Electron correlation and nuclear charge dependence of parity-violating properties in open-shell diatomic molecules

T.A. Isaev and R. Berger

Clemens-Schöpf Institute, TU Darmstadt,
Petersenstr. 22, 64287 Darmstadt, Germany

(Dated: May 2, 2014)

Abstract

The scaling of nuclear spin-dependent parity violating effects with increasing nuclear charge $Z$ is discussed in two series of isovalent open-shell diatomic molecules. The parameter $W_a$ characterising the strength of parity violation in diatomic molecules is calculated in the framework of the zeroth-order regular approximation (ZORA) and found to be in good agreement with the $R(Z)Z^k$ scaling law derived for atoms in which $R(Z)$ represents a relativistic enhancement factor. The influence of electron correlation is studied on the molecular level, with spin-polarisation effects being conveniently accounted for by a previously established approximate relation between the hyperfine coupling tensor and $W_a$. For high accuracy predictions of parity violating effects in radium fluoride the necessity for systematically improvable correlation calculations is emphasised.
INTRODUCTION

Molecular properties depending strongly on the behaviour of the electronic wavefunction in the vicinity of the nuclei display a pronounced dependence on the nuclear charge \( Z \). This is known for a long time and often employed in atomic physics to obtain qualitative estimates (see e.g. Ref. [1]). For systems with more complicated electronic structure, in particular for molecules bearing nuclei with various \( Z \) values, a simple \( Z \)-scaling of such molecular properties is not a priori guaranteed, as molecular properties are also depending on the specific nuclear arrangement, which could in principle hamper a direct comparison (see e.g. discussion in Ref. [2]). Establishing general scaling laws also for complex molecules would present a great advantage, as scaling laws can be used for inexpensive order-of-magnitude estimates. Quantum chemical calculations allow to scrutinise proposed scaling laws for a given property and investigate the form of the dependence on \( Z \). This has been applied in some detail in Ref. [3] for nuclear spin-independent parity violating effects in chiral molecules containing atoms from various rows of the periodic table (see Refs. [4–6] for reviews on molecular parity violation). In the present article we are calculating nuclear spin-dependent parity violation interaction in alkaline earth metal monofluorides (Mg-Ra)F (group II monofluorides) and (Zn-Cn)H (group XII monohydrides) as an example for open-shell systems. Results and conclusions presented below were reported by the authors on several workshops and conferences during the years 2010 and 2011 and explicitly foreshadowed in Ref. [7]. A recent paper took up the idea that we reported on those occasions, which motivates us to present here our results and to comment, in particular, on the inclusion of electron correlation effects in molecular systems.

NUCLEAR SPIN-DEPENDENT PARITY VIOLATION

One of the properties that is predicted to depend heavily on \( Z \) is the nuclear spin-dependent parity-odd (\( P \)-odd) interaction (\( \mathcal{NPD} – \mathcal{PV} \)), whose effective operator looks in a four-component (relativistic) framework like [8]:

\[
\hat{h}_{\text{pv}}^I = \frac{G_F}{\sqrt{2}} \sum_{A,i} k_{A,A} \vec{\alpha} \cdot \vec{I}_A \rho_A(r_i),
\]

where \( G_F \) is Fermi’s constant of the weak interaction, \( k_{A,A} \) is an effective parameter describing \( \mathcal{NPD} – \mathcal{PV} \) interactions for nucleus \( A \) (caused both by the nuclear anapole moment and
by weak electron-nucleon interactions, see Ref. [9]). $I_A$ and $\rho_A$ are the spin and nuclear spin density distribution of nucleus $A$, respectively. For $\tilde{\alpha}$ one uses

$$
\tilde{\alpha} = \begin{pmatrix}
0 & \vec{\sigma} \\
\vec{\sigma} & 0
\end{pmatrix}
$$

with $\vec{\sigma}$ being a vector of the $2 \times 2$ Pauli spin matrices $\sigma_x$, $\sigma_y$, $\sigma_z$ and with $\mathbf{0}$ being a $2 \times 2$ zero matrix. The anapole moment was proposed by Zeldovich [10, 11] quickly after the discovery of parity violation in processes mediated by the fundamental weak interaction. The nuclear anapole moment [12] has received great interest in atomic and molecular physics as it is caused by parity violating interaction within the nucleus, but should favourably be probed in atomic and molecular experiments. In atoms with stable nuclei, nuclear-spin independent terms caused by exchange of $Z^0$ bosons between nucleus and electrons typically dominate parity violating effects and often mask those effects depending on the nuclear spin that are significantly smaller. Thus, as of yet, only for one nucleus, namely $^{133}\text{Cs}$, nuclear spin-dependent parity violating effects could be determined in atomic experiments [13]. In linear open-shell molecules, the special electronic structure itself suppresses the contribution from nuclear spin-independent $P$-odd terms and offers, in principle, convenient access to nuclear-spin dependent $P$-odd contributions for a variety of nuclei, including those with an odd number of neutrons instead of an odd number of protons. A complementary route would be the detection of $NSD - PV$ in polyatomic chiral molecules by nuclear magnetic resonance techniques [14–23]. As of yet, however, molecular parity violation has not been detected, which underlines the particular need for identification of promising molecular candidate systems by theoretical means.

In open-shell diatomic molecules, the contribution from interactions in Eq. (1) to the effective molecular spin-rotational Hamiltonian can be parametrised by the term $W_a k_A \left[ \vec{\lambda} \times \vec{S}_{\text{eff}} \right] \cdot \vec{I}$ [24], a parity-violating contribution to the hyperfine coupling tensor, where $\vec{\lambda}$ is the unit vector pointing along the molecular axis, $\vec{S}_{\text{eff}}$ is the effective electron spin and $W_a$ is a single constant characterising the $P$-odd electron spin-nuclear spin coupling for a given nucleus with nuclear spin $\vec{I}$. In the basis of the degenerate molecular states $| \Omega \rangle$ and $|-\Omega \rangle$ ($\Omega$ is the projection of the total electronic momentum on the molecular axis coinciding with the $z$ axis) $W_a$ is approximately (see discussion below) proportional to the non-diagonal matrix
element of the operator in Eq. (1):

$$W_a = \frac{1}{k_A (\vec{\lambda} \times S_{\text{eff}})_{x,y}} \langle \Omega | \frac{\partial \hat{h}_{\text{pv}}}{\partial I} | -\Omega \rangle_{x,y},$$

(3)

where it was accounted for that $\vec{\lambda}$ has only a non-vanishing $z$-component. In contrast to $W_a$, components of the hyperfine coupling tensor $A$ can be computed also as diagonal matrix elements in the $|\Omega\rangle$ and $|-\Omega\rangle$ basis, which we will exploit below to estimate spin-polarisation effects on $W_a$.

To calculate $W_a$ we utilise a quasi-relativistic two-component zeroth-order regular approximation (ZORA) approach to electroweak quantum chemistry, which proved to perform well in calculations of the spin-independent $P$-odd energy differences for chiral compounds when compared to four-component treatment [23, 25, 26]. Details of the ZORA approach for one and multielectron cases can be found elsewhere [3, 25–27] and below we give only the final expression of $N_{SD-PV}$ terms in the ZORA approach in the self-consistent field (SCF) framework of Hartree–Fock–Coulomb and Kohn–Sham–Coulomb. The derivation of these terms together with common consideration of the parity violation problem in open-shell polyatomic molecules can be found in Ref. [28].

**TABLE I: Parity violating terms in ZORA Hamiltonian.**

| Term Name | Expression |
|-----------|------------|
| $s_{\mu}^{(0)}$ | $\frac{1}{2} Q_A \{ \vec{\sigma} \cdot \vec{p}, \vec{\lambda} \cdot \vec{A}_\mu(\vec{r}) \}$ |
| $s_{\mu}^{(1)}$ | $\frac{1}{2} Q_A \{ e \vec{\sigma} \cdot \vec{A}_\mu(\vec{r}), \vec{\lambda} \cdot \vec{A}_\mu(\vec{r}) \}$ |
| $s_{\mu \nu + \mu}^{(1)}$ | $\frac{1}{2} k_{A,A} \{ \vec{\sigma} \cdot \vec{p}, \vec{\lambda} \cdot \vec{I}_\mu(\vec{r}), \vec{\lambda} \cdot \vec{A}_\mu(\vec{r}) \}$ |
| $s_{\mu \nu + \mu}^{(2)}$ | $\frac{1}{2} k_{A,A} \{ e \vec{\sigma} \cdot \vec{A}_\mu(\vec{r}), \vec{\lambda} \cdot \vec{I}_\mu(\vec{r}), \vec{\lambda} \cdot \vec{A}_\mu(\vec{r}) \}$ |

In Table I, $Q_A$ is the weak charge of nucleus $A$, $Q_A = N_A - (1 - 4 \sin^2 \theta_W)Z_A$, where $N_A$ is the number of neutrons in nucleus $A$, $Z_A$ the nuclear charge, $\sin^2 \theta_W$ the Weinberg parameter, for which we employ the numerical value $\sin^2 \theta_W = 0.2319$, and $\vec{A}_\mu$ is the magnetic vector potential from the point-like nuclear magnetic moments $\vec{\mu}_A = h\gamma_A \vec{I}_A$ with $\vec{A}_\mu(\vec{r}) = (\mu_0/4\pi) \sum_{A} \vec{\mu}_A \times (\vec{r} - \vec{R}_A)/(|\vec{r} - \vec{R}_A|)^3$, $\gamma_A$ being the gyromagnetic ratio and $\mu_0$ being the vacuum permeability. The symbol $e$ denotes the elementary charge (charge of a positron), $m_e$ the mass of the electron, $\hbar = h/(2\pi)$ the reduced Planck constant and $\{x, y\} = xy + yx$ the anticommutator. The ZORA factor $\tilde{\omega}$ is also used, $\tilde{\omega} = 1/\left(2m_e - \tilde{V}/c^2\right)$, where $\tilde{V}$ is the model potential (with additional damping [29]) proposed by van Wülken [30], which alleviates the gauge-dependence of ZORA. To calculate $W_a$, the terms of the ZORA Hamiltonian which
are first order in $\vec{I}$ have to be accounted for, namely

$$z_{hf}^{(0,1)} + z_{sd}^{(1,1)} = \sum_A \frac{G_F}{2\sqrt{2}} \left( Q_A \{ e \vec{\sigma} \cdot \vec{A}_p(r), \frac{\tilde{\omega}}{c} \rho_N(r) \} + 2k_{A,A} \{ \vec{\sigma} \cdot \vec{p}, \frac{\tilde{\omega}}{c} \vec{\sigma} \cdot \vec{I}_A \rho_A(r) \} \right).$$  

(4)

An advantage of the ZORA approach is that one of the terms coupling the $\mathcal{P}$-even hyperfine interaction with the $\mathcal{P}$-odd nuclear spin-independent weak interaction (the first term in Eq. (4)) naturally appears after the transition from a four-component to a two-component framework. In our calculations we neglect this term together with accompanying response terms, however, as in atomic calculations it was shown to give corrections on the order of a few percent for heavy atoms.

The $Z$-dependent scaling behaviour of the matrix element of the nuclear spin-independent $\mathcal{P}$-odd interaction was first obtained in [1] and, for nuclear spin-dependent $\mathcal{P}$-odd interaction, in [8]:

$$\langle s_1/2 | \hat{h}_{pv} | p_{1/2} \rangle \sim Z^2 R(Z) \quad \text{(5)}$$

$$R(Z) = \frac{4}{3} \frac{2 \sqrt{1 - (Z\alpha)^2} + 1}{\Gamma(2 \sqrt{1 - (Z\alpha)^2} + 1)^2} \left( \frac{a_0}{2ZA^{1/3} \cdot r_0} \right)^{(2-2\sqrt{1-(Z\alpha)^2})}, \quad \text{(6)}$$

where $a_0$ is the Bohr radius, $\alpha$ the fine structure constant and $r_0 = 1.2$ fm a nuclear size parameter. The analytic form of the relativistic enhancement factor $R(Z)$ was obtained from a model treatment, such that $R(Z)$ can either be tabulated and used in approximate treatments or be calculated directly in atomic relativistic vs. non-relativistic calculations. As is shown in Fig. [11] on a double logarithmic scale, $R(Z)$ depends heavily on $Z$ (here the analytic form was used). The proposed scaling behaviour for atomic systems can subsequently be studied in explicit calculations for molecular systems as we will show below.

**CALCULATION DETAILS AND RESULTS**

The results of our study are summarised in Table III. We calculated the absolute value of the parameter $W_a$ for the ground $\Sigma_{1/2}$ states of the alkaline earth metal monofluorides ($\text{Mg-Ra}F$) and group XII monohydrides ($\text{Zn-Cn}H$). In addition, we report results for $\text{YbF}$ for comparison with other approaches. In all our computations we used for the alkaline earth metal atoms a basis set of uncontracted Gaussians with the exponent coefficients (EC)
FIG. 1: Relativistic enhancement factor $R(Z)$ as a function of the nuclear charge $Z$ shown on a double logarithmic scale.

composed as an even-tempered series. This sequence was generated according to $\alpha_i = \gamma \beta^{N-i}$, $i = 1, \ldots, N$. For s,p-functions $\beta$ was taken equal to 2.0 for basis sets centred on the heavier alkaline earth metal nuclei (Sr, Ba, Ra) as well as on ytterbium and $(5/2)^{1/25} \times 10^{2/5} \approx 2.6$ for the group XII nuclei (Zn, Cd, Hg, Cn) and the lighter group II nuclei (Mg, Ca). For all sets of d-functions and f-functions $\beta = (5/2)^{1/25} \times 10^{2/5} \approx 2.6$ was chosen. The tighter basis sets for s- and p-functions were employed, because the $P$-odd operator mixes mainly s- and p-waves on the heavy nucleus. For the ECs and the resulting basis set dimensions, see Table II. On the fluorine atom in all cases an uncontracted ANO basis set of triple-zeta quality [31] and on hydrogen an s,p-subset of an uncontracted correlation-consistent basis set of quadruple-zeta quality [31] were used with the ECs given explicitly in Table II.

The nuclear density was modelled by a spherical Gaussian distribution $\rho(R) = \rho_0 e^{-\frac{3}{\pi} R^2}$, where $\xi$ is the mean root square radius of the corresponding nucleus computed according to the empirical formula $\xi = (0.836A^{1/3} + 0.57) \text{ fm} = (1.5798A^{1/3} + 1.077) 10^{-5} a_0$, where $A$ is the given mass number of the respective isotope. Within this work we employed mass numbers corresponding to the standard relative atomic mass rounded to the nearest integer, namely
$^1$H, $^{19}$F, $^{24}$Mg, $^{40}$Ca, $^{65}$Zn, $^{88}$Sr, $^{112}$Cd, $^{137}$Ba and $^{201}$Hg. The radium nucleus with atomic mass number 225 was taken and the copernicium nucleus with atomic mass number 284. As computed $W_a$ values do not depend too strongly on the atomic mass number (for $^{213}$RaF, $^{223}$RaF and $^{225}$RaF changes in $|W_a|$ were found on the order of a few Hz [7]), we report only one value for $|W_a|$, even though the specific isotope corresponding to the standard relative atomic mass may have a nuclear spin quantum number of $I = 0$. A modified version [23, 25, 26, 28] of the program package TURBOMOLE [32] was used for the complex generalised SCF (Hartree–Fock or Kohn–Sham) calculations. As spatial symmetry was not exploited, we also calculated the value of the projection $\Omega$ of the total electron angular momentum on the molecular axis. In the two-component generalised Hartree–Fock (GHF) calculations $\Omega = 0.5 \pm 10^{-3}$, in the two-component density functional theory (DFT) calculations within the generalised Kohn–Sham (GKS) framework $\Omega = 0.5 \pm 10^{-4}$. The value of $|W_a|$ was calculated according to Eq. (3). In the ZORA calculations $|\Omega\rangle$ and $|-\Omega\rangle$ are many-electron functions and the Löwdin formula [33] for calculations of the matrix elements between non-orthogonal one-determinantal (OD) functions was applied:

$$\langle \Psi_1 | \hat{W} | \Psi_2 \rangle = \sum_k \sum_l \langle \tilde{\psi}_k | \hat{w} | \psi_l \rangle D(k|l),$$

(7)

where $|\Psi_1\rangle$ and $|\Psi_2\rangle$ can be either orthonormalised or non-orthonormalised OD functions, $\langle \tilde{\psi}_l | \hat{w} | \psi_k \rangle$ is the matrix element of the one-electron operator $\hat{w}$ between members of the two sets of molecular spin-orbitals with $\langle \tilde{\psi}_i | \tilde{\psi}_j \rangle = \delta_{ij}, \langle \psi_i | \psi_j \rangle = \delta_{ij}$, that are occupied in the OD wavefunctions $\Psi_1$ and $\Psi_2$, respectively, and $D(k|l)$ is the minor of $S$ of rank $n - 1$ ($n$ is the number of electrons) which is obtained from the original OD wavefunctions by crossing out in the overlap matrix $S$ (that has the matrix elements $s_{kl} = \langle \tilde{\psi}_k | \psi_l \rangle$) the $k$-th row and $l$-th column with subsequently forming the determinant of the resulting submatrix. We note in passing that in the direct application of the present complex GHF/GKS approach only the absolute value of $W_a$ is immediately accessible, whereas determination of its sign requires an additional symmetrisation procedure, which is for the purpose of the present study, however, not required.

In calculations of the (Mg-Ra)F row two different exchange-correlation (XC) functionals were used in a generalised Kohn–Sham DFT framework: 1) the local density approximation LDA and 2) the Becke 3-parameter hybrid functional containing Becke’s exchange functional together with Lee-Yang-Parr’s (LYP) correlation functional B3LYP. This latter hybrid XC
functional, which contains an admixture of about 20% non-local Fock exchange, was used in the form employed in the Gaussian 03 program package \cite{34} with an approximation (VWN3) to the correlation functional of the homogeneous electron gas. The equilibrium distance for all diatomic molecules was taken from experimental data, except for RaF, where the distance was obtained in \cite{4} from four-component relativistic coupled cluster calculations in the Fock space (FS-RCC-SD) and CnH, where we used the bond length obtained in the two-component GHF framework.

One can see from Table I two main trends when accounting for correlations by DFT: 1) systematic increase in the value of $|W_a|$ from B3LYP to LDA XC functionals and 2) relative decrease in correlation contributions from 33% for MgF to about 12% for RaF. Both these dependences are consistent with previous observations and anticipations. The former trend was observed for parity violating energy differences between enantiomers of chiral molecules \cite{26}, the latter is also not surprising as the main contribution in this class of heavy-atom open-shell diatomic molecules is expected to arise from spin-polarisation effects, which cannot (fully) be accounted for by direct calculation of non-diagonal matrix elements between complex GHF wavefunctions at least for $\mathcal{T}$-odd operators, for which thus results of essentially paired GHF quality are obtained. A discussion of the influence of symmetry breaking for OD wavefunctions on matrix elements of different operators can be found in Ref. \cite{35}. Finally we plotted on a double logarithmic scale (Fig. 2) instead of $|W_a|$ the values of $|W_a/R(Z)|$ obtained on the GHF level against $Z$, as we have argued previously \cite{3, 7} that one should correct for the relativistic enhancement factors when attempting to extract $Z^k$ scaling laws from quasi-relativistic and relativistic calculations. Fitting of the points in Fig. 2 by a linear function gives a slope equal 1.75 for (Mg-Ra)F and 2.68 for (Zn-Cn)H which is indeed close to the scaling factor for $N_{SD-\mathcal{P}V}$ interaction matrix element.

Our current results have been mainly confirmed by recent four-component calculations of $W_a$ in the series of diatomic radicals (Mg-Ra)F \cite{36}. The authors of \cite{36} have also observed the $Z^k$ scaling (also with $k$ close to 2) for $W_a/R(Z)$. Besides performing Dirac–Hartree–Fock–Coulomb and Dirac–Kohn–Sham calculations in a paired GHF and paired GKS framework, which can not account for core-polarisation effects, the authors of Ref. \cite{36} employed some approximate atom based schemes to roughly estimate part of electron correlation effects via scaling factors. Our treatment, however, is based on the complex GHF/GKS framework and thus allows to capture part of the electron correlation effects directly within
the molecular calculations (see also below), whereas some contributions are not included due to calculation via off-diagonal matrix elements between time-reversed wavefunctions. Our direct DFT-based estimates for $|W_a|$ in MgF, CaF and SrF can reasonably well be reproduced by the indirect procedure employed in Ref. [36]. For BaF and RaF we find, however, only a modest electron correlation contribution on the DFT level of theory whereas in Ref. [36] significant changes are reported for RaF. Even without the subsequent attempts to account for further electron correlation effects, in Ref. [36] DHF and DKS values for $|W_a|$ in RaF differ by more than 15% (and by about 30% for LDA XC functional) and in BaF only by 2%. As it was mentioned, the latter result (for BaF) is actually in agreement with the earlier calculations in Ref. [37], in which the authors found that the main contribution comes from the spin-polarisation effects, though further accounting for electron correlation gives minor contribution. We note in passing that in Ref. [36] the data are mixed up for the calculations without accounting for spin-polarisation (SCF in notations of the authors of Ref. [37], $W_a = 111$ Hz), with the accounting for spin-polarisation (SCF-EO, $W_a = 181$ Hz) and electron correlation + spin-polarisation (RASSCF-EO, $W_a = 175$ Hz). In Ref. [36] Faegri’s energy-optimised basis sets were employed, which required augmenting with additional functions to be used in calculations of properties that depend on the behaviour of the electronic wavefunction near the nucleus. To check the influence of the basis set choice, we performed calculations with two additional basis sets (see below for basis set specifications) for Ra together with an uncontracted aug-cc-pVTZ basis set 11s6p3d2f on fluorine nucleus. The first Ra basis set (Basis S in Table III) was Faegri’s uncontracted basis set 25s21p14d9f recommended for relativistic calculations [38] and another one (Basis L) was a large even-tempered basis set 36s33p22d15f generated according to recommendation of the article [39]. The result of the calculations with these basis sets clearly shows that with the extension of the basis set from Basis S to Basis L the difference between GHF and GKS results of essentially paired generalised SCF quality decreases from 38% to 20% for LDA XC functional, getting close to the values reported by us ($\approx 12\%$) for the basis sets we used herein and in Ref. [7]. This provides some indication that the pronounced electron correlation effects reported in Ref. [36] for the DFT framework might primarily be caused by the special choice of basis set therein.

To estimate spin-polarisation contributions within the GHF approach we use scaling relations from the semiempirical molecular model by Kozlov [40], which is known to reproduce
ab initio parameters of the $P, T$-odd spin-rotational Hamiltonian for ground states of BaF, YbF and some other molecules with an accuracy of 10-15%. For this model some simple (approximate) relations can be established between the parameters of the electronic structure, required for calculations of $W_a$ of the linear diatomic molecules employed in the current work in their $\Sigma_{1/2}$ ground states, and the hyperfine coupling tensor terms $A_{\text{iso}}$ (isotropic) and $A_d$ (dipole). For our purpose and the current set of molecules, however, more important is that the relation between $W_a$ obtained for different approximations (e.g. complex and paired generalised Hartree–Fock wavefunctions, cGHF and pGHF, respectively) is approximately equal to the ratio between the square root of the products of $A_{\text{iso}}$ and $A_d$ (see equations (33),(34) and (10) in Ref. [40]; assuming that signs of $A_{\text{iso}}, A_d$ are identical):

$$
\frac{W_a^{\text{cGHF}}}{W_a^{\text{pGHF}}} \approx \left[ \frac{(A_{\text{iso}} \cdot A_d)^{\text{cGHF}}}{(A_{\text{iso}} \cdot A_d)^{\text{pGHF}}} \right]^{1/2}.
$$

(8)

Thus, by calculating the hyperfine tensors with accounting for spin-polarisation (in our case as diagonal matrix elements within the complex GHF scheme) and without accounting for it (as non-diagonal matrix elements, leading to results of essentially paired GHF quality) we can restore spin-polarisation contributions, which are expected to be most important for RaF. The results of this scaling are presented in Table IV. One can observe that for molecules with a valence electronic structure similar to RaF the relative deviation of our scaling for $W_a$ parameters is better than 10 % when judged from the corresponding RASSCF/EO results or about 10 % in comparison with the semiempirical estimates for HgH by Kozlov [40]. This finding is particularly encouraging for the identification of promising molecular candidates, although we expect the accuracy in general to be somewhat lower than implied by the present results. Thus, for reliable estimates of electron correlation and spin-polarisation effects on the value of $W_a$ (and other properties depending on the behaviour of the wavefunction near the nucleus) in RaF one has to employ high-order correlation calculations, for instance similar to those in Ref. [41]. It is also interesting to note that in the group XII monohydrides series the spin-polarisation contribution should suppress rather than enhance the $NSD – PV$ interaction, at least for the two heavy representatives reported in Table IV.

Finally, we emphasise that although the treatment of relativistic effects in the four- and two-component framework is different, deviations between results for $NSD – PV$ operators are not expected to be significantly larger than 3 % for the heavier nuclei (row 4–7) when judged on the basis of earlier calculations [23, 26], provided appropriate basis sets are used...
FIG. 2: Scaling of $|W_a/R(Z)|$ GHF values (in Hz) with $Z$ for the (Mg-Ra)F and (Zn-Cn)H series (orange line, blue dots and red line, green dots, respectively) on a double logarithmic scale. The slope of the lines is 1.75 for (Mg-Ra)F and 2.68 for (Zn-Cn)H, which implies a $R(Z)Z^k$ scaling law for $W_a$ with $k = 1.75$ and $k = 2.68$, respectively.
TABLE II: Basis sets parameters for ZORA HF/DFT calculations. Even-tempered basis sets of uncontracted Gaussians are given in the form $N_{bas}; l; (E_{C_{\text{max}}}; E_{C_{\text{min}}})$, where $N_{bas}$ is the number of Gaussians, $l$ is s, p, d or f and represents the angular momentum quantum numbers 0, 1, 2 or 3. $E_{C_{\text{max}}}$ and $E_{C_{\text{min}}}$ are the largest and smallest exponent coefficients, respectively.

| Mg  | Ca  | Sr, Ba, Yb | Ra  |
|-----|-----|------------|-----|
| 27; s; (500000000; 0.00769) | 27; s; (500000000; 0.00769) | 37; s; (2000000000; 0.0291) | 39; s; (2000000000; 0.00728) |
| 25; p; (191890027; 0.02000) | 25; p; (191890027; 0.02000) | 34; p; (500000000; 0.0582) | 34; p; (500000000; 0.0582) |
| 4; d; (3.750; 0.21336) | 13; d; (13300.758; 0.135789) | 14; d; (13300.758; 0.0521) | 14; d; (13300.758; 0.0521) |
| 9; f; (751.8368350; 0.3546) | 9; f; (751.8368350; 0.3546) |

| Zn, Cd, Hg, Cu |
|----------------|
| 27; s; (500000000; 0.0077) |
| 25; p; (191890027; 0.0200) |
| 14; d; (13300.758; 0.0521) |
| 8; f; (751.8368350; 0.9219352) |

| F ANO basis | H basis |
|-------------|---------|
| s | p | d | s | p |
| 103109.46 | 245.33029 | 5.000000 | 82.640 | 2.292000 |
| 15281.007 | 56.919005 | 1.750000 | 12.410 | 0.838000 |
| 3441.5392 | 17.604568 | 0.612500 | 2.8240 | 0.292000 |
| 967.09483 | 6.2749950 | 0.214375 | 0.7977 |
| 314.03534 | 2.4470300 | 0.080419 | 0.2581 |
| 113.44230 | 0.9950600 | 0.08989 |
| 44.644727 | 0.4039730 |
| 18.942874 | 0.1548100 |
| 8.5327430 | 0.0541840 |
| 3.9194010 |
| 1.5681570 |
| 0.6232900 |
| 0.2409610 |
| 0.0843010 |

12
TABLE III: Calculated $P$-odd parameter $|W_a|$ (in Hz) for open-shell diatomic molecules together with the charge number $Z$ of the heavy nucleus and the equilibrium distance $R_e$ employed.

|        | $Z$ | $R_e/a_0$ | $|W_a|$/Hz         |
|--------|-----|-----------|-------------------|
|        |     |           | GHF               | GKS/B3LYP | GKS/LDA |
| MgF    | 12  | 3.30      | 3.9               | 4.9       | 5.2     |
| CaF    | 20  | 3.71      | 8.0               | 9.2       | 9.5     |
| SrF    | 38  | 3.92      | $3.9 \times 10^1$ | $4.6 \times 10^1$ | $4.8 \times 10^1$ |
| BaF    | 56  | 4.07      | $1.11 \times 10^2$ | $1.19 \times 10^2$ | $1.25 \times 10^2$ |
| RaF    | 88  | 4.24      | $1.30 \times 10^3$ | $1.42 \times 10^3$ | $1.47 \times 10^3$ |
| RaF (Basis S) | 88 | 4.24      | $1.07 \times 10^3$ |           | $1.48 \times 10^3$ |
| RaF (Basis L) | 88 | 4.24      | $1.24 \times 10^3$ |           | $1.50 \times 10^3$ |
| ZnH    | 30  | 3.01      | $4.7 \times 10^1$  |
| CdH    | 48  | 3.36      | $2.23 \times 10^2$ |
| HgH    | 80  | 3.33      | $3.30 \times 10^3$ | c         |
| CnH    | 112 | 3.10      | $4.88 \times 10^4$ |

- a) In Ref. 7 111 Hz were obtained with a slightly different basis set.
- b) In Ref. 7 1.3 kHz were reported for a slightly different basis set.
- c) In Ref. 7 3.3 kHz were reported for a slightly smaller basis set.
TABLE IV: Calculated and scaled *ab initio* values for the parameter $|W_a|$ in BaF, YbF and RaF together with scaling factor $f = \left[ \frac{(A_{iso} - A_d)^{GHF}}{(A_{iso} - A_d)^{EO}} \right]^{1/2}$. Additional *ab initio* results and calculation methods are taken from the corresponding references. A bond length of 3.80 $a_0$ was used in the calculation for YbF.

|     | $|W_a|$/$\text{Hz}$ | Method | Ref. |
|-----|-------------------|--------|------|
|     | $\text{GHF}$ | $\text{Scaled}$ | $\text{ab initio}$ | $f$ |
| BaF | $1.11 \times 10^2$ | $1.9 \times 10^2$ | $1.81 \times 10^2$ | 1.68 | SCF/EO | [37] |
|     | | | $1.75 \times 10^2$ | $1.9 \times 10^2$ | RASSCF/EO | [37] |
| YbF | $4.65 \times 10^2$ | $6.1 \times 10^2$ | $6.34 \times 10^2$ | 1.31 | RASSCF/EO | [42] |
| RaF | $1.30 \times 10^3$ | $2.1 \times 10^3$ | | 1.65 |
| HgH | $3.30 \times 10^3$ | $2.0 \times 10^3$ | $3.1 \times 10^4$ | 0.63 |
| CnH | $4.88 \times 10^4$ | $3.1 \times 10^4$ | | 0.63 |

a) Semi-empirical estimate of Ref. [40] based on spectroscopic parameters of $^{199}\text{HgH}$ and $^{201}\text{HgH}$:

$W_a = 1800 \text{ Hz}$ and $W_a = 1940 \text{ Hz}$, respectively.
CONCLUSIONS

We have reported herein a numerical study on nuclear charge dependent scaling of molecular properties in open-shell diatomic molecules. After we have accounted for a relativistic enhancement factor $R(Z)$, which grows non-polynominally with the nuclear charge $Z$, we obtain an approximate $Z^2$ scaling behaviour for the nuclear spin-dependent parity violating parameter $W_a$ computed at the respective equilibrium structures. This term contributes to the effective spin-rotational Hamiltonian used for high-resolution studies which aim for the first detection of molecular parity violation. The present confirmation of a simple scaling law is excellent news as it allows for quick estimates of parity violating effects in a whole series of diatomic molecules. Within the complex generalised Kohn–Sham framework employed in this work, part of electron correlation effects on this molecular property can be accounted for, although some contributions are still missing. Spin-polarisation effects can approximately be included within a simple, but powerful molecular scaling scheme utilised previously for semi-empirical estimates. For high accuracy calculations, more sophisticated molecular electron correlation approaches are clearly needed, but given the present experimental status, the current approximate approaches allow to identify promising molecular candidates such as RaF, which was proposed in Ref. [7].

ACKNOWLEDGEMENT

We are indebted to Mikhail Kozlov and Sophie Nahrwold for discussions and are particularly thankful for numerous discussions at the 2010 ECT* workshop on “Violations of discrete symmetries in atoms and nuclei” in Trento. Financial support by the Volkswagen Foundation and computer time provided by the Center for Scientific Computing (CSC) Frankfurt are gratefully acknowledged.

* timur.isaev@tu-darmstadt.de
† robert.berger@tu-darmstadt.de

[1] M. A. Bouchiat and C. Bouchiat, J. Phys. (Paris) 35, 899 (1974).
[2] A. Bakasov, R. Berger, T.-K. Ha, and M. Quack, Int. J. Quantum Chem. 99, 393 (2004).
[3] R. Berger, J. Chem. Phys. 129, 154105 (2008).

[4] R. Berger, in Relativistic Electronic Structure Theory, Part: 2, Applications, edited by P. Schwerdtfeger (Elsevier, Netherlands, 2004), pp. 188–288.

[5] M. Quack and M. Willeke, Helv. Chim. Acta 86, 1641 (2003).

[6] J. Crassous, C. Chardonnet, T. Saue, and P. Schwerdtfeger, Org. Biomol. Chem. 3, 2218 (2005).

[7] T. A. Isaev, S. Hoekstra, and R. Berger, Phys. Rev. A 82, 052521 (2010).

[8] A. N. Moskalev, R. M. Ryndin, and I. B. Khriplovich, Uspekhi. Phys. 118, 409 (1976).

[9] V. V. Flambaum and I. B. Khriplovich, Phys. Lett. B 146, 367 (1984).

[10] B. Y. Zel'dovich, J. Exptl. Theoret. Phys. (U. S. S. R) 33, 1531 (1957).

[11] I. B. Zel'dovich, Sov. Phys. JETP 6, 1184 (1958).

[12] V. V. Flambaum and I. B. Khriplovich, Sov. Phys. JETP 52, 835 (1980).

[13] C. S. Wood and et al, Science 275, 1759 (1997).

[14] V. G. Gorshkov, M. G. Kozlov, and L. N. Labzowsky, Sov. Phys. JETP 55, 1042 (1982).

[15] A. L. Barra, J. B. Robert, and L. Wiesenfeld, Phys. Lett. A 115, 443 (1986).

[16] A. L. Barra, J. B. Robert, and L. Wiesenfeld, Europhys. Lett. 5, 217 (1988).

[17] A. L. Barra and J. B. Robert, Mol. Phys. 88, 875 (1996).

[18] G. Laubender and R. Berger, ChemPhysChem 4, 395 (2003).

[19] A. Soncini, F. Faglioni, and P. Lazzеретти, Phys. Rev. A 68, 033402 (2003).

[20] V. Weijo, P. Manininen, and J. Vaara, J. Chem. Phys. 123, 054501 (2005).

[21] G. Laubender and R. Berger, Phys. Rev. A 74, 032105 (2006).

[22] R. Bast, P. Schwerdtfeger, and T. Saue, J. Chem. Phys. 125, 064504 (2006).

[23] S. Nahrwold and R. Berger, J. Chem. Phys. 130, 214101 (2009).

[24] M. Kozlov and L. Labzowsky, J. Phys. B 28, 1933 (1995).

[25] R. Berger, N. Langermann, and C. van Wüllen, Phys. Rev. A 71, 042105 (2005).

[26] R. Berger and C. van Wüllen, J. Chem. Phys. 122, 134316 (2005).

[27] E. van Lenthe, E. J. Baerendas, and J. G. Snijders, J. Chem. Phys 101, 9783 (1994).

[28] T. A. Isaev, S. Nahrwold, and R. Berger (2012), to be published soon.

[29] W. Liu, C. van Wüllen, F. Wang, and L. Li, J. Chem. Phys. 116, 3626 (2002).

[30] C. van Wüllen, J. Chem. Phys. 109, 392 (1998).

[31] Https://bse.pnl.gov/bse/portal.
[32] R. Alrichs, M. Bär, M. Häser, H. Horn, and C. Köhnel, Chem. Phys. Lett. 162, 165 (1989).
[33] P.-O. Löwdin, Phys. Rev. 97, 1474 (1955).
[34] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
[35] T. A. Isaev and R. Berger (2012), to be published soon.
[36] A. Borschevsky, M. Ilias, V. A. Dzuba, K. Beloy, V. V. Flambaum, and P. Schwerdtfeger, Phys. Rev. A 85 (2012).
[37] M. G. Kozlov, A. V. Titov, N. S. Mosyagin, and P. V. Souchko, Phys. Rev. A 56, R3326 (1997).
[38] K. Faegri, http://folk.uio.no/knutf/bases/four/.
[39] K. Faegri, Chemical Physics 311, 25 (2005).
[40] M. G. Kozlov, Sov. Phys.–JETP 62, 1114 (1985).
[41] T. A. Isaev, A. N. Petrov, N. S. Mosyagin, A. V. Titov, E. Eliav, and U. Kaldor, Phys. Rev. A 69, 030501(R) (2004).
[42] N. S. Mosyagin, M. G. Kozlov, and A. V. Titov, J. Phys. B 31, L763 (1998).