_D^{(\lambda=0)} | X | \Psi_D^{(\lambda=0)} \rangle. \quad (5)$$

Hence, the unperturbed wave function is sufficient in a four-component (and consequently also in a two-component) framework for the calculation of linear response quantities. Note that Eq. (5) requires that the wave function employed fulfills the Hellmann-Feynman theorem.

In a quasirelativistic scheme, we block diagonalize the unperturbed Dirac-Hamiltonian H_D by a suitably chosen unitary transformation U ,

$$H_{bd} = UH_DU^\dagger = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix} = \sum_{k=0}^{\infty} \mathcal{E}_k, \quad (6)$$

yielding a (2×2) Hamiltonian h_+ that describes only electronic states of the positive-energy spectrum (note that this notation includes the electronic bound states). In DKH theory, U is built up by a sequence of infinitely many unitary matrices U_m . Each unitary matrix U_m is expanded in terms of a power series of the parameter W_m according to the most general ansatz,⁵

$$U_m = \sum_{j=0}^{\infty} a_{m,j} W_m^j = 1 + \sum_{j=1}^{\infty} a_{m,j} W_m^j. \quad (7)$$

The expansion parameter W_m has to be anti-Hermitian and is chosen such that the off-diagonal blocks are diminished order by order in the external potential. The set of expansion coefficients $\{a_{m,j}\}$ must guarantee unitarity of U_m . The so-called *optimum* parametrization given in Ref. 5 allows us to provide a set of expansion coefficients $\{a_{m,j}\}$, which yields truncated unitary transformations that fulfill the condition of unitarity as close as possible upon truncation of the series in Eq. (7) after a given order. Although it is not a crucial part of DKH theory, several sets of expansion coefficients $\{a_{m,j}\}$ were devised, among them the square-root parametrization first introduced by Douglas and Kroll.³

The transformation U must also be applied to the unperturbed four-component wave function,

$$U\Psi_D^{(\lambda=0)} = U \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix} = \begin{pmatrix} \Phi_L \\ 0 \end{pmatrix}, \quad (8)$$

eliminating its small-component part Ψ_S of the 4-spinor and yielding the exact two-component DKH wave function Φ_L . Taking into account the first-order correction to the energy given by Eq. (5), which requires exclusively the unperturbed wave function, we obtain

$$E_D^{(1)} = \langle U\Psi_D^{(\lambda=0)} | UXU^\dagger | U\Psi_D^{(\lambda=0)} \rangle = \langle \Phi_L | X_{DKH^\infty}^{LL} | \Phi_L \rangle. \quad (9)$$

So far Eq. (9) does not contain any approximation. In practice, however, DKH transformations are truncated with respect to a predefined order in the external potential, resulting in a systematic approximation hierarchy for the desired expectation value,

$$\langle X(n,m) \rangle = \langle \Phi_L^{\text{DKH}n} | \sum_{k=0}^m X_{\mathcal{E},k} | \Phi_L^{\text{DKH}n} \rangle, \quad (10)$$

where n and m refer to the DKH order of the orbitals (determined from an n th order Hamiltonian) and property operator, respectively.

The procedure for the calculation of electric-field-dependent DKH properties discussed so far was demonstrated within a one-component formalism for radial momenta as property operators.^{24,25} We may note that Malkin *et al.* applied a similar low-order scheme for the calculation of magnetic properties which they called back transformation.²⁶ We should, however, note that these authors actually did not use a truly four-component framework in this case, but actually considered the transformation of the four-component property operator.²⁷ Nonetheless, it is in principle possible²³ to return to the original Dirac picture starting from Eq. (8), in which the DKH-transformed unperturbed two-component wave function is obtained, by applying the inverse transformation,

$$U^{-1} \begin{pmatrix} \Phi_L \\ 0 \end{pmatrix} = \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix}. \quad (11)$$

According to this ansatz the evaluation of the expectation value $\langle X \rangle$ then takes place in the original four-component framework. The advantage of this procedure is that it is an intrinsically picture-change-free formalism. Within a standard DKH program, which follows Hess' original implementation,⁴ this alternative cannot be implemented as no explicit representation of U , which would require the introduction of a small-component basis in one way or another, is available.

One should not confuse this particular four-component approach with the term "back transformation" as used in Ref. 21, referring to a general application of perturbation-independent unitary transformations U_m . Following Neese *et al.*,²¹ a "forward transformation," however, would feature an *explicit* dependence of the unitary transformations $U_m(\lambda)$ on the perturbation strength λ . As both procedures involve unitary transformations, they must be identical at infinite order. At low order, however, they may deviate. We should stress that we consider perturbation-independent unitary matrices, $U_m(\lambda=0)$, i.e., those called back transformation matrices in Ref. 21, as the proper choice as these would exactly produce the unperturbed wave function of the four-component approach, as required by Eq. (5).²³ The preceding considerations reflect a general treatment of electric-field-like properties within the DKH framework, which has been explicated in detail in Ref. 23. We now focus on the calculation of picture-change-corrected electric field gradients. The perturbing one-electron operator, which accounts for the *electronic* contribution to the EFG at nucleus A , is given by

$$X_{A,\mu\nu} = \sum_i \frac{3r_{iA,\mu}r_{iA,\nu} - r_{iA}^2\delta_{\mu\nu}}{|r_{iA}|^5}, \quad (12)$$

where $r_{iA} = r_i - R_A$ defines the position of electron i relative to nucleus A . The calculation of the nuclear contribution to the EFG, which is skipped in Eq. (12), is trivial in the regime of

the Born-Oppenheimer approximation, as it merely yields an additive constant.

Note that all what has been discussed so far is valid for the one-electron case. It is straightforward to generalize all statements for the N -electron case, where the one-electron perturbation operator enters the sum of N such one-electron operators. Accordingly, all what has been said for the one-electron wave function transfers to molecular spinors and orbitals, which set up the many-electron wave function. The scalar-relativistic, i.e., one-component, expressions of the DKH-transformed property operator in basis set representation are obtained after separation and neglect of all spin-dependent terms.²⁴

III. COMPUTATIONAL DETAILS

All scalar-relativistic calculations were carried out with the MOLCAS electronic structure package,²⁸ into which we implemented our arbitrary-order DKH property module.²⁴ The bond distances of the hydrogen halides series were taken from Ref. 21 and are given in bohrs as follows (we use Hartree atomic units throughout): HF: 1.732 549, HCl: 2.408 502, HBr: 2.672 946, HI: 3.040 798, and HAT: 3.250 392.

The accurate calculation of the EFG requires large decontracted basis sets which is a sensitive issue. Note that many previous papers did either not provide the full list of exponents but a rather vague description of the quality of the basis set or recursively refer to rather old papers which makes it difficult to reproduce the results published. Therefore, the construction of the basis sets used in this work is described in detail in Sec. IV. In particular, we provide all exponents.

The overall basis set sizes used in the benchmark calculations are At (37s/32p/22d/15f/4g), I (35s/28p/19d/8f/4g), Br (30s/22p/14d/8f/3g), Cl (24s/19p/7d/5f), F (23s/17p/6d/4f), and H (20s/5p/4d). Tight convergence criteria were imposed on the calculation of the wave function. The maximum allowed difference in total energy was set to 10^{-10} hartree, and the maximally allowed changes in the density matrix elements and Fock matrix elements were chosen to be 10^{-6} and 0.5×10^{-7} a.u., respectively. The norm of the orbital displacement vector used in the C²-DIIS procedure was fixed to 0.2×10^{-7} . The Dirac-Hartree-Fock calculations were performed with the DIRAC (Ref. 29) program package using the same bond distances, basis sets, and finite-nucleus exponents as in the one-component calculations. The small-component exponents were obtained from applying the atomic kinetic balance condition to the large component basis set and using both the upward and downward generated derivatives.

IV. BASIS SET CONSTRUCTION AND BASIS SET DEPENDENCE OF THE EFG

The basis sets already introduced in Sec. III were primarily generated to yield an accurate EFG close to the limit within the approximations involved, i.e., under neglect of spin-orbit coupling and using a single Slater determinant as an approximation for the wave function. They were not fully

TABLE I. *s* and *p* exponents of the decontracted basis sets used in all nonrelativistic, DKH, and four-component calculations.

At	I	Br	Cl	F	H
<i>s</i> exponents					
1.014 307 2E+09	3.023 925 1E+08	1.004 151 6E+08	3.102 440 0E+07	2.126 736 0E+05	1.162 937 7E+05
2.415 017 1E+08	7.753 654 2E+07	2.668 351 6E+07	1.410 200 0E+07	7.089 120 0E+04	4.186 575 9E+04
6.037 542 7E+07	2.060 522 7E+07	9.161 227 9E+06	6.410 000 0E+06	2.531 828 7E+04	1.268 659 3E+04
1.607 567 3E+07	7.049 668 0E+06	3.548 718 9E+06	9.596 000 0E+05	9.737 802 7E+03	4.228 864 5E+03
5.507 564 5E+06	2.684 767 7E+06	1.526 392 3E+06	2.183 000 0E+05	4.057 417 8E+03	1.510 308 7E+03
2.100 414 3E+06	1.112 957 7E+06	6.936 569 2E+05	6.181 000 0E+04	1.690 590 7E+03	5.808 879 9E+02
8.791 700 1E+05	4.854 140 3E+05	3.212 165 9E+05	2.014 000 0E+04	7.684 503 4E+02	2.525 599 9E+02
3.904 561 8E+05	2.208 265 5E+05	1.493 491 3E+05	7.264 000 0E+03	3.659 287 3E+02	1.147 999 9E+02
1.827 355 2E+05	1.037 876 5E+05	7.019 834 3E+04	2.832 000 0E+03	1.829 643 7E+02	5.466 666 6E+01
8.883 817 8E+04	5.020 235 9E+04	3.357 214 8E+04	1.175 000 0E+03	9.629 703 5E+01	2.733 333 2E+01
4.461 610 6E+04	2.490 171 4E+04	1.639 245 5E+04	5.126 000 0E+02	5.349 835 3E+01	1.438 596 4E+01
2.297 925 2E+04	1.264 625 2E+04	8.171 162 4E+03	2.330 000 0E+02	3.057 048 7E+01	8.462 331 7E+00
1.209 513 8E+04	6.564 646 0E+03	4.153 622 4E+03	1.095 000 0E+02	1.698 360 4E+01	5.288 957 3E+00
6.490 797 3E+03	3.477 787 3E+03	2.151 003 0E+03	5.286 000 0E+01	9.990 355 3E+00	3.111 151 3E+00
3.552 482 4E+03	1.878 384 0E+03	1.133 602 0E+03	2.584 000 0E+01	5.876 679 6E+00	1.637 448 0E+00
1.984 558 9E+03	1.034 244 4E+03	6.071 623 9E+02	1.217 000 0E+01	3.456 870 3E+00	8.618 147 8E-01
1.132 373 1E+03	5.812 603 3E+02	3.299 791 6E+02	6.030 000 0E+00	2.033 453 1E+00	4.535 867 3E-01
6.601 726 7E+02	3.346 718 5E+02	1.814 894 0E+02	3.012 000 0E+00	1.196 148 9E+00	2.387 298 5E-01
3.939 258 9E+02	2.002 323 1E+02	1.004 232 5E+02	1.511 000 0E+00	6.465 669 7E-01	1.256 472 9E-01
2.402 153 1E+02	1.336 376 0E+02	5.495 630 8E+01	6.604 000 0E-01	3.592 038 7E-01	6.980 400 0E-02
1.490 065 2E+02	8.864 208 2E+01	3.080 702 6E+01	2.926 000 0E-01	1.995 577 0E-01	
9.400 091 9E+01	5.548 972 4E+01	1.739 173 7E+01	1.254 000 0E-01	9.977 885 0E-02	
5.969 982 1E+01	3.371 889 8E+01	9.757 985 6E+00	6.270 000 0E-02	4.988 942 5E-02	
3.769 607 8E+01	2.029 488 0E+01	5.257 583 5E+00	3.135 000 0E-02		
2.338 652 9E+01	1.257 641 3E+01	2.868 306 3E+00			
1.528 499 9E+01	7.925 900 0E+00	1.549 511 8E+00			
9.402 809 6E+00	4.992 856 1E+00	7.479 470 2E-01			
5.929 223 3E+00	3.048 260 7E+00	3.847 054 0E-01			
3.870 601 0E+00	1.831 461 1E+00	1.888 560 6E-01			
2.217 795 3E+00	1.058 657 7E+00	8.933 786 0E-02			
1.340 572 9E+00	5.594 202 6E-01				
8.430 933 1E-01	2.965 386 7E-01				
5.653 104 1E-01	1.500 080 4E-01				
2.931 847 5E-01	7.260 990 8E-02				
1.482 336 9E-01	3.209 713 5E-02				
7.050 650 4E-02					
2.747 088 2E-02					
<i>p</i> exponents					
7.225 140 7E+07	4.443 722 1E+07	3.153 669 4E+06	2.888 919 0E+05	2.634 291 0E+03	4.395 000 0E+00
2.493 285 4E+07	1.031 696 2E+07	4.658 429 8E+05	1.313 145 0E+05	1.145 343 9E+03	1.995 000 0E+00
8.893 737 6E+06	2.827 669 0E+06	9.999 918 0E+04	5.968 840 0E+04	5.206 108 7E+02	9.060 000 0E-01
3.345 410 0E+06	8.651 317 3E+05	2.694 310 7E+04	2.713 110 4E+04	2.263 525 5E+02	4.110 000 0E-01
1.314 044 4E+06	2.873 981 9E+05	8.659 960 5E+03	1.233 232 0E+04	1.077 869 2E+02	1.866 000 0E-01
5.360 813 2E+05	1.026 896 6E+05	3.199 731 4E+03	5.605 600 0E+03	5.389 346 4E+01	
2.260 347 4E+05	3.921 176 1E+04	1.314 860 0E+03	2.480 000 0E+03	2.836 498 1E+01	
9.828 670 9E+04	1.595 505 6E+04	5.851 663 7E+02	6.037 000 0E+02	1.575 832 3E+01	
4.405 261 4E+04	6.907 893 4E+03	2.766 697 0E+02	1.956 000 0E+02	9.269 601 7E+00	
2.035 561 7E+04	3.168 031 4E+03	1.371 320 1E+02	7.415 000 0E+01	5.149 778 7E+00	
9.703 123 3E+03	1.527 457 4E+03	7.035 870 7E+01	3.094 000 0E+01	2.860 988 1E+00	
4.775 837 5E+03	7.682 604 9E+02	3.701 474 0E+01	1.369 000 0E+01	1.505 783 2E+00	
2.426 690 0E+03	4.002 985 7E+02	1.981 598 0E+01	6.229 000 0E+00	8.365 462 2E-01	
1.271 052 6E+03	2.144 215 8E+02	1.059 948 9E+01	2.878 000 0E+00	4.647 479 0E-01	
6.840 792 4E+02	1.172 911 2E+02	5.584 693 8E+00	1.282 000 0E+00	2.446 041 5E-01	
3.769 316 6E+02	6.524 930 4E+01	2.920 689 7E+00	5.641 000 0E-01	1.287 390 3E-01	
2.119 490 1E+02	3.652 410 3E+01	1.509 962 1E+00	2.348 000 0E-01	6.602 001 5E-02	
1.207 574 9E+02	2.031 342 6E+01	7.168 223 2E-01	9.312 000 0E-02		
6.930 438 4E+01	1.148 056 8E+01	3.363 481 9E-01	4.655 600 0E-02		
4.052 441 4E+01	6.488 439 3E+00	1.526 336 9E-01			
2.359 836 8E+01	3.601 133 6E+00	6.672 435 0E-02			

TABLE I. (Continued.)

At	I	Br	Cl	F	H
1.349 783 5E+01	1.958 980 3E+00	2.738 609 4E-02			
7.807 620 8E+00	1.046 601 7E+00				
4.466 743 5E+00	5.150 390 0E-01				
2.521 171 6E+00	2.501 806 2E-01				
1.399 328 0E+00	1.174 067 7E-01				
7.596 631 1E-01	5.315 840 3E-02				
3.901 775 8E-01	2.247 577 1E-02				
1.931 586 5E-01					
9.322 940 2E-02					
4.340 915 5E-02					
1.842 079 7E-02					

optimized with respect to the electronic energy, but they perform better with respect to the energy and EFG than the basis sets used in previous studies^{21,30} on the halogen series.

As already mentioned, the basis set information was not fully provided in previous work by other groups. For this reason we explicitly give all exponents of our basis sets of primitive Gaussians in Tables I and II.

The optimization of the basis sets was carried out by successively extending a primary basis set. Additional exponents were incorporated until the change of the EFG was below a predefined tight threshold and convergence was ascertained. This procedure, thus, corresponds to an individual optimization of additional exponents. In the case of the heavier elements (Br, I, At), we chose to take the *s*, *p*, *d*, and *f* exponents (including the diffuse functions) from the relativistic quadruple-zeta basis sets devised by Dyal³¹ as starting point. For At the extension comprised two tight *s* exponents and four *g* functions derived from a geometric progression. The iodine basis set was augmented by one tight *s* function, the valence and core correlating *f* functions of the original basis set, two additional tight *f* functions, and four *g* functions consisting of the same exponents as in the case of At. For Br the valence and core correlating *f* functions of the original basis set, two additional tight *f* functions, and three *g* functions were appended. The Cl basis set was generated from the cc-pV5Z basis set³² by supplementing the original exponents by two tight and two diffuse *s* functions, six tight and one diffuse *p* functions, three steep *d* functions, and finally two steep *f* functions. The *s* and *p* functions of the F basis set were generated by using an increasing ratio of subsequent exponents ranging from 2 to 3 in the case of the *s* functions and from 1.95 to 2.3 in the case of *p* functions. The *d* and *f* exponents were taken from the standard cc-pV5Z basis set and extended by two additional tight *d* functions and one steep *f* exponent. The *s* exponents of the H basis set were generated in the same fashion using a ratio ranging from 1.8 to 2.78, and the *p* and *d* exponents were provided by a cc-pV6Z (Ref. 33) basis set. It is noteworthy that the EFG depends to a large extent on steep higher angular momentum exponents centered at the nucleus the EFG calculation is performed on. Diffuse exponents of the same angular momentum, however, practically do not contribute to the EFG. This can be understood by considering the fact that the EFG operator features a r^{-3} dependence, where *r* denotes the

electron-nucleus distance, and hence probes the core region. Nevertheless diffuse functions on nearby atoms may contribute to the electric field gradient calculated at a specific nucleus, which has to be considered when investigating extended molecules.

V. RESULTS AND DISCUSSION

A. Convergence of the DKH electric field gradient

The results of the scalar-relativistic DKH-Hartree-Fock and the Dirac-Hartree-Fock (DHF) calculation are presented in Tables III–VII.

1. Light homologues: HF, HCl

In the case of the lighter elements relativistic effects are, as expected, negligible. A nonrelativistic EFG calculation on HF recovers already 99.7% of the DKH(7,7) value and 99.6% of the four-component DHF treatment, respectively. A DKH(2,2) calculation reproduces the four-component DHF reference within a deviation of 5×10^{-4} a.u. The absolute picture-change error (PCE), approximated by the difference of the DKH(7,0) and DKH(7,7) expectation values according to the following formula

$$\text{PCE}(q_{zz}) = q_{zz}(7,0) - q_{zz}(7,7), \quad (13)$$

comprises less than 5×10^{-3} a.u. The relative picture-change error estimated from the ratio

$$\text{PCE}_{\text{rel}}(q_{zz}) = \left(\frac{q_{zz}(7,0)}{q_{zz}(7,7)} \times 100 \% \right) - 100 \% \quad (14)$$

is found to be smaller than 0.2% in the case of HF.

A nonrelativistic calculation of the EFG at the Cl nucleus in HCl covers about 99.6% of the DKH(7,7) and DHF reference values. A DKH(2,2) calculation of the EFG shows an accuracy of $1.1 \cdot 10^{-3}$ a.u. compared to a DIRAC DHF calculation. With an absolute value of 0.03 a.u. and a relative value of 0.8%, the PCE is comparatively small.

2. Heavy homologues: HBr, HI, HAt

For the Br nucleus in HBr relativistic effects, however, begin to affect the expectation value of the EFG remarkably. Calculating the EFG in HBr from a nonrelativistic wave function reproduces merely about 93% of the DKH(7,7)

TABLE II. *d*, *f*, and *g* exponents of the decontracted basis sets used in all nonrelativistic, DKH, and four-component calculations.

At	I	Br	Cl	F	H
<i>d</i> exponents					
1.903 494 9E+05	2.453 194 4E+04	2.071 641 5E+03	1.811 700 0E+02	1.263 300 0E+02	4.974 000 0E+00
4.457 226 0E+04	6.156 122 7E+03	5.899 266 1E+02	4.117 500 0E+01	2.871 199 9E+01	2.215 000 0E+00
1.428 275 7E+04	2.150 914 0E+03	2.230 081 6E+02	1.247 730 0E+01	7.760 000 0E+00	9.860 000 0E-01
5.466 223 9E+03	8.917 882 8E+02	9.737 598 1E+01	3.781 000 0E+00	3.032 000 0E+00	4.390 000 0E-01
2.362 092 5E+03	4.118 430 8E+02	4.618 362 9E+01	1.529 000 0E+00	1.185 000 0E+00	
1.115 029 7E+03	2.048 529 3E+02	2.304 057 4E+01	6.180 000 0E+01	4.630 000 0E-01	
5.618 300 5E+02	1.071 147 4E+02	1.189 737 3E+01	2.500 000 0E+01		
2.968 281 6E+02	5.812 822 2E+01	6.208 363 1E+00			
1.626 902 8E+02	3.232 980 2E+01	3.234 217 4E+00			
9.135 128 3E+01	1.821 441 3E+01	1.679 137 4E+00			
5.229 901 2E+01	1.038 538 8E+01	8.702 667 8E-01			
3.018 626 7E+01	5.904 395 3E+00	4.599 294 7E-01			
1.735 276 7E+01	3.293 227 5E+00	1.952 511 7E-01			
9.925 612 3E+00	1.814 770 0E+00	7.460 607 1E-02			
5.653 321 6E+00	1.003 792 9E+00				
3.166 008 2E+00	6.050 331 0E-01				
1.730 928 7E+00	3.725 168 9E-01				
9.510 506 6E-01	1.558 008 0E-01				
5.715 961 8E-01	6.031 522 0E-02				
3.376 139 9E-01					
1.389 246 8E-01					
5.354 779 2E-02					
<i>f</i> exponents					
2.983 211 1E+03	1.097 288 2E+02	4.298 010 3E+02	2.191 200 0E+01	1.997 259 9E+01	
9.883 464 5E+02	2.887 600 6E+01	8.954 188 3E+01	4.980 000 0E+00	5.398 000 0E+00	
4.190 045 1E+02	8.021 112 8E+00	2.035 042 8E+01	1.345 000 0E+00	2.078 000 0E+00	
2.004 800 9E+02	3.180 084 4E+00	7.230 603 1E+00	6.560 000 0E-01	8.000 000 0E-01	
1.036 583 3E+02	1.304 467 1E+00	2.648 744 8E+00	3.200 000 0E-01		
5.591 791 3E+01	5.882 749 8E-01	8.269 465 7E-01			
3.112 787 6E+01	2.502 012 1E-01	3.416 628 6E-01			
1.754 230 8E+01	1.487 455 1E-01	1.890 058 2E-01			
9.886 373 7E+00					
5.518 439 5E+00					
2.990 438 2E+00					
1.518 976 7E+00					
5.477 684 6E-01					
2.310 511 9E-01					
1.314 299 2E-01					
<i>g</i> exponents					
1.000 000 0E+00	1.000 000 0E+00	1.000 000 0E+00			
4.000 000 0E+00	4.000 000 0E+00	4.000 000 0E+00			
1.600 000 0E+01	1.600 000 0E+01	1.600 000 0E+01			
6.400 000 0E+01	6.400 000 0E+01				

value and DHF reference. The DKH(2,2) value differs only 4×10^{-3} a.u. from the DHF reference. An absolute PCE of about 0.3 a.u. resulting in a relative effect of the order of 4%, however, gives rise to larger deviations, when neglecting the property transformation.

For the two heaviest molecules HI and HAt in our study, the influence of relativity on the EFG is far greater than in the cases mentioned before. A nonrelativistic treatment of the property integrals in HI leads to a drop of the EFG by almost 17% when compared to the DKH(7,7) or the DHF calculation. In the case of HAt a nonrelativistic expression for the EFG underestimates the DHF result by about 41%. The

DKH(2,2) approach yields compared to the DHF reference a deviation of 0.01 a.u. for HI and a deviation of 0.36 a.u. for HAt, respectively. The absolute PCE is about 1.24 a.u. in the case of HI, which increases to 9.90 a.u. for HAt, leading to a significant relative PCE of 11% for the EFG on the iodine nucleus, which rises to about 37% for HAt. An overview of the relative amount of scalar-relativistic effects and the relative size of the picture-change error for all molecules under investigation is given in Table VIII.

According to these results a relativistic treatment avoiding the PCE of the molecular property is mandatory for the heavier molecules (HBr, HI, HAt). As has already been

TABLE III. Electronic energy and the principal component of the diagonalized electric field gradient tensor (q_{zz}) in HF (in a.u.) calculated at the F nucleus.

DKH n	Energy	$q_{zz}(n,0)$	$q_{zz}(n,1)$	$q_{zz}(n,2)$	$q_{zz}(n,3)$	$q_{zz}(n,4)$	$q_{zz}(n,5)$	$q_{zz}(n,6)$	$q_{zz}(n,7)$
Point charge nucleus/Optimum parametrization									
Nonrel	-100.070 710 71	2.799 747							
DKH2	-100.157 491 39	2.813 983	2.809 265	2.809 265					
DKH3	-100.157 559 59	2.813 984	2.809 265	2.809 266	2.809 266				
DKH4	-100.157 558 80	2.813 984	2.809 265	2.809 266	2.809 266	2.809 266			
DKH5	-100.157 558 82	2.813 984	2.809 265	2.809 266	2.809 266	2.809 266	2.809 266		
DKH6	-100.157 558 82	2.813 984	2.809 265	2.809 266	2.809 266	2.809 266	2.809 266	2.809 266	
DKH7	-100.157 558 82	2.813 984	2.809 265	2.809 266	2.809 266	2.809 266	2.809 266	2.809 266	2.809 266
Finite nucleus/Optimum parametrization									
Nonrel	-100.070 687 38	2.799 746							
DKH2	-100.157 467 60	2.813 983	2.809 265	2.809 265					
DKH3	-100.157 535 77	2.813 984	2.809 265	2.809 266	2.809 266				
DKH4	-100.157 534 98	2.813 984	2.809 265	2.809 266	2.809 266	2.809 266			
DKH5	-100.157 535 00	2.813 984	2.809 265	2.809 266	2.809 266	2.809 266	2.809 266		
DKH6	-100.157 535 00	2.813 984	2.809 265	2.809 266	2.809 266	2.809 266	2.809 266	2.809 266	
DKH7	-100.157 535 00	2.813 984	2.809 265	2.809 266	2.809 266	2.809 266	2.809 266	2.809 266	2.809 266
4-component									
DHF	-100.162 573 87								2.809 754

pointed out by Malkin *et al.*,²⁰ a first-order property transformation, i.e., the free-particle Foldy-Wouthuysen transformation, contributes to a large extent to the correction for the picture-change effect. Higher-order terms decline rapidly with increasing order. The standard DKH(2,2) approach can be regarded as a suitable choice for lighter elements including iodine, where the deviation from a DKH(7,7) EFG data adds up to 0.07 a.u., which is smaller than the computational error introduced by the finite basis set. For At already DKH(4,4) offers a fast and accurate alternative.

Spin-orbit effects are small for the closed-shell species under study, excepting HAt where spin-orbit coupling tends to diminish the EFG by some 0.5 a.u. An explanation for that was given by Pyykkö and Seth by addressing the so-called

spin-orbit tilting effect.³⁴ For the lighter homologs, however, the DKH(7,7) results do not deviate much from the DHF ones.

B. Effects of a finite-nucleus model on the EFG

Tables III–VII also provide the results for the EFG of the set of HX molecules within different DKH(n,m) models, as obtained with a finite nuclear charge distribution. The Gaussian charge distribution model of Visscher and Dyall was chosen to represent the nucleus in our study.³⁵ The very same finite-nucleus model exponents were also applied in all four-component calculations. Switching from a point charge nucleus to a finite-nucleus model does not show a significant

TABLE IV. Electronic energy and principal component of the diagonalized electric field gradient tensor (q_{zz}) in HCl (in a.u.) calculated at the Cl nucleus.

DKH n	Energy	$q_{zz}(n,0)$	$q_{zz}(n,1)$	$q_{zz}(n,2)$	$q_{zz}(n,3)$	$q_{zz}(n,4)$	$q_{zz}(n,5)$	$q_{zz}(n,6)$	$q_{zz}(n,7)$
Point charge nucleus/Optimum parametrization									
Nonrel	-460.112 660 42	3.541 586							
DKH2	-461.522 947 27	3.619 627	3.590 193	3.590 205					
DKH3	-461.526 290 83	3.619 629	3.590 195	3.590 207	3.590 207				
DKH4	-461.526 187 04	3.619 629	3.590 195	3.590 207	3.590 207	3.590 207			
DKH5	-461.526 195 58	3.619 629	3.590 195	3.590 207	3.590 207	3.590 207	3.590 207		
DKH6	-461.526 194 83	3.619 629	3.590 195	3.590 207	3.590 207	3.590 207	3.590 207	3.590 207	
DKH7	-461.526 194 89	3.619 629	3.590 195	3.590 207	3.590 207	3.590 207	3.590 207	3.590 207	3.590 207
Finite nucleus/Optimum parametrization									
Nonrel	-460.112 214 60	3.541 586							
DKH2	-461.522 468 83	3.619 626	3.590 191	3.590 204					
DKH3	-461.525 795 34	3.619 628	3.590 193	3.590 205	3.590 205				
DKH4	-461.525 692 87	3.619 628	3.590 193	3.590 205	3.590 205	3.590 205			
DKH5	-461.525 701 22	3.619 628	3.590 193	3.590 205	3.590 205	3.590 205	3.590 205		
DKH6	-461.525 700 50	3.619 628	3.590 193	3.590 205	3.590 205	3.590 205	3.590 205	3.590 205	
DKH7	-461.525 700 55	3.619 628	3.590 193	3.590 205	3.590 205	3.590 205	3.590 205	3.590 205	3.590 205
4-component									
DHF	-461.568 450 82								3.591 314

TABLE V. Electronic energy and principal component of the diagonalized electric field gradient tensor (q_{zz}) in HBr (in a.u.) calculated at the Br nucleus.

DKH n	Energy	$q_{zz}(n,0)$	$q_{zz}(n,1)$	$q_{zz}(n,2)$	$q_{zz}(n,3)$	$q_{zz}(n,4)$	$q_{zz}(n,5)$	$q_{zz}(n,6)$	$q_{zz}(n,7)$
Point charge nucleus/Optimum parametrization									
Nonrel	-2573.052 255 97	7.009 477							
DKH2	-2604.911 957 60	7.840 219	7.537 429	7.536 201					
DKH3	-2605.122 055 55	7.840 417	7.537 597	7.536 368	7.536 551				
DKH4	-2605.108 392 61	7.840 403	7.537 585	7.536 356	7.536 539	7.536 520			
DKH5	-2605.110 856 54	7.840 405	7.537 587	7.536 358	7.536 541	7.536 522	7.536 524		
DKH6	-2605.110 394 36	7.840 404	7.537 586	7.536 358	7.536 540	7.536 521	7.536 523	7.536 523	
DKH7	-2605.110 467 52	7.840 404	7.537 586	7.536 358	7.536 540	7.536 521	7.536 523	7.536 523	7.536 523
Finite nucleus/Optimum parametrization									
Nonrel	-2573.038 943 88	7.009 468							
DKH2	-2604.894 274 63	7.840 026	7.537 244	7.536 047					
DKH3	-2605.101 634 19	7.840 222	7.537 410	7.536 213	7.536 390				
DKH4	-2605.088 392 57	7.840 208	7.537 398	7.536 201	7.536 378	7.536 360			
DKH5	-2605.090 711 33	7.840 210	7.537 400	7.536 203	7.536 380	7.536 362	7.536 364		
DKH6	-2605.090 295 40	7.840 209	7.537 399	7.536 203	7.536 380	7.536 361	7.536 363	7.536 363	
DKH7	-2605.090 357 88	7.840 209	7.537 399	7.536 203	7.536 380	7.536 361	7.536 363	7.536 363	7.536 363
4-component									
DHF	-2605.633 124 16								7.540 289

effect in case of all molecules with the exception of HAt, where a finite nucleus accounts for a decrease of the EFG by 0.18 a.u. EFG calculations on *heavy* elements are thus sensitive to the type of nucleus chosen, i.e., whether it features the singular attraction potential of a point charge (with its well-known effect on the short-range expansion of the spherically averaged spinor) or the finite potential of an extended charge distribution.³⁶ For heavier atoms than At, the effect of a finite nuclear charge distribution can be expected to be even larger. Therefore, a careful choice of the nucleus model chosen might be a crucial issue in calculations on heavy and superheavy atoms. It is likely that different finite-nucleus models such as a homogeneously charged sphere or

a Fermi nucleus will not change the qualitative picture obtained from the Gaussian model (compare to the results of Ref. 35).

C. EFG calculated with standard basis sets

Since basis sets of sizes as used in the present study are unfeasible for standard applications, we repeated the DKH(2,2) and DKH(4,3) calculations on the whole hydrogen halide series with ANO-RCC (Ref. 37) basis sets, as implemented in MOLCAS. These generally contracted basis sets were especially derived for scalar-relativistic one-component calculations by using a second-order DKH Hamiltonian.

TABLE VI. Electronic energy and principal component of the diagonalized electric field gradient tensor (q_{zz}) in HI (in a.u.) calculated at the I nucleus.

DKH n	Energy	$q_{zz}(n,0)$	$q_{zz}(n,1)$	$q_{zz}(n,2)$	$q_{zz}(n,3)$	$q_{zz}(n,4)$	$q_{zz}(n,5)$	$q_{zz}(n,6)$	$q_{zz}(n,7)$
Point charge nucleus/Optimum parametrization									
Nonrel	-6918.574 867 07	9.670 500							
DKH2	-7111.459 293 89	12.873 105	11.655 929	11.618 554					
DKH3	-7113.627 304 38	12.874 893	11.657 317	11.619 930	11.628 742				
DKH4	-7113.412 672 21	12.874 679	11.657 134	11.619 748	11.628 560	11.626 853			
DKH5	-7113.475 811 88	12.874 721	11.657 173	11.619 787	11.628 600	11.626 892	11.627 224		
DKH6	-7113.457 201 05	12.874 707	11.657 162	11.619 776	11.628 589	11.626 881	11.627 213	11.627 152	
DKH7	-7113.461 609 43	12.874 710	11.657 165	11.619 778	11.628 591	11.626 884	11.627 216	11.627 155	11.627 166
Finite nucleus/Optimum parametrization									
Nonrel	-6918.480 825 83	9.670 452							
DKH2	-7111.275 741 93	12.857 503	11.643 874	11.614 194					
DKH3	-7113.388 091 20	12.859 200	11.645 247	11.615 560	11.622 568				
DKH4	-7113.185 138 62	12.858 992	11.645 080	11.615 393	11.622 401	11.621 046			
DKH5	-7113.241 557 67	12.859 028	11.645 115	11.615 428	11.622 437	11.621 081	11.621 348		
DKH6	-7113.226 118 20	12.859 016	11.645 106	11.615 419	11.622 427	11.621 072	11.621 338	11.621 288	
DKH7	-7113.229 473 46	12.859 019	11.645 108	11.615 421	11.622 429	11.621 074	11.621 340	11.621 290	11.621 299
4-component									
DHF	-7116.386 133 82								11.623 332

TABLE VII. Electronic energy and principal component of the diagonalized electric field gradient tensor (q_{zz}) in HAt (in a.u.) calculated at the At nucleus.

DKHn	Energy	$q_{zz}(n,0)$	$q_{zz}(n,1)$	$q_{zz}(n,2)$	$q_{zz}(n,3)$	$q_{zz}(n,4)$	$q_{zz}(n,5)$	$q_{zz}(n,6)$	$q_{zz}(n,7)$
Point charge nucleus/Optimum parametrization									
Nonrel	-21 267.467 071 51	15.358 363							
DKH2	-22 846.393 604 06	37.171 665	27.425 119	26.409 692					
DKH3	-22 877.971 823 32	37.200 149	27.446 665	26.430 743	26.782 486				
DKH4	-22 873.130 856 58	37.194 075	27.441 024	26.425 127	26.776 879	26.659 425			
DKH5	-22 875.918 074 19	37.197 022	27.442 715	26.426 715	26.778 503	26.661 037	26.699 892		
DKH6	-22 874.502 887 35	37.195 213	27.441 822	26.425 900	26.777 661	26.660 204	26.699 056	26.686 713	
DKH7	-22 875.005 641 74	37.195 680	27.442 169	26.426 249	26.778 012	26.660 555	26.699 407	26.687 064	26.690 805
Finite nucleus/Optimum parametrization									
Nonrel	-21 266.618 586 32	15.358 042							
DKH2	-22 840.664 598 10	36.391 780	26.978 222	26.335 521					
DKH3	-22 869.976 352 86	36.416 796	26.997 685	26.354 736	26.572 096				
DKH4	-22 865.658 508 92	36.410 276	26.993 094	26.350 251	26.567 579	26.497 028			
DKH5	-22 867.809 612 48	36.412 034	26.994 367	26.351 501	26.568 836	26.498 282	26.521 140		
DKH6	-22 866.841 604 69	36.411 008	26.993 782	26.350 940	26.568 267	26.497 716	26.520 573	26.513 359	
DKH7	-22 867.141 640 46	36.411 262	26.993 964	26.351 129	26.568 457	26.497 906	26.520 763	26.513 548	26.515 799
4-component									
DHF	-22 910.394 500 51								25.979 844

They might, however, not offer an optimal description of core orbitals in heavy elements, when higher-order DKH transformations are involved. We chose the DKH(2,2) and DKH(4,3) approaches for this comparison because both do not depend on the parametrization of the unitary matrices. While DKH(2,2) calculations represent the “standard” DKH model, DKH(4,3) provides the highest order possible if a dependence on the parametrization of the unitary matrices shall be avoided. As can be seen from Table IX, reliable values for the EFG are obtained even with basis sets of modest size. For the two heaviest elements the error due to the incompleteness of the basis set is 1%–2%. Thus for Br and its heavier homologs, the error introduced by the picture-change effect is by far larger than the inaccuracies owing to the limited basis set size and has to be considered explicitly.

D. Dependence of the EFG on the parametrization of the unitary transformation

Different parametrization schemes characterized by different sets of expansion coefficients $a_{m,j}$ of Eq. (7) do not have significant impact on the calculation of the EFG, as can be demonstrated on the basis of Table X. We chose two different models DKH(5,4) and DKH(6,6) in order to demonstrate the magnitude of this effect as depending on the DKH order.

TABLE VIII. Percent scalar-relativistic effect on q_{zz} and relative picture-change error as defined by Eq. (14).

Molecule	Scalar-relativistic effect on q_{zz} (%)	PCE _{rel} (%)
HF	0.3	0.2
HCl	0.4	0.8
HBr	7	4
HI	17	11
HAt	41	37

The five different parametrization schemes compared for DKH(6,6) taking the heavy hydrogen halides HI and HAt as examples reveal an absolute dependence of the EFG on the parametrization of the order of magnitude less than 10^{-4} a.u., which can be below the accuracy of the electronic structure method. The same holds for the DKH(5,4) calculations where the largest parameter dependence is expected. Thus the choice of parametrization affects the electronic energy to a greater extent than the molecular property in this example.

E. Comparison to data from the literature

A sensible comparison of our results to data from the literature on the EFG in the hydrogen halide series is only appropriate for the data given by Malkin *et al.*²⁰ and Neese *et al.*,²¹ because they both provide results obtained with an analytical treatment of the DKH property transformation. Since only the electronic contribution to the EFG was published by Malkin *et al.*, we have evaluated the missing nuclear contribution and complemented the original data set. In addition, we compare to the finite-field results of Visscher *et al.*,³⁰ which depend on this numerical model but incorporate electron correlation effects. The corresponding data can be found in Table XI.

First of all we should like to draw attention to the deviation of results obtained with the forward and back transformation schemes in the cases of HI and HAt in Ref. 21. For these two heaviest elements, our results do not confirm the back transformation results of Ref. 21, but show that our back transformation approach agrees well with the DHF reference as it should be [compare Eq. (5)]. The agreement is even better in the case of HAt if we contrast the DKH(2,2) EFG of 26.409 692 a.u. with the spin-free DHF EFG of 26.588 178 a.u. (see Ref. 38 for this spin-free variant of DHF). On the contrary, it is surprising to note that the electric-field-dependent forward transformation agrees well with our results and DHF. In most cases our results are

TABLE IX. Electronic energy and principal component of the diagonalized electric field gradient tensor (q_{zz}) in the halogen halide series (in a.u.) calculated with a DKH(2,2) and DKH(4,3) formalism at the halogen nucleus with standard ANO-RCC basis sets (Ref. 37). Relative differences (in %) to the DKH(2,2) and DKH(4,3) values obtained with large decontracted basis sets are given for comparison.

Molecule	Energy	DKH(n,m)	$q_{zz}(n,m)$	$\Delta q_{zz}(n,m)$ (%)	Basis set (heavy element) ^a
HF	-100.157 138 04	(2,2)	2.867 641	2.1	14s9p4d3f2g/8s7p4d3f2g
	-100.157 199 10	(4,3)	2.867 645	2.1	
HCl	-461.521 148 15	(2,2)	3.631 357	1.1	17s12p5d4f2g/8s7p5d4f2g
	-461.524 101 33	(4,3)	3.631 356	1.1	
HBr	-2 604.909 591 42	(2,2)	7.503 138	0.4	20s17p11d4f2g/9s8p6d4f2g
	-2 605.104 997 75	(4,3)	7.503 860	0.4	
HI	-7 111.449 015 84	(2,2)	11.486 758	1.1	22s19p13d5f3g/10s9p8d5f3g
	-7 113.392 019 77	(4,3)	11.493 198	1.2	
HAt	-22 846.012 724 39	(2,2)	26.137 657	1.0	25s22p16d12f4g/11s10p9d6f4g
	-22 872.405 129 85	(4,3)	26.383 652	1.5	

Hydrogen basis set: 8s4p3d1f/6s4p3d1f^b

^aReference 37.

^bReference 39.

smaller than those published by Neese *et al.*,²¹ Malkin *et al.*,²⁰ and Visscher *et al.*³⁰ This is likely to be due to the additional tight polarization functions in our work. Steep functions of higher angular momentum hardly contribute to the electronic energy of the molecules under investigation, but they tend to diminish the expectation value of the EFG. This effect was also observed by Visscher *et al.*³⁰ The basis sets used in Ref. 20 are, in general, considerably smaller than those employed in the other studies under consideration. This

gives rise to somewhat larger deviations when comparing our results to the data provided by Ref. 20, especially in case of the EFG at the fluorine nucleus in HF and the chlorine nucleus in HCl. Note that if electron correlation is taken into account, a change of about 7% for the EFG in HI was estimated by Visscher *et al.*³⁰

TABLE X. Electronic energy and principal component of the diagonalized electric field gradient tensor (q_{zz}) in HI and HAt (in a.u.) calculated with the DKH(6,6) and DKH(5,4) protocols at the I and At nucleus, using different parametrization schemes. These schemes provide different sets of expansion coefficients $\{a_{m,j}\}$ given in Ref. 5. Note that the energy is classified by n and hence either of sixth or fifth order. The fifth order is below the sixth order following the oscillatory convergence in Ref. 10.

Parametrization	DKH(n,m)	Energy	$q_{zz}(n,m)$
HI			
Cayley	(6,6)	-7 113.457 176 25	11.627 143
	(5,4)	-7 113.476 046 96	11.626 883
Exponential	(6,6)	-7 113.457 196 21	11.627 150
	(5,4)	-7 113.475 857 78	11.626 891
McWeeny	(6,6)	-7 113.457 116 38	11.627 120
	(5,4)	-7 113.476 614 51	11.626 860
Optimum	(6,6)	-7 113.457 201 05	11.627 152
	(5,4)	-7 113.475 811 88	11.626 892
Square root	(6,6)	-7 113.457 236 14	11.627 166
	(5,4)	-7 113.475 479 44	11.626 906
HAt			
Cayley	(6,6)	-22 874.499 553 11	26.686 711
	(5,4)	-22 875.942 067 58	26.661 039
Exponential	(6,6)	-22 874.502 236 24	26.686 713
	(5,4)	-22 875.922 758 82	26.661 029
McWeeny	(6,6)	-22 874.491 506 27	26.686 705
	(5,4)	-22 876.000 012 44	26.661 067
Optimum	(6,6)	-22 874.502 887 35	26.686 713
	(5,4)	-22 875.918 074 19	26.661 037
Square root	(6,6)	-22 874.507 603 81	26.686 715
	(5,4)	-22 875.884 150 57	26.661 010

VI. CONCLUSION

Quantum chemical calculations of energies and molecular properties on molecules containing heavy elements require a consistent treatment of relativistic effects. For the closed-shell molecules under investigation spin-orbit effects can be shown to be rather small, excluding HAt, where they diminish the expectation value of the EFG by more than 0.5 a.u. A scalar-relativistic treatment is thus sufficient for all studied molecules with the exception of HAt. A DKH(2,2) calculation, which may be considered the standard approach for the analytical determination of the electric field gradient on molecules up to a nuclear charge of $Z \approx 50$, provides reliable results within the accuracy of the computational method chosen. A complete neglect of the property transformation is in no case acceptable because the error introduced by the picture-change effect leads to an overestimation of the EFG, which lies in the order of magnitude of the relativistic corrections. For heavier elements a DKH(3,3) or even higher-order schemes can be regarded as an appropriate choice for performing scalar-relativistic calculations. Moreover, the choice of the nuclear charge distribution model affects the calculation of the electric field gradient with increased nuclear charge Z and should be considered, especially for heavy atoms. However, the errors introduced due to the incompleteness of standard basis set can be far larger than the corrections to the EFG provided by higher-order property transformations. Hence time and memory-consuming high-order corrections in case of a conventional DKH implementation are out of all proportion to the gain in

TABLE XI. Principal component of the diagonalized electric field gradient tensor (q_{zz}) in the hydrogen halides series HX (in a.u.) at the halogen nucleus compared to EFG values calculated by Neese *et al.* (Ref. 21), Malkin *et al.* (Ref. 20), and Visscher *et al.* (Ref. 30). Bond distances and basis sets are given for comparison. (FT)/(BT) refer to “forward transformation” and “back transformation,” respectively. The “basis” is the uncontracted basis set at the halogen atom and the bond distance (in bohrs) is denoted as d . All four-component DHF and CCSD(T) [denoted as 4-c-CCSD(T)] calculations were performed with a Gaussian nuclear charge distribution, while the DKH(2,2) results were obtained with a point-charge nucleus model.

	Neese <i>et al.</i>	Malkin <i>et al.</i>	Visscher <i>et al.</i>	This work
HF				
d	1.732 549	1.733	1.7328	1.732 549
Basis	23s/16p/3d/1f	9s/5p/1d	aug-cc-pVTZ	23s/17p/6d/4f
4-c-CCSD(T)	2.696	...
DHF	2.881	...	2.870	2.809 754
HF DKH(2,2)	2.879 9(BT) 2.880 1(FT)	2.963	...	2.809 265 (BT)
HCl				
d	2.408 502	2.409	2.409	2.408 502
Basis	26s/19p/3d/1f	11s/7p/2d	aug-cc-pVTZ	24s/19p/7d/5f
4-c-CCSD(T)	3.377	...
DHF	3.660	...	3.638	3.591 314
HF [DKH(2,2)]	3.656 1(BT) 3.658 7(FT)	3.803	...	3.590 205 (BT)
HBr				
d	2.672 946	2.673	2.673	2.672 946
Basis	29s/23p/16d/3f	15s/12p/7d/2f	23s/16p/12d/3f	30s/22p/14d/8f/3g
4-c-CCSD(T)	7.035	...
DHF	7.602	...	7.603	7.540 289
HF DKH(2,2)	7.536 5(BT) 7.599 8(FT)	7.560	...	7.536 201 (BT)
HI				
d	3.040 798	3.040	3.040	3.040 798
Basis	31s/26p/19d/3f	17s/13p/9d/2f	27s/21p/15d/4f	35s/28p/19d/8f/4g
4-c-CCSD(T)	10.751	...
DHF	11.679	...	11.658	11.623 332
HF DKH(2,2)	11.290 1(BT) 11.700 4(FT)	11.560	...	11.618 554 (BT)
HAt				
d	3.250 392	3.250 392
Basis	31s/27p/21d/15f	37s/32p/22d/15f/4g
4-c-CCSD(T)
DHF	25.976	25.979 844
HF DKH(2,2)	21.423 1(BT) 26.966 5(FT)	26.409 692 (BT)

accuracy. The choice of the parametrization scheme for the unitary matrices in the DKH approach does hardly affect the expectation value of the EFG, and has thus not to be considered when setting up a calculation. While the standard DKH(2,2) model is likely to perform well for most cases, we may recommend the DKH(4,3) model, which is still independent of the chosen parametrization, as valid for the whole of the Periodic Table. In conclusion, we should emphasize that the field-independent unitary transformation is the appropriate approach to match results from four-component first-order perturbation theory. In standard DKH calculations, however, one neglects all spin-dependent terms which then, of course, introduces additional sources of error.

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