

# Relativistic effects on Sternheimer shieldings and the polarizabilities of the electric-field gradient at the nucleus: HX (X = F, Cl, Br, I, At) and Br<sub>2</sub>

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## Abstract

We investigate the relativistic effects on the electric field gradient (EFG) at the nucleus, the generalized Sternheimer shielding constants, and the EFG polarizabilities using analytic quadratic response theory at the four-component Dirac–Hartree–Fock level of theory. Particular attention is paid to the basis set requirements for calculations at the four-component level of theory of these higher-order properties involving operators that probe both the near-nucleus and the outer regions of the electron density. Our results show that relativistic effects become non-negligible for the hydrogen halides starting with hydrogen bromide and the heavier members of the group 17 halides. Interestingly, the relativistic effects are much more pronounced for the heavy-atom in hydrogen bromide, being about 10% for most of the generalized EFG polarizabilities, than in the homonuclear diatomic molecule Br<sub>2</sub>, where relativistic effects in general are much less than 10%.

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## 1. Introduction

Intermolecular interactions remain a challenging and important subject in modern chemistry. Understanding these interactions will enable better understanding and rationalization of observed temperature and pressure dependencies of molecular properties, as

well as provide some insight into the mechanisms involved in solvation. Although some of this insight in general can be obtained from pressure studies and thereby from the virial coefficients of the system [1], it is in general difficult to design experiments where one can easily disentangle the effects of the intermolecular interactions from those arising from the electronic structure of the molecule itself.

One approach for obtaining detailed knowledge of intermolecular interactions has been the use of microwave spectroscopy [2], and in particular of

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the nuclear quadrupole coupling constants (NQCCs) [3] that can be observed in molecular species with quadrupolar nuclei. The microwave technique provides a unique testing ground for the study of intermolecular interactions, since it allows for a very accurate determination of molecular properties such as rotational constants, NQCCs, and spin–rotation constants for gaseous species. By observing the changes in these properties in weak van der Waals complexes, much insight into the nature of the intermolecular interactions—free of most other sources of complications—can be obtained.

Of particular interest here is the study of the effects of intermolecular interactions on the NQCCs—or equivalently on the electric field gradient (EFG) experienced at the nuclei, which can be combined with the NQCCs to yield the nuclear quadrupole moments [4,5]—in van der Waals complexes, a technique pioneered by Legon and coworkers [6–19]. Since the EFG at the nucleus depends only on the density of the molecular system (*vide infra*), any change to the ground state density of a molecule by a perturbing complexing molecule is easily reflected in the observed NQCC. Furthermore, the form of the NQCC operator also favors changes in the electronic structure close to the quadrupolar nucleus, and thus a clever design of the interacting molecules and the possible use of different interaction sites for the van der Waals complex may give a very complete picture of the effects of intermolecular interactions on the electronic structure of a molecule.

However, although the effects of the intermolecular interactions can easily be observed in the NQCCs or EFG at the nuclei, it is not necessarily obvious how to relate these changes to changes in the electronic structure or properties of the molecule itself and how this would affect the strength of the interaction. Assuming the interaction to be weak, and thus ignoring all possible overlap effects, intermolecular perturbation theory can often be a useful starting point. This means in our case expanding the EFG at the nucleus in terms of so-called generalized Sternheimer shielding constants [12,20–23]. As demonstrated by Legon, Fowler and coworkers [11,15], these quantities can be related to the parameters entering the Townes–Dailey model for charge flow in weak intermolecular complexes [24].

The subject of the interaction of electric fields with the EFG at the nucleus, based on the theory developed in Refs. [12,21–23], has been one of many subjects on which David Bishop has given seminal contributions [25,26]. We have also been active in this field, with studies of the EFG at the nuclei, Sternheimer (anti)shields, and EFG polarizabilities in some reference molecular systems (including HCl, which is also analyzed here) employing first multi-configurational self consistent field (MCSCF) response [27] and, quite recently, a hierarchy of coupled cluster (CC) response models including the widely employed CC singles and doubles (CCSD) approach and also the highly accurate CC3 approximation [28]. Aspects such as the effect of both valence and core electron correlation, basis set requirements, and vibrational corrections have been addressed in some detail.

Many of the systems investigated by Legon and his coworkers concern complexes involving dihalogen molecules or hydrogen halides, since most of the isotopes of the halogens have a nuclear quadrupole moment. Many of these dihalogens or hydrogen halides contain quite heavy atoms [16], where one might expect relativistic effects to become important, in particular considering the fact that the NQCC probes the electronic structure close to the nuclei, where scalar relativistic effects are expected to be the largest [29,30].

Hydrogen halides and dihalogens are a favorite area for the study of relativistic effects on molecular properties. Bond lengths, harmonic frequencies, dissociation energies [31,32], dipole moments, electric dipole polarizabilities, and hyperpolarizabilities [33,34], and very recently also Raman scattering spectra [34] have been computed and discussed in recent years. Relativistic effects on the EFG at the nuclei have also been investigated recently by Visscher et al. [30], both at the four-component level of theory, as well as using more approximate relativistic models involving one- or two-component wave functions. In the latter case one can also expect that picture-change effects may become important, although recent studies into this question indicate that these effects are rather small [35]. The effect of relativity on the EFG and Sternheimer-type properties in the molecule BrCl was studied by Fowler and coworkers by employing a Douglas–Kroll ‘no-pair’ model [13]. However, to our knowledge there has not

been any systematic study of the relativistic effects on the Sternheimer (anti)shields and generalized EFG polarizabilities. In this work we rectify this situation by performing analytical four-component Dirac–Hartree–Fock (DHF) calculations of the first and second EFG shielding polarizabilities and Sternheimer shields using a recently developed quadratic response DHF code [36].

The remainder of this paper is divided into four sections. In Section 2, we present the definitions of the generalized Sternheimer shielding constants and EFG polarizabilities resulting from a perturbation expansion of the EFG. In Section 3 we briefly summarize the computational details of our study, before presenting the results in Section 4. In Section 5 we give some concluding remarks.

## 2. Theory

In the traceless form, the EFG at a nucleus  $P$  can be computed as an expectation value [22,23]

$$V_{\alpha\beta}^P = \langle \psi | \sum_i \frac{\{3(r_{i\alpha} - R_{P\alpha})(r_{i\beta} - R_{P\beta}) - |\mathbf{r}_i - \mathbf{R}_P|^2 \delta_{\alpha\beta}\}}{|\mathbf{r}_i - \mathbf{R}_P|^5} | \psi \rangle - \sum_{Q \neq P} Z_Q \frac{\{3(R_{Q\alpha} - R_{P\alpha})(R_{Q\beta} - R_{P\beta}) - |\mathbf{R}_Q - \mathbf{R}_P|^2 \delta_{\alpha\beta}\}}{|\mathbf{R}_Q - \mathbf{R}_P|^5}, \quad (1)$$

with the vectors  $\mathbf{r}_i$  and  $\mathbf{R}_Q$  denoting the positions of the  $i$ th electron and of the  $Q$ th nucleus, respectively. In a static, non-uniform electric field  $F$ , the EFG at the nucleus  $P$  can be expanded as (using Einstein summation over repeated indices and retaining explicitly only the terms of relevance to our discussion) [22]

$$V_{\alpha\beta}^P(F) = V_{\alpha\beta}^P + g_{\alpha\beta,\gamma}^P F_\gamma + \frac{1}{2} \epsilon_{\alpha\beta,\gamma\delta}^P F_\gamma F_\delta + \left[ \frac{1}{2} (\delta_{\alpha\delta} \delta_{\beta\gamma} + \delta_{\alpha\gamma} \delta_{\beta\delta}) + g_{\alpha\beta,\gamma\delta}^P \right] F_{\gamma\delta} + \dots \quad (2)$$

$V_{\alpha\beta}^P$  denotes the EFG at the nucleus  $P$  in the unperturbed molecule;  $F_\alpha$  is the  $\alpha$  component of the electric field vector and  $F_{\alpha\beta}$  the  $\alpha\beta$  component of the EFG defined with respect to a given origin. Eq. (2) has been generalized also to time-dependent

electric fields [22]. The tensors  $g_{\alpha\beta,\gamma}$  and  $g_{\alpha\beta,\gamma\delta}$ —often referred to as *generalized Sternheimer shielding constants* since they were first discussed by Sternheimer in 1950 [20]—describe the main linear response of the EFG at the nucleus  $P$  to the electric field perturbation, whereas  $\epsilon_{\alpha\beta,\gamma\delta}$  [21] represents a contribution arising from a quadratic response and is an example of an *EFG (hyper)polarizability* [21]. The tensor  $g_{\alpha\beta,\gamma}^P$  is called *Sternheimer shielding* or *antishielding*, depending on its positive or negative sign, respectively.

The generalized Sternheimer shielding constants, related to the linear response of the EFG to the electric field ( $g_{\alpha\beta,\gamma}^P$ ) and to the electric-field gradient ( $g_{\alpha\beta,\gamma\delta}^P$ ), can be written, in the notation and convention of Ref. [37], as

$$g_{\alpha\beta,\gamma}^P = \langle V_{\alpha\beta}^P; r_\gamma \rangle_0, \quad (3)$$

$$g_{\alpha\beta,\gamma\delta}^P = \frac{1}{3} \langle V_{\alpha\beta}^P; \Theta_{\gamma\delta} \rangle_0, \quad (4)$$

with

$$\Theta_{\alpha\beta} = -\frac{1}{2} \sum_i (3r_{i\alpha} r_{i\beta} - r_{i\gamma} r_{i\gamma} \delta_{\alpha\beta}), \quad (5)$$

denoting the electric quadrupole moment operator in its traceless form. The EFG electric dipole polarizability tensor ( $\epsilon_{\alpha\beta,\gamma\delta}^P$ ) is analogously identified as

$$\epsilon_{\alpha\beta,\gamma\delta}^P = \langle V_{\alpha\beta}^P; r_\gamma, r_\delta \rangle_{0,0}. \quad (6)$$

The symmetry properties of the different tensors have been discussed in detail in Refs. [22,23], where also higher-order members of the perturbation expansion Eq. (2) have been analyzed. For linear molecules the number of independent components of the tensors for nuclei in a  $C_{\infty v}$  site symmetry reduces to one for  $V_{\alpha\beta}^P$ , two for  $g_{\alpha\beta,\gamma}^P$ , three for  $g_{\alpha\beta,\gamma\delta}^P$  and four for  $\epsilon_{\alpha\beta,\gamma\delta}^P$ . A choice of independent components which has been

also adopted elsewhere [22,23,27,28] is

$$\begin{aligned} &V_{zz}^P, \\ &g_{zz,z}^P, g_{xz,x}^P, \\ &g_{zz,zz}^P, g_{xy,xy}^P, g_{xz,xz}^P, \\ &\epsilon_{zz,z,z}^P, \epsilon_{xx,x,x}^P, \epsilon_{xz,x,z}^P, \epsilon_{xy,x,y}^P. \end{aligned} \quad (7)$$

To ease the discussion, these tensors are most often discussed in terms of their rotational averages defined as

$$\bar{g}^P = \frac{1}{5} g_{\alpha\beta,\alpha\beta}^P, \quad \bar{\epsilon}^P = \frac{2}{15} \epsilon_{\alpha\beta,\alpha\beta}^P, \quad (8)$$

and which in our case, due to the relationships between non-zero components [22], reduce to

$$\bar{g}^P = \frac{1}{10} (3g_{zz,zz}^P + 8g_{xy,xy}^P + 8g_{xz,xz}^P), \quad (9)$$

$$\bar{\epsilon}^P = \frac{2}{15} (\epsilon_{zz,z,z}^P + 2\epsilon_{xx,x,x}^P + 4\epsilon_{xz,x,z}^P + 2\epsilon_{xy,x,y}^P). \quad (10)$$

In Eq. (2), the response functions that involve multipole operators carry as usual a dependence on the origin of the electric field [22,23]. As is customary [22,23,27,28], we here place the origin at the nucleus of interest when calculating the  $g_{\alpha\beta,\gamma\delta}^P$  tensor components and the corresponding averages. As the origin moves from  $\mathbf{O}$  to  $\mathbf{O}' = \mathbf{O} + \mathbf{R}$ , the change in the response is given by

$$\begin{aligned} g_{\alpha\beta,\gamma\delta}^P(\mathbf{O}') &= g_{\alpha\beta,\gamma\delta}^P(\mathbf{O}) - \frac{1}{2} g_{\alpha\beta,\gamma}^P R_\delta - \frac{1}{2} g_{\alpha\beta,\delta}^P R_\gamma \\ &\quad + \frac{1}{3} \delta_{\alpha\beta} g_{\alpha\beta,\sigma}^P R_\sigma. \end{aligned} \quad (11)$$

All our results are in atomic units. Conversion factors to SI units are given in Ref. [27,38].

### 3. Computational details

All calculations employ electron uncorrelated, single determinant, reference states with molecular orbitals that are either real scalar functions or complex four-component spinors. The two approximations are known as the Hartree–Fock (HF) and the DHF approximation, respectively. The nuclei are represented by Gaussian charge distributions and the electron–electron interactions are represented by the instantaneous Coulomb interaction in

the non-relativistic as well as the relativistic case. A discussion of the relativistic Dirac–Coulomb Hamiltonian may be found in Refs. [39,40].

The molecular properties are calculated by means of the linear and quadratic response functions which collect terms to a field dependent quantum mechanical expectation value that are of first- and second-order in the perturbation, respectively. These response functions include only the responses of the electrons in the systems and thus leave out effects of for instance nuclear relaxation in the presence of the external fields, another field of theoretical research pioneered by David Bishop [41–44]. In other words, our calculations refer to a field-dependent EFG ( $V^P(F)$ ) in Eq. (2) evaluated at a fixed nuclear configuration.

The choice of basis set in a relativistic calculation is a difficult one. It is clearly inappropriate to use basis set contractions based on non-relativistic optimizations in this case due to the relativistic contractions and de-contractions of atomic orbitals. Basis sets of systematically improved quality have yet to be developed for four-component property calculations. Due to this fact we have been lead to use uncontracted basis sets based on the exponents taken from the work of Sadlej and co-workers [45–49]. These basis sets are further augmented by diffuse and polarizing functions using a geometric sequence in order to meet the demands for calculations of the properties of interest, see footnotes to the tables for details.

Molecular structures for the monohydrides are optimized at the density functional theory level using the hybrid B3LYP exchange correlation functional and relativistic effective core potentials [33]. The optimized internuclear distances are (in Å): HF 0.9312, HCl 1.3011, HBr 1.4334, HI 1.6347, and HAt 1.7279. For Br<sub>2</sub> the chosen internuclear distance was 2.281 Å, corresponding to the experimental datum of Ref. [50].

For all calculations we have used a locally modified version of the Dirac program [36,51,52].

### 4. Results and discussion

We first discuss the convergence of the molecular properties with respect to the basis set. In Tables 1 and 2 we present an investigation of the basis set dependence for the properties of HI. The reference

Table 1  
HI. Sternheimer shieldings, antishieldings and EFG polarizabilities

	Hartree–Fock							Dirac–Hartree–Fock						
	Unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>	+3spdf <sup>c</sup>	+sp <sup>d</sup>	+/2sp <sup>e</sup>	+3spdf <sup>f</sup> /sp <sup>f</sup>	Unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>	+3spdf <sup>c</sup>	+sp <sup>d</sup>	+/2sp <sup>e</sup>	+3spdf <sup>f</sup> /sp <sup>f</sup>
$V_{zz}^H$	0.17286	−0.00007	−0.00004	−0.00004	0.00001	0.00002	−0.00002	0.16554	−0.00007	−0.00003	−0.00003	0.00001	0.00002	−0.00001
$g_{zz,z}^H$	0.6807	−0.0012	−0.0016	−0.0016	0.0000	0.0000	−0.0017	0.6884	−0.0013	−0.0018	−0.0018	0.0000	0.0000	−0.0019
$g_{xz,x}^H$	0.2051	0.0029	0.0019	0.0019	0.0001	0.0001	0.0020	0.2034	0.0033	0.0024	0.0024	0.0000	0.0001	0.0024
$g_{zz,zz}^H$	0.8034	−0.0080	−0.0173	−0.0175	−0.0004	−0.0004	−0.0169	0.8267	−0.0072	−0.0164	−0.0166	−0.0004	−0.0004	−0.0162
$g_{xy,xy}^H$	−0.0094	0.0969	0.1208	0.1208	0.0000	0.0001	0.1207	−0.0069	0.0964	0.1204	0.1204	0.0000	0.0001	0.1203
$g_{xz,xz}^H$	0.2963	−0.0505	−0.0328	−0.0328	−0.0002	−0.0002	−0.0328	0.3011	−0.0497	−0.0328	−0.0328	−0.0002	−0.0002	−0.0329
$\bar{g}^H$	0.4705	0.0347	0.0653	0.0652	−0.0003	−0.0003	0.0653	0.4834	0.0352	0.0652	0.0651	−0.0002	−0.0002	0.0651
$\epsilon_{zz,zz}^H$	1.338	0.031	0.068	0.069	−0.012	−0.016	0.059	1.210	0.030	0.067	0.069	−0.013	−0.017	0.059
$\epsilon_{xx,xx}^H$	0.340	−0.267	−0.422	−0.423	−0.008	−0.009	−0.419	0.284	−0.269	−0.426	−0.427	−0.008	−0.009	−0.424
$\epsilon_{xz,x,z}^H$	−2.887	0.002	−0.102	−0.102	0.004	0.005	−0.102	−3.060	−0.003	−0.101	−0.100	0.004	0.005	−0.101
$\epsilon_{xy,xy}^H$	0.146	−0.278	−0.447	−0.447	−0.002	−0.002	−0.446	0.110	−0.279	−0.450	−0.450	−0.002	−0.002	−0.449
$\epsilon^H$	−1.232	−0.140	−0.277	−0.277	−0.002	−0.003	−0.277	−1.366	−0.144	−0.278	−0.279	−0.002	−0.003	−0.279
$V_{zz}^I$	9.9957	−0.0170	−0.0177	−0.0176	0.0004	0.0003	−0.0173	11.805	−0.019	−0.020	−0.020	0.000	0.000	−0.020
$g_{zz,z}^I$	68.589	0.033	0.040	0.040	0.006	0.004	0.046	81.417	0.051	0.060	0.060	0.007	0.004	0.066
$g_{xz,x}^I$	−13.592	0.069	0.082	0.082	−0.008	−0.009	0.079	−8.755	0.064	0.078	0.078	−0.008	−0.012	0.076
$g_{zz,zz}^I$	−125.566	0.928	1.235	1.237	−0.039	−0.048	1.191	−146.891	1.015	1.360	1.362	−0.042	−0.051	1.312
$g_{xy,xy}^I$	−85.103	1.294	1.390	1.395	−0.022	−0.024	1.351	−98.020	1.396	1.502	1.507	−0.023	−0.026	1.459
$g_{xz,xz}^I$	−26.220	−0.637	−0.868	−0.862	0.038	0.049	−0.873	−30.921	−0.769	−1.031	−1.025	0.042	0.053	−1.037
$\bar{g}^I$	−126.728	0.804	0.788	0.797	0.001	0.005	0.739	−147.221	0.806	0.784	0.795	0.003	0.007	0.731
$\epsilon_{zz,zz}^I$	35.38	0.08	−1.67	−1.66	0.16	0.17	−1.56	20.38	0.20	−1.83	−1.81	0.17	0.17	−1.69
$\epsilon_{xx,xx}^I$	1554.72	−4.82	−4.66	−4.55	1.59	1.93	−3.30	1867.30	−4.89	−4.71	−4.58	1.78	2.15	−3.19
$\epsilon_{xz,x,z}^I$	447.55	0.58	2.14	2.12	−0.52	−0.65	2.16	560.85	0.61	2.35	2.32	−0.57	−0.73	2.36
$\epsilon_{xy,xy}^I$	1020.10	−3.94	−4.07	−3.98	1.10	1.21	−3.21	1243.03	−4.05	−4.17	−4.07	1.24	1.37	−3.20
$\epsilon^I$	930.03	−2.01	−1.41	−1.37	0.46	0.51	−0.79	1131.26	−2.03	−1.36	−1.31	0.52	0.57	−0.67

Use of the augmented uncontracted Sadlej basis. For both Hartree–Fock and Dirac–Hartree–Fock we report the results in the uncontracted Sadlej basis sets and the differences with respect to these results when augmenting the set.

<sup>a</sup> Uncontracted Sadlej set plus 1s,1p,1d and 1f (geometrical sequence) diffuse functions on the heavy atom.

<sup>b</sup> Uncontracted Sadlej set plus 2s,2p,2d and 2f (geometrical sequence) diffuse functions on the heavy atom.

<sup>c</sup> Uncontracted Sadlej set plus 3s,3p,3d and 3f (geometrical sequence) diffuse functions on the heavy atom.

<sup>d</sup> Uncontracted Sadlej set plus 1s,1p (geometrical sequence) diffuse functions on hydrogen.

<sup>e</sup> Uncontracted Sadlej set plus 2s,2p (geometrical sequence) diffuse functions on hydrogen.

<sup>f</sup> The set of footnote c plus 1s and 1p (geometrical sequence) diffuse functions on hydrogen.

Table 2

HI. Sternheimer shieldings, antishieldings and EFG polarizabilities

	Hartree–Fock				Dirac–Hartree–Fock			
	Unc. Sadlej	+t(spdf) <sup>a</sup>	+t(sp) <sup>b</sup>	+t(spdf) + t(sp) <sup>c</sup>	Unc. Sadlej	+t(spdf) <sup>a</sup>	+t(sp) <sup>b</sup>	+t(spdf) + t(sp) <sup>c</sup>
$V_{zz}^H$	0.17286	−0.00020	−0.00015	−0.00036	0.16554	−0.00020	−0.00014	−0.00035
$g_{zz,z}^H$	0.6807	−0.0003	0.0052	0.0050	0.6884	−0.0003	0.0050	0.0047
$g_{xz,x}^H$	0.2051	0.0000	0.0009	0.0010	0.2034	0.0000	0.0008	0.0009
$g_{zz,zz}^H$	0.8034	0.0001	0.0043	0.0044	0.8267	0.0001	0.0043	0.0044
$g_{xy,xy}^H$	−0.0094	0.0001	−0.0008	−0.0007	−0.0069	0.0002	−0.0008	−0.0006
$g_{xz,xz}^H$	0.2963	−0.0004	0.0004	0.0001	0.3011	−0.0004	0.0003	0.0000
$g^H$	0.4705	−0.0002	0.0009	0.0008	0.4834	−0.0001	0.0009	0.0008
$e_{zz,zz}^H$	1.338	0.003	−0.040	−0.037	1.210	0.002	−0.041	−0.039
$e_{xz,x,x}^H$	0.340	0.000	−0.010	−0.010	0.284	−0.001	−0.010	−0.011
$e_{xz,x,z}^H$	−2.887	0.000	−0.043	−0.043	−3.060	0.000	−0.043	−0.043
$e_{xy,x,y}^H$	0.146	0.000	−0.007	−0.007	0.110	−0.001	−0.007	−0.008
$V_{zz}^I$	−1.232	0.000	−0.033	−0.033	−1.366	0.000	−0.033	−0.033
$e^I$	9.9957	0.0032	0.0015	0.0046	11.8054	0.1201	0.0018	0.1217
$g_{zz,z}^I$	68.589	0.438	0.001	0.437	81.417	1.221	0.000	1.219
$g_{xz,x}^I$	−13.592	0.045	−0.003	0.042	−8.755	−0.020	−0.003	−0.023
$g_{zz,zz}^I$	−125.566	0.099	0.002	0.101	−146.891	−1.232	0.003	−1.229
$g_{xy,xy}^I$	−85.103	0.184	−0.002	0.182	−98.020	−0.804	−0.002	−0.807
$g_{xz,xz}^I$	−26.220	0.280	0.004	0.286	−30.921	−0.022	0.006	−0.015
$g^I$	−126.728	0.401	0.002	0.404	−147.221	−1.031	0.004	−1.026
$e_{zz,zz}^I$	35.38	0.17	0.04	0.18	20.38	−0.43	0.03	−0.43
$e_{xz,x,x}^I$	1554.72	5.22	0.15	5.43	1867.30	23.50	0.17	23.73
$e_{xz,x,z}^I$	447.55	1.77	−0.03	1.74	560.85	7.29	−0.05	7.23
$e_{xy,x,y}^I$	1020.10	3.38	0.11	3.47	1243.03	16.07	0.12	16.17
$e^I$	930.03	3.26	0.06	3.32	1131.26	14.38	0.06	14.44

Use of the augmented tight–function uncontracted Sadlej basis. For both Hartree–Fock and Dirac–Hartree–Fock we report the results in the uncontracted Sadlej basis sets and the differences with respect to these results when augmenting the set with tight functions.

<sup>a</sup> Uncontracted Sadlej set plus 1s,1p,1d and 1f (geometrical sequence) tight functions on the heavy atom.

<sup>b</sup> Uncontracted Sadlej set plus 1s,1p (geometrical sequence) tight functions on Hydrogen.

<sup>c</sup> Uncontracted Sadlej set plus both 1s,1p (geometrical sequence) tight functions on the Hydrogen and 1s, 1p, 1d and 1f (geometrical sequence) tight on the heavy atom.

uncontracted polarized basis set by Sadlej contains diffuse s, p, and d-functions and polarizing (but not diffuse) f-functions, giving a total size of [19s15p12d4f]. It is seen from Table 1 that the larger electron density in the vicinity of the heavy atom results in an EFG at iodine that is almost two orders of magnitude larger than the EFG at the position of the proton (9.9957 and 0.17286 a.u., respectively). Similar differences in magnitude are observed for the induced EFGs.

With respects to improvements in the basis set, based on the physical argument that the single electron of the hydrogen does not contribute much to the electric field at the other nucleus, we do not expect that an improved description of the electron of

the hydrogen should have any significant effect on the EFG at the position of the heavy atom. A comparison of the results obtained with the use of the uncontracted basis set (denoted by ‘unc. Sadlej’) to those obtained with the doubly augmented hydrogen basis set (denoted by ‘+ /2sp’) confirms our intuitive reasoning both at the non-relativistic level as well as at the relativistic four-component level of theory; we observe discrepancies no greater than 0.3% (the largest discrepancy observed for  $e_{zz,zz}^I$ ). The situation for the EFG at the hydrogen nucleus is not much different, and this may, from the physical argument advocated above, be a bit counterintuitive. The results are also in this case quite stable with respects to improvements in the hydrogen basis set. However,

there are examples of greater discrepancies such as the component  $\epsilon_{zz,z}^H$  which is lowered by about 1%.

If we turn to the basis set of the heavy atom we may expect larger basis set effects, since, as described above, the main contribution to the EFG and the induced EFG come from the electrons of the heavy atom. The diffuse electron density might contribute significantly to the EFG at the hydrogen nucleus. Indeed, large differences between results obtained with various basis sets can be seen in Table 1 for the generalized Sternheimer shielding  $g_{\alpha\beta,\delta\gamma}$  and the EFG polarizability  $\epsilon_{\alpha\beta,\delta\gamma}$  at the hydrogen nucleus. A fair convergence with respect to the basis set on the heavy atom is achieved only with at least two sets of additional diffuse basis functions. This observation holds both at the non-relativistic and the relativistic level of theory.

The effect that additional tight basis functions have on the properties of hydrogen iodide can be discussed with reference to Table 2, where the results obtained with the uncontracted polarized basis set by Sadlej are compared to those given by sets augmented (i) with an extra tight function on the heavy atom, (ii) with an extra tight function on the hydrogen atom, and (iii) with both extra tight functions. For iodine, the effect of tight functions is stronger in the relativistic case than in the non-relativistic calculations. This is understandable, since we are augmenting a basis set optimized with respect to non-relativistic electron densities, and therefore not allowing for an equally adequate description of decontracted relativistic orbitals. For the hydrogen atom, the effect of tight functions is of the same order of magnitude at the HF and the DHF level. As can be expected, extra tight

Table 3  
HF. Sternheimer shieldings, antishieldings and EFG polarizabilities

	Hartree–Fock			Dirac–Hartree–Fock		
	unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>	unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>
$V_{zz}^H$	0.50748	0.50748	0.50748	0.50706	0.50706	0.50706
$g_{zz,z}^H$	0.7562	0.7563	0.7564	0.7572	0.7574	0.7575
$g_{xz,x}^H$	0.1917	0.1919	0.1918	0.1917	0.1919	0.1918
$g_{yz,y}^H$	0.4646	0.4639	0.4643	0.4656	0.4648	0.4653
$g_{xy,xy}^H$	0.0311	0.0310	0.0309	0.0311	0.0309	0.0309
$g_{xz,xz}^H$	0.2224	0.2226	0.2227	0.2227	0.2229	0.2230
$g_{yz,yz}^H$	0.3422	0.3421	0.3422	0.3427	0.3425	0.3427
$\epsilon_{zz,z}^H$	2.685	2.687	2.686	2.690	2.692	2.690
$\epsilon_{xz,x}^H$	−0.474	−0.474	−0.475	−0.476	−0.476	−0.477
$\epsilon_{yz,y}^H$	−1.308	−1.312	−1.313	−1.312	−1.317	−1.317
$\epsilon_{xy,xy}^H$	−0.161	−0.161	−0.161	−0.162	−0.162	−0.162
$\epsilon_{xx,xx}^H$	−0.509	−0.511	−0.512	−0.511	−0.513	−0.514
$V_{zz}^F$	2.89315	2.89358	2.89359	2.90161	2.90204	2.90205
$G_{zz,z}^F$	8.8014	8.8020	8.8030	8.8479	8.8485	8.8495
$g_{xz,x}^F$	1.6261	1.6268	1.6265	1.6526	1.6532	1.6530
$g_{yz,y}^F$	−10.8953	−10.8990	−10.8989	−10.9304	−10.9341	−10.9340
$g_{xy,xy}^F$	−6.1170	−6.1207	−6.1197	−6.1339	−6.1376	−6.1366
$g_{xz,xz}^F$	−5.7986	−5.8047	−5.8047	−5.8154	−5.8215	−5.8215
$g_{yz,yz}^F$	−12.8011	−12.8100	−12.8091	−12.8386	−12.8475	−12.8467
$\epsilon_{zz,z}^F$	52.917	52.896	52.896	53.133	53.113	53.113
$\epsilon_{xz,x}^F$	60.564	60.633	60.649	60.923	60.992	61.008
$\epsilon_{yz,y}^F$	39.453	39.532	39.537	39.690	39.770	39.774
$\epsilon_{xy,xy}^F$	43.016	43.073	43.085	43.277	43.334	43.345
$\epsilon_{xx,xx}^F$	55.719	55.792	55.802	56.039	56.112	56.122

<sup>a</sup> Uncontracted Sadlej set plus 1s,1p and 1d (geometrical sequence) diffuse functions on the heavy atom and 1s, 1p on the hydrogen.

<sup>b</sup> Uncontracted Sadlej set plus 2s,2p and 2d (geometrical sequence) diffuse functions on the heavy atom. No extra functions on hydrogen.



functions on a given nucleus affect the properties of that nucleus to a non-negligible extent, whereas they are of little influence for the properties of the other nucleus. The largest differences are observed for the EFG polarizabilities, where the addition of an extra tight function on iodine changes  $\bar{\epsilon}^I$  by  $\approx 1.2\%$ , whereas adding a tight function to the set centered on hydrogen increases (in absolute value)  $\bar{\epsilon}^H$  by  $\approx 2.4\%$ .

The conclusion of the basis set analysis is therefore that the doubly augmented basis set on the heavy atoms (denoted by ‘+ 2spdf’) can be considered to be adequate for the determination of the Sternheimer shieldings and EFG polarizabilities to within an accuracy of a few percent at the uncorrelated level.

Let us now turn to the effects of relativity on the EFGs, Sternheimer shieldings, and EFG polarizabilities. Considering first the hydrogen fluoride

molecule, for which the results are collected in Table 3, we observe that the relativistic effects are overall negligible, and also that the results show very little dependence on the choice of basis set, both at the HF and the DHF levels of theory. An interesting observation to make is that although the absolute values of the relativistic corrections increase going from the EFG at fluorine, to the generalized Sternheimer shieldings and to the EFG polarizability, the relative corrections introduced by relativity remain approximately constant at about 0.5%. As we will see, this constancy of the relative relativistic corrections to the properties—irrespective of their order of interaction—appear to be a rather general feature for these properties, indicating that the relativistic effects mainly affect the EFG at the nucleus, and that they are carried through from this property to all the higher-order responses. We note,

Table 4  
HCl. Sternheimer shieldings, antishieldings and EFG polarizabilities

	Hartree–Fock			Dirac–Hartree–Fock		
	unc. Sadlej	+ spdf <sup>a</sup>	+ 2spdf <sup>b</sup>	unc. Sadlej	+ spdf <sup>a</sup>	+ 2spdf <sup>b</sup>
$V_{zz}^H$	0.27979	0.27979	0.27979	0.27898	0.27897	0.27897
$g_{zz,z}^H$	0.7093	0.7088	0.7085	0.7111	0.7106	0.7103
$g_{xz,x}^H$	0.2362	0.2362	0.2375	0.2361	0.2361	0.2374
$g_{zz,zz}^H$	0.5693	0.5700	0.5692	0.5721	0.5728	0.5719
$g_{xy,xy}^H$	–0.0014	–0.0014	–0.0011	–0.0015	–0.0015	–0.0013
$g_{xz,xz}^H$	0.3314	0.3319	0.3347	0.3321	0.3326	0.3354
$g^H$	0.4348	0.4354	0.4376	0.4361	0.4367	0.4389
$\epsilon_{zz,zz}^H$	2.324	2.312	2.307	2.327	2.315	2.309
$\epsilon_{xz,x,x}^H$	0.051	0.051	0.052	0.050	0.050	0.052
$\epsilon_{xz,xz}^H$	–2.288	–2.295	–2.306	–2.303	–2.311	–2.322
$\epsilon_{xy,x,y}^H$	0.036	0.036	0.031	0.036	0.035	0.031
$\epsilon^H$	–0.887	–0.893	–0.900	–0.895	–0.901	–0.909
$V_{zz}^{Cl}$	3.7258	3.7260	3.7254	3.7736	3.7738	3.7731
$G_{zz,z}^{Cl}$	18.644	18.645	18.609	18.954	18.955	18.918
$g_{xz,x}^{Cl}$	–0.574	–0.572	–0.560	–0.446	–0.444	–0.428
$g_{zz,zz}^{Cl}$	–28.926	–28.912	–28.950	–29.316	–29.302	–29.341
$g_{xy,xy}^{Cl}$	–18.593	–18.588	–18.594	–18.815	–18.810	–18.815
$g_{xz,xz}^{Cl}$	–11.168	–11.172	–11.154	–11.296	–11.300	–11.280
$g^{Cl}$	–32.487	–32.482	–32.483	–32.883	–32.878	–32.878
$\epsilon_{zz,zz}^{Cl}$	66.30	66.02	65.85	67.11	66.83	66.67
$\epsilon_{xz,x,x}^{Cl}$	272.34	272.23	273.11	277.39	277.28	278.18
$\epsilon_{xz,xz}^{Cl}$	111.01	111.12	111.08	113.24	113.35	113.31
$\epsilon_{xy,x,y}^{Cl}$	184.66	184.60	183.91	188.26	188.21	187.50
$\epsilon^{Cl}$	189.91	189.89	189.89	193.51	193.49	193.50

<sup>a</sup> Uncontracted Sadlej set plus 1s, 1p, 1d and 1f (geometrical sequence) diffuse functions on the heavy atom and 1s, 1p on the hydrogen.

<sup>b</sup> Uncontracted Sadlej set plus 2s, 2p, 2d and 2f (geometrical sequence) diffuse functions on the heavy atom. No extra functions on hydrogen.



however, that a slightly different behavior of the relativistic corrections to the EFG properties at the hydrogen nucleus can in general be observed (vide infra).

Although the relativistic effects are beginning to become noticeable for the heavy nucleus in HCl (Table 4), they are still a rather modest 2%. As for HF, the relative change in the various properties are almost identical. Although these changes may be important for instance in calculations aimed at determining the nuclear quadrupole moments [53, 54], the effect of relativity still remains so small for HCl that it can be safely neglected for studies of intermolecular interactions using microwave spectroscopy. No significant effects of relativity is observed for the hydrogen nucleus in HCl.

As we proceed to HBr, for which the results are collected in Table 5, we see that the relativistic effects

become significant and non-negligible, amounting on average to 5–10% for the bromine nucleus. Some components of the Sternheimer shieldings are, however, exceptionally strongly affected by the relativistic effects, such as  $g_{xz,x}^{\text{Br}}$ , which is reduced by more than a factor of two, although the reduction is fairly small in absolute terms. We also notice that this component does not contribute to the rotational averages of the generalized Sternheimer shieldings. Although the relativistic effects still are fairly small for the hydrogen nucleus—being in general less than a percent of the total correction— $\epsilon^{\text{H}}$  experiences for instance a relativistic correction of about 4%. The effects observed for HBr become even more evident in hydrogen iodide, where the relativistic corrections become almost 20% for the iodine nucleus. One rather interesting observation that can be drawn from the results collected for this molecule in Table 6 is that

Table 5  
HBr. Sternheimer shieldings, antishieldings and EFG polarizabilities

	Hartree–Fock			Dirac–Hartree–Fock		
	unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>	unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>
$V_{zz}^{\text{H}}$	0.23434	0.23420	0.23372	0.23000	0.22987	0.22940
$g_{zz,z}^{\text{H}}$	0.7249	0.7244	0.7239	0.7304	0.7299	0.7295
$g_{xz,x}^{\text{H}}$	0.2158	0.2161	0.2162	0.2152	0.2155	0.2154
$g_{zz,zz}^{\text{H}}$	0.6841	0.6839	0.6831	0.6952	0.6950	0.6943
$g_{xy,xy}^{\text{H}}$	−0.0132	−0.0131	−0.0129	−0.0128	−0.0127	−0.0125
$g_{xz,xz}^{\text{H}}$	0.3280	0.3284	0.3285	0.3299	0.3304	0.3305
$g^{\text{H}}$	0.4570	0.4574	0.4574	0.4623	0.4627	0.4627
$\epsilon_{zz,z,z}^{\text{H}}$	1.862	1.863	1.870	1.856	1.857	1.865
$\epsilon_{xx,x,x}^{\text{H}}$	0.197	0.196	0.195	0.180	0.179	0.180
$\epsilon_{xz,x,z}^{\text{H}}$	−2.632	−2.634	−2.633	−2.692	−2.694	−2.695
$\epsilon_{xy,x,y}^{\text{H}}$	0.099	0.097	0.096	0.090	0.088	0.087
$\epsilon^{\text{H}}$	−1.077	−1.079	−1.078	−1.116	−1.118	−1.118
$V_{zz}^{\text{Br}}$	7.2824	7.2856	7.2973	7.7868	7.7900	7.8021
$G_{zz,z}^{\text{Br}}$	42.141	42.159	42.223	45.486	45.506	45.577
$g_{xz,x}^{\text{Br}}$	−2.499	−2.488	−2.465	−1.135	−1.122	−1.085
$g_{zz,zz}^{\text{Br}}$	−70.899	−70.731	−70.838	−75.669	−75.489	−75.613
$g_{xy,xy}^{\text{Br}}$	−46.238	−46.169	−46.181	−48.934	−48.857	−48.883
$g_{xz,xz}^{\text{Br}}$	−22.561	−22.647	−22.648	−23.942	−24.030	−24.030
$g^{\text{Br}}$	−76.309	−76.272	−76.315	−81.001	−80.956	−81.014
$\epsilon_{zz,z,z}^{\text{Br}}$	109.42	107.61	108.45	115.33	113.43	114.31
$\epsilon_{xx,x,x}^{\text{Br}}$	755.08	752.79	753.14	817.42	814.93	815.78
$\epsilon_{xz,x,z}^{\text{Br}}$	269.69	270.83	270.87	295.25	296.43	296.62
$\epsilon_{xy,x,y}^{\text{Br}}$	507.38	506.22	506.53	551.88	550.58	551.19
$\epsilon^{\text{Br}}$	495.08	494.53	494.84	537.99	537.36	537.97

<sup>a</sup> Uncontracted Sadlej set plus 1s,1p,1d and 1f (geometrical sequence) diffuse functions on the heavy atom and 1s, 1p on the hydrogen.

<sup>b</sup> Uncontracted Sadlej set plus 2s,2p,2d and 2f (geometrical sequence) diffuse functions on the heavy atom. No extra functions on hydrogen.

Table 6

HI. Sternheimer shieldings, antishieldings and EFG polarizabilities

	Hartree–Fock			Dirac–Hartree–Fock		
	unc. Sadlej	+ spdf <sup>a</sup>	+ 2spdf <sup>b</sup>	unc. Sadlej	+ spdf <sup>a</sup>	+ 2spdf <sup>b</sup>
$V_{zz}^H$	0.17286	0.17282	0.17282	0.16554	0.16551	0.16550
$g_{zz,z}^H$	0.6807	0.6797	0.6790	0.6884	0.6873	0.6866
$g_{xz,x}^H$	0.2051	0.2080	0.2070	0.2034	0.2067	0.2057
$g_{zz,zz}^H$	0.8034	0.7947	0.7861	0.8267	0.8188	0.8103
$g_{xy,xy}^H$	−0.0094	0.0874	0.1114	−0.0069	0.0895	0.1135
$g_{xz,xz}^H$	0.2963	0.2458	0.2635	0.3011	0.2514	0.2683
$g^H$	0.4705	0.5050	0.5358	0.4834	0.5184	0.5485
$e_{zz,zz,z}^H$	1.338	1.359	1.406	1.210	1.229	1.277
$e_{xx,x,x,x}^H$	0.340	0.075	−0.082	0.284	0.018	−0.142
$e_{xz,x,z}^H$	−2.887	−2.883	−2.990	−3.060	−3.061	−3.161
$e_{xy,x,y}^H$	0.146	−0.132	−0.302	0.110	−0.168	−0.340
$e^H$	−1.232	−1.372	−1.509	−1.366	−1.509	−1.644
$V_{zz}^I$	9.9957	9.9791	9.9779	11.8054	11.7866	11.7854
$G_{zz,z}^I$	68.589	68.630	68.628	81.417	81.476	81.477
$g_{xz,x}^I$	−13.592	−13.529	−13.510	−8.755	−8.697	−8.677
$g_{zz,zz}^I$	−125.566	−124.695	−124.331	−146.891	−145.938	−145.531
$g_{xy,xy}^I$	−85.103	−83.852	−83.713	−98.020	−96.672	−96.519
$g_{xz,xz}^I$	−26.220	−26.846	−27.087	−30.921	−31.679	−31.952
$g^I$	−126.728	−125.967	−125.940	−147.221	−146.462	−146.436
$e_{zz,zz,z}^I$	35.38	35.62	33.70	20.38	20.77	18.56
$e_{xx,x,x,x}^I$	1554.72	1551.88	1550.07	1867.30	1864.62	1862.59
$e_{xz,x,z}^I$	447.55	448.02	449.69	560.85	561.32	563.20
$e_{xy,x,y}^I$	1020.10	1017.37	1016.03	1243.03	1240.33	1238.86
$e^I$	930.03	928.83	928.62	1131.26	1130.13	1129.90

<sup>a</sup> Uncontracted Sadlej set plus 1s,1p,1d and 1f (geometrical sequence) diffuse functions on the heavy atom and 1s, 1p on the hydrogen.<sup>b</sup> Uncontracted Sadlej set plus 2s,2p,2d and 2f (geometrical sequence) diffuse functions on the heavy atom. No extra functions on hydrogen.

due to relativistic effects,  $\epsilon_{zz,zz,z}^I$  is reduced to approximately half of its non-relativistic value at the four-component level of theory. Not only is this change significantly larger both in relative and absolute terms compared to the lighter members of the hydrogen halide series, but relativistic effects lead to a *decrease* in the value of this component for hydrogen iodide. This is a rather surprising result, since we can observe from the results for HAt in Table 7 that the same component is significantly increased by relativity also for the heavier member of the hydrogen halide series investigated here.

The relativistic effects become non-negligible in hydrogen iodide also for the hydrogen nucleus. Here we start to observe another interesting trend: the effects of relativity on the EFG at the nucleus and the generalized Sternheimer shielding constants are in

general much smaller than the effects on the EFG polarizability  $\epsilon_{\alpha\beta,\alpha,\beta}^H$ . This should be an effect caused by changes to the excited state energy spectrum caused by relativity. Such an explanation is corroborated by the findings of a recent study of the relativistic effects on the electric (hyper)polarizabilities of the same series of molecules [33], in which only very small relativistic effects were observed for the linear polarizabilities, but significantly larger effects were observed for the first-order hyperpolarizabilities. In the sum-over-states expressions for the linear and quadratic response functions [37], we observe that whereas the linear response function only contains transition moments from the ground to the excited states, the quadratic response functions involve also transition moments between excited states. Relativistic effects thus appear to have

Table 7

HAt. Sternheimer shieldings, antishieldings and EFG polarizabilities

	Hartree–Fock			Dirac–Hartree–Fock		
	unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>	unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>
$V_{zz}^H$	0.17651	0.17420	0.15795	0.15686	0.15468	0.13983
$g_{zz,z}^H$	0.6937	0.6915	0.6704	0.6995	0.6984	0.6839
$g_{xz,x}^H$	0.1879	0.1907	0.1920	0.1740	0.1776	0.1822
$g_{zz,zz}^H$	0.8225	0.8244	0.8541	0.8702	0.8706	0.9139
$g_{xy,xy}^H$	–0.0325	–0.0315	–0.0083	–0.0122	–0.0113	0.0114
$g_{xz,xz}^H$	0.3089	0.3115	0.2708	0.3229	0.3267	0.2900
$\bar{g}^H$	0.4679	0.4713	0.4662	0.5097	0.5134	0.5153
$\epsilon_{zz,z,z}^H$	0.316	0.375	0.726	–1.221	–1.166	–0.657
$\epsilon_{xx,x,x}^H$	0.538	0.534	0.456	0.279	0.267	0.205
$\epsilon_{xz,x,z}^H$	–2.993	–2.981	–3.031	–3.702	–3.690	–3.757
$\epsilon_{xy,x,y}^H$	0.231	0.233	0.188	–0.033	–0.033	–0.067
$\bar{\epsilon}^H$	–1.349	–1.335	–1.348	–2.071	–2.061	–2.055
$V_{zz}^{At}$	15.759	15.708	15.566	25.583	25.500	25.317
$G_{zz,z}^{At}$	116.11	116.09	116.10	173.58	173.62	174.07
$g_{xz,x}^{At}$	–28.81	–28.63	–28.34	7.25	7.52	7.61
$g_{zz,zz}^{At}$	–223.95	–223.43	–220.82	–320.69	–320.68	–318.81
$g_{xy,xy}^{At}$	–155.85	–156.06	–153.52	–239.23	–239.26	–236.45
$g_{xz,xz}^{At}$	–34.30	–33.11	–32.68	–57.57	–56.28	–57.02
$\bar{g}^{At}$	–219.30	–218.37	–215.20	–333.65	–332.63	–330.42
$\epsilon_{zz,z,z}^{At}$	–70.9	–71.7	–72.3	–673.8	–666.5	–657.3
$\epsilon_{xx,x,x}^{At}$	3010.1	3021.0	2992.8	5268.2	5266.0	5230.3
$\epsilon_{xz,x,z}^{At}$	774.3	769.3	764.3	1481.4	1470.5	1463.2
$\epsilon_{xy,x,y}^{At}$	1956.3	1966.0	1948.4	3579.8	3582.1	3558.8
$\bar{\epsilon}^{At}$	1727.9	1730.6	1715.6	3059.7	3054.9	3036.5

<sup>a</sup> Uncontracted Sadlej set plus 1s,1p,1d and 1f (geometrical sequence) diffuse functions on the heavy atom and 1s, 1p on the hydrogen.<sup>b</sup> Uncontracted Sadlej set plus 2s,2p,2d and 2f (geometrical sequence) diffuse functions on the heavy atom. No extra functions on hydrogen.

a greater relative influence on the separation between the excited states than on their separation from the ground electronic state.

This analysis is further accentuated for HAt, see Table 7. The effect is made especially visible in Fig. 1, where we note that the relativistic effects on the EFG polarizabilities at the hydrogen nucleus are now almost as large as for the EFG properties at the astatine nucleus, whereas the relative relativistic changes to the EFG and to the generalized Sternheimer shieldings at the hydrogen nucleus are almost an order of magnitude smaller than for the EFG polarizabilities. For the astatine nucleus, the effects of relativity on the electronic structure close to the nucleus leads to large changes in the EFG properties of the nucleus. However, the enhancement due to relativity of the EFG polarizability as compared to the EFG and generalized Sternheimer shieldings are also

visible for this heavy nucleus, although significantly less clearly than for the hydrogen nucleus (Fig. 1).

Let us finally discuss a very different system from the hydrogen halides, namely the bromine molecule. This system is important in microwave studies of weak intermolecular forces involving the NQCCs of the bromine atom, since the symmetry allows one to study the changes in the electronic structure at two nuclei that are identical in the isolated molecule, but become inequivalent as the molecule is involved in the formation of a complex. Indeed, the simple Townes–Daily model [24] predicts that the changes in the NQCCs as the molecule forms a complex will be of equal magnitude but oppositely directed for the two nuclei, a prediction largely confirmed by theoretical calculations [15].

Intuitively, one might expect similar or possibly larger relativistic effects in this homonuclear

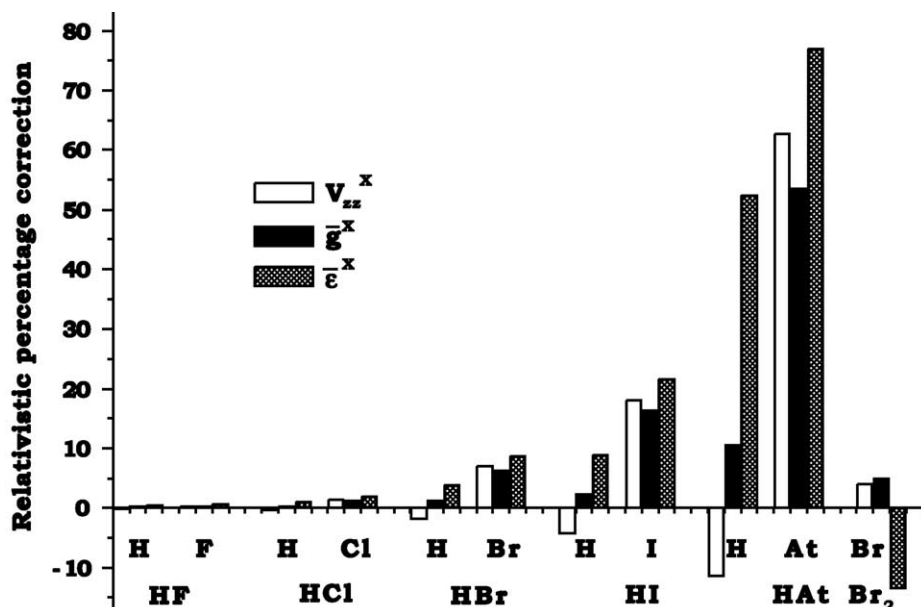


Fig. 1. The relative changes in  $V_{zz}^X$ ,  $g_{zz}^X$ , and  $\epsilon^X$  when going from the Hartree–Fock to the Dirac–Hartree–Fock level of theory

diatomic compared to the corresponding hydrogen halide. However, as seen from our results in Table 8, the relativistic effects for the bromine nucleus are actually smaller than what is observed in hydrogen bromide, the changes caused by relativity being about 3–5%. Larger changes can however be observed for some of the components of the EFG polarizability.

## 5. Summary and conclusions

We have presented the first study of relativistic effects on generalized Sternheimer shielding constants and EFG polarizabilities for the hydrogen halide series as well as for the bromine molecule. We have used analytic quadratic response theory at the four-component DHF level of theory.

Table 8  
Br<sub>2</sub>. Sternheimer shieldings, antishieldings and EFG polarizabilities

	Hartree–Fock			Dirac–Hartree–Fock		
	unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>	unc. Sadlej	+spdf <sup>a</sup>	+2spdf <sup>b</sup>
$V_{zz}^{\text{Br}}$	1.81115	1.81095	1.81093	1.88286	1.88267	1.88258
$g_{zz,z}^{\text{Br}}$	0.7531	0.7562	0.7494	0.7542	0.7572	0.7504
$g_{xz,x}^{\text{Br}}$	0.4585	0.4590	0.4559	0.4985	0.4990	0.4961
$g_{zz,zz}^{\text{Br}}$	–3.7030	–3.7075	–3.6977	–3.8182	–3.8225	–3.8123
$g_{xy,xy}^{\text{Br}}$	–2.7957	–2.7955	–2.7962	–2.9361	–2.9359	–2.9366
$g_{xz,xz}^{\text{Br}}$	–0.4467	–0.4241	–0.4574	–0.4895	–0.4669	–0.5004
$g_{zz}^{\text{Br}}$	–3.7048	–3.6879	–3.7122	–3.8859	–3.8690	–3.8933
$\epsilon_{zz,zz}^{\text{Br}}$	0.751	0.751	0.751	0.811	0.811	0.811
$\epsilon_{xx,xx}^{\text{Br}}$	0.801	0.799	0.810	0.853	0.851	0.862
$\epsilon_{xz,xz}^{\text{Br}}$	–1.227	–1.308	–1.302	–1.232	–1.312	–1.307
$\epsilon_{xy,xy}^{\text{Br}}$	0.594	0.595	0.592	0.634	0.634	0.632
$\epsilon^{\text{Br}}$	–0.182	–0.226	–0.220	–0.153	–0.196	–0.191

<sup>a</sup> Uncontracted Sadlej set plus 1s,1p,1d and 1f (geometrical sequence) diffuse functions on Bromine.

<sup>b</sup> Uncontracted Sadlej set plus 2s,2p,2d and 2f (geometrical sequence) diffuse functions on Bromine.

The effects of relativity are found to be significant for hydrogen halides containing bromine or heavier members of group 17, and they cannot in general be neglected if a proper account of the electronic structure of these molecules—as described by the EFG at the nuclei and by its electric field and EFG polarizabilities—is of interest. Indeed, for the heaviest member of the group 17 halides analyzed in this work, HAt, the relativistic effects lead to an increase in the EFG properties by 60–80%. Interestingly, the relativistic effects on the heavy-atom nucleus appear to be stronger in hydrogen bromide than in the homonuclear diatomic analogue Br<sub>2</sub> where they are about half of those observed for HBr.

An interesting observation arising from this study is that the behavior of the generalized Sternheimer shieldings and of the EFG polarizabilities for the hydrogen nucleus follows to a large extent that observed previously for electric (hyper)polarizabilities. This has been rationalized in terms of the effects of relativity on the excited states of these molecules, whereas the changes due to relativistic effects close to the hydrogen nucleus are, as expected, very small.

Our results indicate, in agreement with previous Douglas–Kroll investigations [13], that relativistic effects may be substantial and non-negligible for these higher-order EFG response functions, and need to be taken into account when comparing theoretical and experimental observations for electronic structure changes induced by molecular complexation when studied using NQCCs measured in microwave spectroscopy and modelled through the higher-order EFG response functions.

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