PHYSICAL REVIEW A **86**, 062515 (2012)

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

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(Received 14 August 2012; published 27 December 2012)

The scaling of nuclear-spin-dependent parity-violating effects with increasing nuclear charge Z is discussed in two series of isoelectronic open-shell diatomic molecules. The parameter W_{a} characterizing the strength of parity violation in diatomic molecules is calculated in the framework of the zeroth-order regular approximation 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-polarization 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 emphasized.

DOI: 10.1103/PhysRevA.86.062515 PACS number(s): 31.30.−i, 37.10.Mn, 12.15.Mm, 21.10.Ky

I. INTRODUCTION

Properties depending strongly on the behavior of the electronic wave function in the vicinity of the nuclei display a pronounced dependence on the nuclear charge Z. This has been known for a long time and is 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 also depend on the specific nuclear arrangement, which could in principle modify the trends (see, e.g., the 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 one to scrutinize 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 (PV)]. In the present article we calculate nuclear-spin-dependent parity-violation interactions in alkaline-earth-metal monofluorides (Mg–Ra)F (group-II monofluorides) and (Zn–Cn)H (group-XII monohydrides) as examples for open-shell systems. Most 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.

II. NUCLEAR-SPIN-DEPENDENT PARITY VIOLATION

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

$$\hat{h}^{I}_{\mathrm{PV}} = \frac{G_{\mathrm{F}}}{\sqrt{2}} \sum_{A,i} k_{\mathcal{A},A}\, \vec{\boldsymbol{\alpha}} \cdot \vec{I}_A\, \rho_A(\vec{r}_i), \tag{1}$$

where G_{F} is Fermi's constant of the weak interaction, $k_{\mathcal{A},A}$ is an effective parameter describing NSD-PV interactions for nucleus A (caused both by the nuclear anapole moment and by weak electron-nucleon interactions; see Ref. [9]), and $\vec{I}_A$ and ρ_A are the spin and nuclear-spin-density distribution of nucleus A, respectively. For $\vec{\boldsymbol{\alpha}}$ one uses

$$\vec{\boldsymbol{\alpha}} = \begin{pmatrix} \mathbf{0} & \vec{\boldsymbol{\sigma}} \\ \vec{\boldsymbol{\sigma}} & \mathbf{0} \end{pmatrix} \tag{2}$$

with $\vec{\boldsymbol{\sigma}}$ being a vector of the 2×2 Pauli spin matrices $\sigma_x,\sigma_y,\sigma_z$ and $\mathbf{0}$ a 2×2 zero matrix. The anapole moment was proposed by Zel'dovich [10,11] soon 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 favorably 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}Cs, have nuclear-spin-dependent parity-violating effects been determined in atomic experiments [13]. In linear open-shell molecules, the special electronic structure itself suppresses the contribution from nuclear-spin-independent $\mathcal{P}$-odd terms and offers, in principle, convenient access to nuclear-spin-dependent $\mathcal{P}$-odd contributions for a variety of nuclei, including those with an odd number of neutrons instead of an odd number of protons. This suppression in these systems results from the fact that in linear molecules the matrix elements of the spin-independent $\mathcal{P}$-odd operator vanish in the subspace of degenerate components of the Kramers doublet. As the components of the Kramers doublet are interconverted both by time reversal and by reflection in the symmetry plane containing all nuclei whereas the $\mathcal{P}$-odd operator is $\mathcal{T}$ even but

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changes sign under mirror reflection, the expectation values of the components of the Kramers doublet (i.e., diagonal matrix elements) must vanish. The nondiagonal matrix elements are also zero for the nuclear-spin-independent $\mathcal{P}$-odd term, because a (pseudo)scalar operator cannot connect states with different projections of the angular momentum. The nuclear-spin-dependent $\mathcal{P}$-odd term, in contrast, can give rise to nonvanishing nondiagonal matrix elements between states with quantum numbers of the projection of the total electronic momentum on the molecular axis differing by 1. Another very attractive feature of diatomics, besides suppression of the otherwise masking contribution, is the closeness of the levels of opposite parity, which greatly enhances a $\mathcal{P}$-odd signal. With external magnetic fields, the levels of opposite parity can in principle be tuned to near-crossing to increase even more the effect induced by parity violation. These favorable enhancement mechanisms in open-shell diatomic molecules were discussed in the pioneering papers [14–16]. A complementary route would be the detection of NSD-PV in polyatomic chiral molecules by nuclear magnetic resonance techniques [17–26]. 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 parametrized by the term $W_\mathrm{a} k_{\mathcal{A}}[\vec{\lambda} \times \vec{S}^{\mathrm{eff}}] \cdot \vec{I}$ [27], a parity-violating contribution to the hyperfine coupling tensor, where $\vec{\lambda}$ is the unit vector pointing along the molecular axis from the heavy to the light nucleus, $\vec{S}^{\mathrm{eff}}$ is the effective electron spin, and W_a is a single constant characterizing the $\mathcal{P}$-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 $|-\Omega\rangle$ (Ω is the projection of the total electronic momentum on the molecular axis coinciding with the z axis), W_a is approximately (see the discussion below) proportional to the nondiagonal matrix element of the operator in Eq. (1):

$$W_\mathrm{a} = \frac{1}{k_{\mathcal{A}}[\vec{\lambda} \times \vec{S}^{\mathrm{eff}}]_{x,y}} \langle \Omega | \frac{\partial \hat{h}^{I}_{\mathrm{PV}}}{\partial \vec{I}} | -\Omega \rangle_{x,y}, \tag{3}$$

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

To calculate W_a we utilize a quasirelativistic two-component zeroth-order regular approximation (ZORA) approach to electroweak quantum chemistry, which proved to perform well in calculations of the spin-independent $\mathcal{P}$-oddenergy differences for chiral compounds when compared to a four-component treatment [26,28,29]. Details of the ZORA approach for the one- and multielectron cases can be found elsewhere [3,28–30] and below we give only the final expression of the NSD-PV terms in the ZORA approach in the Hartree-Fock-Coulomb and Kohn-Sham-Coulomb self-consistent-field (SCF) frameworks. The derivation of these terms together with common consideration of the parity-violation problem in open-shell polyatomic molecules can be found in Ref. [31].

In Table I, Q_A is the weak charge of nucleus A, $Q_A = N_A - (1 - 4\sin^2\theta_\mathrm{W})Z_A$, where N_A is the number of neutrons in nucleus A, Z_A the nuclear charge, $\sin^2\theta_\mathrm{W}$ the Weinberg parameter, for which we employ the numerical value $\sin^2\theta_\mathrm{W} = 0.2319$, and $\vec{A}_\mu$ the magnetic vector potential from the point-like nuclear magnetic moments $\vec{\mu}_A = \hbar\gamma_A \vec{I}_A$ with $\vec{A}_\mu(\vec{r}) = (\mu_0/4\pi)\sum_A \vec{\mu}_A \times (\vec{r} - \vec{R}_A)/(|\vec{r} - \vec{R}_A|)^3$, γ_A being the gyromagnetic ratio and μ_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, $\tilde{\omega} = 1/(2m_\mathrm{e} - \tilde{V}/c^2)$, where $\tilde{V}$ is the model potential (with additional damping [32]) proposed by van Wüllen [33], 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,

$$z^{(1,1)}_{\mathrm{hf}} + z^{(1,1)}_{\mathrm{sd}} = \sum_A \frac{G_\mathrm{F}}{2\sqrt{2}} \left(Q_A \left\{ e\,\vec{\boldsymbol{\sigma}} \cdot \vec{A}_\mu(\vec{r}), \frac{\tilde{\omega}}{c}\rho_N(\vec{r}) \right\} + 2k_{\mathcal{A},A} \left\{ \vec{\boldsymbol{\sigma}} \cdot \vec{p}, \frac{\tilde{\omega}}{c}\vec{\boldsymbol{\sigma}} \cdot \vec{I}_A \rho_A(\vec{r}) \right\} \right). \tag{4}$$

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

$$\langle s_{1/2} | \hat{h}^{I}_{\mathrm{PV}} | p_{1/2} \rangle \sim Z^2 R(Z), \tag{5}$$

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

TABLE I. Parity-violating terms in the ZORA Hamiltonian.

Term	Name	Expression
$z^{(0,1)}_{\mathrm{s}}$	Scalar $\mathcal{P}$-odd interaction	$\frac{G_\mathrm{F}}{2\sqrt{2}} Q_A \{\vec{\boldsymbol{\sigma}} \cdot \vec{p}, \frac{\tilde{\omega}}{c}\rho_A(\vec{r})\}$
$z^{(1,1)}_{\mathrm{hf}}$	Scalar $\mathcal{P}$-odd and hyperfine $\mathcal{P}$-even interaction	$\frac{G_\mathrm{F}}{2\sqrt{2}} Q_A \{e\,\vec{\boldsymbol{\sigma}} \cdot \vec{A}_\mu(\vec{r}), \frac{\tilde{\omega}}{c}\rho_A(\vec{r})\}$
$z^{(1,1)}_{\mathrm{sd}}$	Nuclear-spin-dependent $\mathcal{P}$-odd interaction	$\frac{G_\mathrm{F}}{2\sqrt{2}} 2k_{\mathcal{A},A} \{\vec{\boldsymbol{\sigma}} \cdot \vec{p}, \frac{\tilde{\omega}}{c}\vec{\boldsymbol{\sigma}} \cdot \vec{I}_A \rho_A(\vec{r})\}$
$z^{(2,1)}_{\mathrm{sdr}}$	Nuclear-spin-dependent $\mathcal{P}$-odd and hyperfine $\mathcal{P}$-even interaction	$\frac{G_\mathrm{F}}{2\sqrt{2}} 2k_{\mathcal{A},A} \{e\,\vec{\boldsymbol{\sigma}} \cdot \vec{A}_\mu(\vec{r}), \frac{\tilde{\omega}}{c}\vec{\boldsymbol{\sigma}} \cdot \vec{I}_A \rho_A(\vec{r})\}$

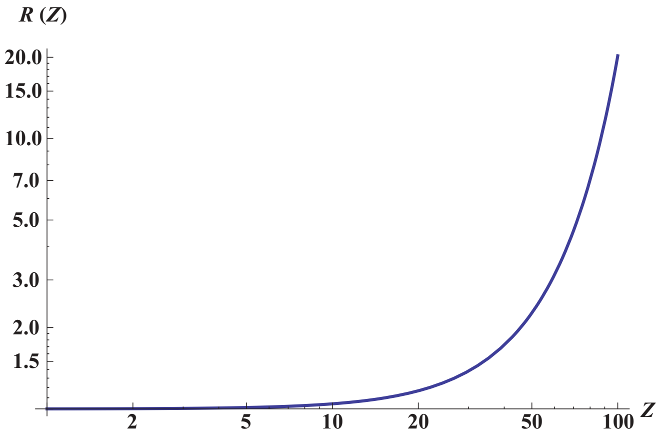

FIG. 1. (Color online) Relativistic enhancement factor $R(Z)$ as a function of the nuclear charge Z shown on a double-logarithmic scale.

where a_0 is the Bohr radius, α 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 nonrelativistic calculations. As is shown in Fig. 1 on a double-logarithmic scale, $R(Z)$ depends heavily on Z (here the analytic form was used). The proposed scaling behavior for atomic systems can subsequently be studied in explicit calculations for molecular systems as we will show below.

III. CALCULATION DETAILS

In all our computations we used for the alkaline-earth-metal atoms a basis set of uncontracted Gaussians with the exponent coefficients (ECs) composed as an even-tempered series. This sequence was generated according to $\alpha_i = \gamma\beta^{N-i}$, $i = 1,\dots,N$. For s and p functions β was taken equal to 2.0 for basis sets centered 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 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 $\mathcal{P}$-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 we used an uncontracted atomic natural orbital (ANO) basis set of triple-ζ quality [34] and on hydrogen an s,p subset of an uncontracted correlation-consistent basis set of quadruple-ζ quality [34] with the ECs given explicitly in Table II.

The nuclear density was modeled by a spherical Gaussian distribution $\rho(R) = \rho_0 e^{-(3/2\xi)R^2}$, where ξ is the root mean square radius of the corresponding nucleus computed according to the empirical formula $\xi = (0.836A^{1/3} + 0.57)$ fm $= (1.5798A^{1/3} + 1.077) \times 10^{-5} a_0$, where A is the given mass number of the respective isotope. Within this work we

TABLE II. Basis set parameters for ZORA HF-DFT calculations. Even-tempered basis sets of uncontracted Gaussians are given in the form N_{bas}; l; (EC$_{\text{max}}$; EC$_{\text{min}}$), 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. EC$_{\text{max}}$ and EC$_{\text{min}}$ are the largest and smallest exponent coefficient (in a_0^{-2}), 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; 0.0200)	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)	10; *f*;	(751.8368350; 0.13638)

Zn,Cd,Hg,Cn	
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	2.2920000
15281.007	56.919005	1.750000	12.410	0.8380000
3441.5392	17.604568	0.612500	2.8240	0.2920000
967.09483	6.2749950	0.214375	0.7977	
314.03534	2.4470300		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				
0.2408610				
0.0843010				

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 $|W_{\mathrm{a}}|$ were found on the order of a few hertz [7]), we report only one value for $|W_{\mathrm{a}}|$, 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 [26,28,29,31] of the program package TURBOMOLE [35] was used for the complex generalized SCF (Hartree-Fock or Kohn-Sham) calculations. As spatial symmetry was not exploited, we also calculated the value of the projection Ω of the total electron angular momentum on the molecular axis. In the two-component generalized Hartree-Fock (GHF) calculations $\Omega \cong 0.5 \pm 10^{-3}$, in the two-component density functional theory (DFT) calculations within the generalized Kohn-Sham (GKS) framework $\Omega \cong 0.5 \pm 10^{-4}$. The value of $|W_{\mathrm{a}}|$ was computed according to Eq. (3). In the ZORA calculations $|\Omega\rangle$ and $|-\Omega\rangle$ are many-electron functions, and the Löwdin formula [36] for calculations of the matrix elements between nonorthogonal one-determinantal (OD) functions was applied:

$$\langle \Psi_1|\widehat{W}|\Psi_2\rangle = \sum_{k}\sum_{l} \langle \tilde{\psi}_k|\widehat{w}|\psi_l\rangle \mathcal{D}(k|l), \qquad (7)$$

where $|\Psi_1\rangle$ and $|\Psi_2\rangle$ can be either orthonormalized or nonorthonormalized OD functions, $\langle \tilde{\psi}_k|\widehat{w}|\psi_l\rangle$ is the matrix element of the one-electron operator $\widehat{w}$ 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 wave functions Ψ_1 and Ψ_2, respectively, and $\mathcal{D}(k|l)$ is the (k,l) cofactor of $\mathbf{S}$ which is obtained from the original OD wave functions by crossing out in the overlap matrix $\mathbf{S}$ (which has the matrix elements $s_{kl} = \langle \tilde{\psi}_k|\psi_l\rangle$) the kth row and lth column, subsequently forming the determinant of the resulting submatrix and multiplying by $(-1)^{k+l}$. 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 symmetrization procedure, which for the purpose of the present study, however, is not required.

In calculations of the (Mg-Ra)F row two different exchange-correlation (XC) functionals were used in a generalized Kohn-Sham DFT framework: (1) the local-density approximation (LDA) and (2) a three-parameter hybrid functional containing Becke's exchange functional together with the Lee-Yang-Parr (LYP) correlation functional B3LYP. This latter hybrid XC functional, which contains an admixture of about 20% nonlocal Fock exchange, was used in the form employed in the GAUSSIAN03 program package [37] with the VWN(III) approximation by Vosko, Wilk, and Nusair for the correlation functional of the homogeneous electron gas. Both XC functionals (LDA and B3LYP) attempt to describe nonlocal exchange-correlation effects by means of an effective (primarily, see below) local interaction. In the case of the LDA this interaction is estimated via a procedure that employs locally the exchange and correlation energy density of a homogeneous electron gas. The B3LYP functional is somewhat more sophisticated in containing additional terms, e.g., ones that account for the local gradient of the density, and includes—being a hybrid functional—also some contribution from nonlocal Fock exchange which attempts to alleviate pronounced errors due to the use of a local exchange term. In some previous studies of parity-violating potentials in chiral molecules containing heavy nuclei, the HF and LD approximations were found to define often the range of corresponding values, with various other functionals such as B3LYP yielding parity-violating potentials typically falling in between these two extremes (see, e.g., Refs. [29,38]).

The equilibrium distance for all diatomic molecules was taken from experimental data, except for RaF, where the distance was obtained in Ref. [7] from four-component relativistic coupled-cluster calculations in the Fock space and CnH, where we used the bond length obtained in the two-component GHF framework.

TABLE III. Calculated $\mathcal{P}$-odd parameter $|W_{\mathrm{a}}|$ (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	$\lvert W_{\mathrm{a}}\rvert$/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	3.9×10^{1}	4.6×10^{1}	4.8×10^{1}
BaF	56	4.07	1.11×10^{2}[a]	1.19×10^{2}	1.25×10^{2}
RaF	88	4.24	1.30×10^{3}[b]	1.42×10^{3}	1.47×10^{3}
RaF (basis S)	88	4.24	1.07×10^{3}		1.48×10^{3}
RaF (basis L)	88	4.24	1.24×10^{3}		1.50×10^{3}
ZnH	30	3.01	4.7×10^{1}		
CdH	48	3.36	2.23×10^{2}		
HgH	80	3.33	3.30×10^{3}[c]		
CnH	112	3.10	4.88×10^{4}		

[a] In Ref. [7] 111 Hz was obtained with a slightly different basis set.
[b] In Ref. [7] 1.3 kHz was reported for a slightly different basis set.
[c] In Ref. [7] 3.3 kHz was reported for a slightly smaller basis set.

IV. RESULTS

The results of our study are summarized 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 (Mg–Ra)F and group-XII monohydrides (Zn–Cn)H. In addition, we report results for YbF for comparison with other approaches. Before discussing details of the results we would like to emphasize that the majority of our calculations are *model* ones. Thus the W_a values provided can primarily be used in assessing the order of magnitude. The exception is the W_a parameter that takes account of the spin-polarization effect from molecular calculations. In this case we provide some theoretical uncertainty estimates (see the corresponding paragraph).

One can see from Table I two main trends when accounting for correlations by DFT: (1) a systematic increase in the value of $|W_a|$ from B3LYP to LDA XC functionals and (2) a 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 [29]; 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-polarization effects, which cannot (fully) be accounted for by direct calculation of nondiagonal matrix elements between complex GHF wave functions 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 wave functions on matrix elements of different operators can be found in Ref. [39]. 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 [3,7] that one should correct for the relativistic enhancement factors when attempting to extract Z^k scaling laws from quasirelativistic and relativistic calculations. Fitting of the points in Fig. 2 by a linear function gives a slope equal to 1.75 for (Mg–Ra)F and 2.68 for (Zn–Cn)H, which are indeed close to the scaling factors for NSD-PV interaction matrix elements.

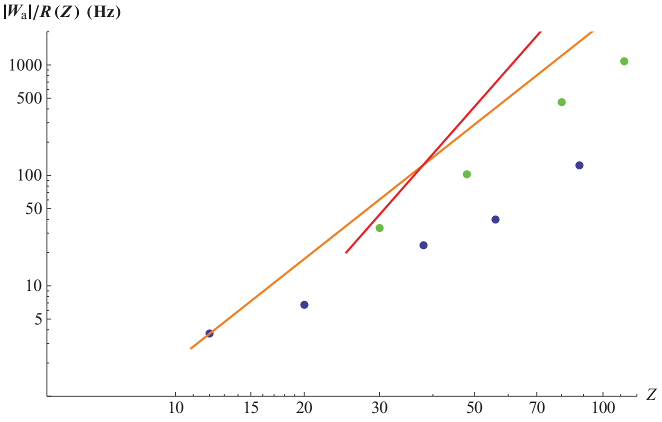

FIG. 2. (Color online) Scaling of $|W_a|/R(Z)$ GHF values with Z for the (Mg–Ra)F and (Zn–Cn)H series [orange (bottom) line, blue dots and red (upper) line, green dots, respectively] on a double-logarithmic scale. The slope of the lines is 1.75 for (Mg–Ra)F and 2.68 for (Zn–Cn)H, which implies an $R(Z)Z^k$ scaling law for W_a with $k = 1.75$ and $k = 2.68$, respectively.

Our current results have been mainly confirmed by recent four-component calculations of W_a in the series of diatomic radicals (Mg–Ra)F [40]. The authors of Ref. [40] have also observed the Z^k scaling (also with k close to 2) for $W_a/R(Z)$. Besides performing Dirac-Hartree-Fock-Coulomb (DHFC) and Dirac-Kohn-Sham (DKS) calculations in a paired GHF and paired GKS framework, which cannot account for core-polarization effects, the authors of Ref. [40] employed some approximate atom-based schemes to roughly estimate part of the electron-correlation effect via scaling factors. Our treatment, however, is based on a complex GHF (GKS) framework and thus allows us to capture part of the electron-correlation effect 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 wave functions. 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. [40]. For BaF and RaF we find, however, only a modest electron-correlation contribution on the DFT level of theory, whereas in Ref. [40] significant changes are reported for RaF. Even without the subsequent attempts to account for further electron-correlation effects, in Ref. [40] DHFC and DKS values for $|W_a|$ in RaF differ by more than 15% (and by about 30% for the LDA XC functional) and in BaF only by 2%. As was mentioned, the latter result (for BaF) is actually in agreement with the earlier calculations in Ref. [41], in which the authors found that the main contribution comes from the spin-polarization effects, although further accounting for electron correlation gives a minor contribution. We note in passing that in Ref. [40] the data got mixed up for the calculations that do not account for spin polarization (SCF calculations in the notations of the authors of Ref. [41], $W_a = 111$ Hz), with those that account for spin polarization [SCF-EO (SCF plus effective operator accounting for spin polarization), $W_a = 181$ Hz] and those that account for electron correlation and spin polarization (Restricted Active Space SCF (RASSCF)-EO, $W_a = 175$ Hz). In Ref. [40] Faegri's energy-optimized basis sets were employed, which required augmenting with additional functions to be used in calculations of properties that depend on the behavior of the electronic wave function near the nucleus. To check the influence of the basis set choice, we performed calculations with two additional basis sets (see below for the basis set specifications) for Ra together with an uncontracted augmented correlation-consistent polarized valence triple-zeta (aug-cc-pVTZ) basis set $11s6p3d2f$ on the fluorine nucleus. The first Ra basis set (basis S in Table III) was Faegri's uncontracted basis set $25s21p14d9f$ recommended for relativistic calculations [42] and another one (basis L) was a large even-tempered basis set $36s33p22d15f$ generated according to recommendation of the article [43]. 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 the GHF and GKS results of essentially paired generalized SCF quality decreases from 38% to 20% for the LDA XC functional, getting close to the values reported by us (≈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. [40] for the DFT framework might primarily be caused by the special choice of basis set therein.

TABLE IV. Calculated and scaled *ab initio* values for the parameter $|W_{\mathrm{a}}|$ in BaF, YbF, and RaF together with the scaling factor $f = [(A_{\mathrm{iso}}A_{\mathrm{d}})^{\mathrm{CGHF}}/(A_{\mathrm{iso}}A_{\mathrm{d}})^{\mathrm{PGHF}}]^{1/2}$. 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.

	$\|W_{\mathrm{a}}\|$/Hz					
	GHF	Scaled	*ab initio*	f	Method	Reference
BaF	1.11×10^2	1.9×10^2	1.81×10^2	1.68	SCF-EO	[41]
			1.75×10^2		RASSCF-EO	[41]
YbF	4.65×10^2	6.1×10^2	6.34×10^2	1.31	RASSCF-EO	[46]
RaF	1.30×10^3	2.1×10^3		1.65		
HgH	3.30×10^3	2.0×10^3	[a]	0.62		
CnH	4.88×10^4	3.1×10^4		0.63		

[a] Semiempirical estimate of Ref. [44] based on spectroscopic parameters of ^{199}HgH and ^{201}HgH: $W_{\mathrm{a}} = 1800$ Hz and $W_{\mathrm{a}} = 1940$ Hz, respectively.

To estimate spin-polarization contributions within the GHF approach we use scaling relations from the semiempirical molecular model by Kozlov [44], which is known to reproduce *ab initio* parameters of the $(\mathcal{P},\mathcal{T})$-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_{iso} (isotropic) and A_{d} (dipole). For our purpose and the current set of molecules, however, it is more important that the relation between W_{a} obtained for different approximations (e.g., complex and paired generalized Hartree-Fock wave functions, CGHF and PGHF, respectively) is approximately equal to the ratio between the square root of the products of A_{iso} and A_{d} [see Eqs. (33), (34), and (10) in Ref. [44]; assuming that the signs of A_{iso} and A_{d} are identical]:

$$\frac{W_{\mathrm{a}}^{\mathrm{CGHF}}}{W_{\mathrm{a}}^{\mathrm{PGHF}}} \approx \left[\frac{(A_{\mathrm{iso}}A_{\mathrm{d}})^{\mathrm{CGHF}}}{(A_{\mathrm{iso}}A_{\mathrm{d}})^{\mathrm{PGHF}}}\right]^{1/2}. \tag{8}$$

Thus, by calculating the hyperfine tensors both taking into account the spin polarization (in our case as diagonal matrix elements within the complex GHF scheme) and not doing so (as nondiagonal matrix elements, leading to results of essentially paired GHF quality) we can restore spin-polarization 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 that of 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 [44]. This finding is particularly encouraging for the identification of promising molecular candidates. We expect, however, that the theoretical uncertainty of our value for W_{a} in RaF is in general somewhat higher than 10%, as the semiempirical model itself provides results with an accuracy of 10%–15% (see above). The uncertainty of the W_{a} parameter for RaF should therefore rather be 15%, which is indeed an estimate, and not a rigorous error bound. Thus, for reliable estimates of electron-correlation and spin-polarization effects on the value of W_{a} (and other properties depending on the behavior of the wave function near the nucleus) in RaF one has to employ high-order correlation calculations, for instance similar to those in Ref. [45]. It is also interesting to note that in the group-XII monohydrides series the spin-polarization contribution should suppress rather than enhance the NSD-PV interaction, at least for the two heavy representatives reported in Table IV.

Finally, we emphasize that although the treatment of relativistic effects in the four- and two-component frameworks is different, deviations between results for NSD-PV operators are not expected to be significantly larger than 3% for the heavier nuclei (rows 4–7) when judged on the basis of earlier calculations [26,29], provided appropriate basis sets are used (see also the discussion in Ref. [3]).

V. 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 nonpolynomially with the nuclear charge Z, we obtain an approximate Z^2 scaling behavior for the nuclear-spin-dependent parity-violating parameter W_{a} computed at the respective equilibrium structure. 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 generalized Kohn-Sham framework employed in this work, part of the electron-correlation effect on this molecular property can be accounted for, although some contributions are still missing. Spin-polarization effects can approximately be included within a simple but powerful molecular scaling scheme utilized previously for semiempirical 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 promising molecular candidates such as RaF to be identified, as was proposed in Ref. [7].

ACKNOWLEDGMENTS

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.

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