Nuclear-spin dependent parity violation in diatomic molecular ions

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Nuclear-spin-dependent (NSD) parity violating (PV) effects can be strongly enhanced in diatomic molecules containing heavy atoms. Future measurements are anticipated to provide nuclear anapole moments and strength constants for PV nuclear forces. In light molecules, the NSD electroweak electron-nucleus interaction may also be detected. Here we calculate NSD PV effects for molecular ions. Our calculations are motivated by rapid developments in trapping techniques for such systems at low temperatures.

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It was previously shown that nuclear spin-dependent (NSD) parity violation (PV) effects are enhanced by a factor of $10^5$ in diatomic molecules with $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ electronic states due to the mixing of close rotational states of opposite parity (Ω-doublet for $^2\Pi_{1/2}$) [1,2]. Demille and co-workers suggested measuring NSD PV effects by using neutral diatomic molecules in a Stark interference experiment to determine the mixing between opposite-parity rotational/hyperfine levels [3]. Another proposal was published in Ref. [5], and corresponding experiments have already started. Recently, it was demonstrated that positive molecular ions may be easily trapped and studied at low temperatures [6], which motivated us to perform calculations on NSD PV effects in such systems.

The term in the Hamiltonian operator arising from the NSD parity violating electron-nucleus interaction is

$$H_A = \kappa_{NSD} \frac{G_F}{\sqrt{2}} \frac{\boldsymbol{\alpha} \cdot \boldsymbol{I}}{I} \rho(\mathbf{r}). \quad (1)$$

Here, and throughout the text, we use atomic units. In Eq. (1), $\kappa_{NSD}$ is the dimensionless strength constant, $G_F = 2.22249 \times 10^{-14} \text{ a.u.}$ is the Fermi constant, $\boldsymbol{\alpha}$ is a vector comprised of the conventional Dirac matrices, $\boldsymbol{I}$ is the nuclear spin, $\rho(\mathbf{r})$ is the displacement of the valence electron from the nucleus, and $\rho(\mathbf{r})$ is the (normalized) nuclear density. There are three sources for this interaction: the first contribution arises from the electroweak neutral coupling between electron vector and nucleon axial-vector currents ($\mathbf{V}_e \boldsymbol{A}_N$) [7]. The second contribution comes from the nuclear-spin-independent weak interaction combined with the hyperfine interaction [8]. Finally, the nuclear anapole moment contribution, which scales with the number of nucleons $A$ as $\kappa_A \sim A^{2/3}$, becomes the dominant contribution in spin-dependent atomic PV effects for a sufficiently large nuclear charge $Z$ [9,10].

The anapole moment was first predicted by Zeldovich [11] in 1958 as a new parity ($P$) violating and time ($T$) reversal conserving moment of an elementary particle. It appears in the second-order multipole expansion of the magnetic vector-potential simultaneously with the $P$- and $T$-violating magnetic quadrupole moment [12]. The nuclear anapole moment was experimentally discovered in the $^{133}\text{Cs}$ atom in 1997 [13] following a proposal by Flambaum and Khriplovich [9], who showed that the nuclear anapole provides the dominant contribution to the nuclear-spin-dependent parity violating effect in atoms and molecules.

The nuclear anapole requires nuclear spin $I \neq 0$ and in a simple valence model has the following value [10],

$$\kappa_A = 1.15 \times 10^{-3} \left( \frac{K}{I+1} \right) A^{2/3} \mu_i g_i. \quad (2)$$

Here, $K = (-1)^{l+\frac{1}{2}-I}(I+1/2)$, $l$ is the orbital angular momentum of the external unpaired nucleon $i = n, p$; $\mu_p = +2.8$, $\mu_n = -1.9$. Theoretical estimates give the strength constant for nucleon-nucleus weak potential $g_p \approx +4.5$ for a proton and $|g_n| \sim 1$ for a neutron [14]. The aim of anapole measurements is to provide accurate values for these constants, thus obtaining important information about hadronic weak coupling.

A number of theoretical investigations of the nuclear spin-dependent parity violation in diatomic molecules have been performed in recent years, using both semiempirical [4] and ab initio methods [5,15,17]. In a recent paper [23] we presented Dirac Hartree-Fock and relativistic density-functional calculations of the electronic $W_A$ factor of the diatomic group-2 and -12 fluorides and a number of other diatomic compounds. In this work we investigate the nuclear spin-dependent parity violation effects in a different type of system, i.e. positively...
charged dimers, as these systems have an experimental advantage of being easily trapped [6]. Diatomic ions have also been proposed for the search for the electron electric-dipole moment (eEDM) [24–26], and the preliminary experiments are currently being conducted [27]. Here we use the combination of methods presented in Ref. [28] to calculate the $W_A$ factors of positively ionized group-13 and group-15 fluorides ($^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ ground states, respectively), and a number of other positive diatomic ions having a $^2\Sigma_{1/2}$ ground state.

For $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ electronic states, the interaction [1] can be replaced by the effective operator, which appears in the spin-rotational Hamiltonian [23, 24].

$$H_{A}^{\text{eff}} = \kappa_{NSD} W_{A} \frac{(n \times S') \cdot \mathbf{I}}{I}, \quad (3)$$

where $S'$ is the effective spin and $n$ is the unit vector directed along the molecular axis from the heavier to the lighter nucleus. The electronic factor $W_{A}$ is found from evaluating the matrix elements of the $\alpha (r)$ operator in the molecular spinor basis [25]. The $^2\Sigma_{1/2}$ and the $^2\Pi_{1/2}$ open-shell electronic states are two-fold degenerate, corresponding to the two possible projections of electronic angular momentum along $n$, i.e. $|\Omega \rangle = \pm |\frac{1}{2}\rangle$. When operating within this degenerate space, the operator $\sum_{\lambda} \alpha (r)$ is equivalent to $W_{A} (n \times S')$ (Eq. (3)). Time-reversal symmetry ensures that only the matrix elements that are off-diagonal in $\Omega$ are non-vanishing. This symmetry rule is encapsulated within the effective operator $H_{A}^{\text{eff}}$ by the angular factor $(n \times S')$. Here the effective spin $S'$ generates rotations in the degenerate subspace analogously to usual spin operator $S$ in a spin-1/2 system.

The calculations were carried out within the open-shell single determinant average-of-configuration Dirac-Hartree-Fock approach (DHF) [29] and within the relativistic density functional theory (DFT) [30], employing quaternion symmetry [31, 32]. A finite nucleus, modeled by the Gaussian charge distribution was used [33]. All the calculations were performed using the developer's version of the DIRAC10 program package [34].

For the lighter elements (boron to phosphorus), uncontracted aug-cc-pVTZ basis sets were used [35, 36]. For the rest of the atoms, we employed Faegri's dual family basis sets [37]. As a good description of the electronic wave function in the nuclear region is essential for obtaining reliable results for parity violating properties [35], we augmented the basis sets with high exponent $s$ and $p$ functions, which brings about an increase of around 10% in the calculated values of $W_{A}$. The basis sets were increased, both in the core and in the valence regions, to convergence with respect to the calculated $W_{A}$ constants. The final basis sets can be found in Table I.

Where available, experimentally determined bond distances $R_{e}$ were used. For molecules where $R_{e}$ is not known experimentally, we optimized the bond distance using relativistic coupled cluster theory with single, double, and perturbative triple excitations, CCSD(T) [39].

Table I. Basis sets employed in the calculation of the $W_{A}$ constants. All elements with $Z > 15$ are described by the Faegri basis sets [37] augmented by high exponent, diffuse, and high angular momentum functions.

| Atom | $Z$ | Basis Set |
|------|-----|-----------|
| B    | 5   | aug-cc-PVTZ |
| N    | 7   | aug-cc-PVTZ |
| O    | 8   | aug-cc-PVTZ |
| F    | 9   | aug-cc-PVTZ |
| Al   | 13  | aug-cc-PVTZ |
| P    | 15  | aug-cc-PVTZ |
| Ga   | 31  | 22s19p10d8f2g |
| As   | 33  | 21s20p11d8f2g |
| Y    | 39  | 21s20p12d9f2g |
| Zr   | 40  | 21s20p12d9f2g |
| In   | 49  | 22s20p12d9f2g |
| Sb   | 51  | 22s21p13d9f2g |
| Hf   | 72  | 25s22p16d10f2g |
| Tl   | 81  | 25s23p15d10f2g |
| Bi   | 83  | 25s24p16d11f2g |
| Ac   | 89  | 26s24p16d11f2g |

| Basis Set | $a$ | augmented by 3 high exponent $p$ functions |
|-----------|-----|----------------------------------|
|           | $b$ | augmented by 4 high exponent $s$ and 3 high exponent $p$ functions |
|           | $c$ | augmented by 4 high exponent $p$ function. |
|           | $d$ | augmented by 1 high exponent $s$ and 3 high exponent $p$ functions |

To reduce the computational effort, we employed an infinite order two-component relativistic Hamiltonian obtained after the Barysz–Sadlej–Snijders (BSS) transformation of the Dirac Hamiltonian in a finite basis set [40, 41]. Our calculated $R_{e}$ are typically within 0.01 Å of the experimental values, where available. The experimental/calculated equilibrium distances can be found in Table II.

In the DFT calculations we used the Coulomb-attenuated B3LYP functional (CAMB3LYP*), the parameters of which were adjusted by Thierfelder et al. [14] to reproduce the PV energy shifts obtained using coupled cluster calculations (the newly adjusted parameters are $\alpha = 0.20$, $\beta = 0.12$, and $\mu = 0.90$).

In our previous work [23] we have examined and compared various schemes for adding electron correlation to the Dirac–Hartree–Fock $W_{A}$ values, and core-polarization contributions to the DFT results. Here, we correct the calculated DHF and DFT $W_{A}$ for core polarization using a scaling parameter, $K_{CP}$. This parameter is obtained from atomic calculations as described in the following. The main contribution to the matrix elements of the NSD interaction for the valence molecular electrons comes from short distances around the heavy nucleus, where the total molecular potential is spherically symmetric to very high precision, and the core of the heavy atom is practically unaffected by the presence of the second atom, justifying our use of the atomic model. The molecular orbitals of the valence electron can thus be expanded in this region, using spherical harmonics
TABLE II. Internuclear distances $R_v$ (taken from CCSD(T) calculations, unless referenced otherwise, \text{Å}), core-polarization scaling parameters $K_{CP}$, the $P$-odd interaction constants $W_A$ (Hz) obtained using DHF and DFT, and the final recommended values, taken as $W_A$(Final) = $(W_A$(DFT))$K_{CP}$ + $W_A$(DHF)$K_{CP}$)/2. Relativistic factors $R_w$ (see Eq. (10)) are also shown.

| $Z$ | $R_v$ (Å) | $K_{CP}$ | $W_A$ (Hz) |
|-----|----------|-----------|------------|
|     |          | DFT       | DFT Final  |

- Group 13 ($2\Sigma_{1/2}$)
  - BF$^+$: 1.01 1.31 1.1 1.74 1.71 1.90
  - AlF$^+$: 13 1.07 1.59 1.2 9.62 10.39 12.0
  - GaF$^+$: 31 1.41 1.68 1.1 94.4 93.5 103.4
  - InF$^+$: 49 2.2 1.91 1.1 370.3 358.3 400.7
  - TlF$^+$: 81 7.4 2.00 1.1 3833 3622 4100

- Group 15 ($2\Pi_{1/2}$)
  - NF$^+$: 7 1.01 1.18 1.1 -0.014 -0.015 -0.016
  - PF$^+$: 15 1.10 1.52 1.2 -0.16 -0.18 -0.20
  - AsF$^+$: 33 1.47 1.66 1.1 -6.48 -7.29 -7.67
  - SbF$^+$: 52 1.3 1.83 1.1 -60.0 -66.1 -71.6
  - BiF$^+$: 83 8.1 2.28 1.1 -2204 -2123 -2380

- Other systems ($2\Sigma_{1/2}$)
  - YF$^+$: 39 1.69 1.85 1.2 45.6 39.4 51.0
  - ZrO$^+$: 40 1.73 1.95 1.2 43.2 31.1 44.6
  - HFO$^+$: 72 5.0 1.70 1.2 662.5 609.1 762.9
  - AcF$^+$: 89 11 2.106 1.2 1654 1614 1961

* Ref. [42]
* Ref. [43]
* Ref. [44]

The core polarization can be understood as the change of the self-consistent DHF potential due to the effect of the extra term (the weak interaction operator $\hat{H}_A$) in the Hamiltonian. The inclusion of the core polarization in a self-consistent way is equivalent to the random-phase approximation (RPA, see, e.g. [46]). The change in the DHF potential is found by solving the RPA-type equations self-consistently for all states in the atomic core,

$$\hat{H}_0 - \epsilon_v)\psi_v = -(\hat{H}_A + \delta V_A)\psi_v.$$

Here, $\hat{H}_0$ is the DHF Hamiltonian (5), index $c$ enumerates the states in the core, $\delta \psi_v$ is the correction to the core state $c$ due to weak interaction $\hat{H}_A$, and $\delta V_A$ is the correction to the self-consistent core potential due to the change of all core functions. Once $\delta V_A$ is found, the core polarization can be included into a matrix element for valence states $v$ and $w$ via the redefinition of the weak interaction Hamiltonian,

$$\langle v|\hat{H}_A|w\rangle \rightarrow \langle v|\hat{H}_A + \delta V_A|w\rangle.$$

We then obtain the scaling parameter for core-polarization effects, $K_{CP}$, from

$$K_{CP} = \frac{\langle \psi_{n\sigma_{1/2}}|\hat{H}_A + \delta V_A|\psi_{n\sigma_{1/2}}\rangle}{\langle \psi_{n\sigma_{1/2}}|\hat{H}_A|\psi_{n\sigma_{1/2}}\rangle}.$$ (9)

It should be noted that for the positively charged group 15 fluorides we have only calculated the correlations between the valence electrons and the core; the correlations between the valence $ns$ and $np$ electrons are not included.

We investigated two types of positively ionized diatomic molecules: those with a $2\Sigma_{1/2}$ ground state, including group 13 fluorides and a number of other systems, and molecular ions with a $2\Pi_{1/2}$ ground state (represented here by group 15 fluorides). The values of $K_{CP}$ for all the systems under study are presented in Table II together with the DHF and the DFT $W_A$ constants. As the final recommended value for the $W_A$ parameter we take an average of $W_A$(DHF)$K_{CP}$ and $W_A$(DFT)$K_{CP}$.

The estimate of the accuracy in our previous work [23] for all core-polarization $W_A$ values has shown that it is about 15% for molecules in the $2\Sigma_{1/2}$ electronic state and 20-30% for the $2\Pi_{1/2}$ state.

The magnitude of $W_A$ in the $2\Sigma_{1/2}$ electronic state is expected to scale as $Z^2 R_w$ [8], where $R_w$ is the relativistic parameter,

$$R_w = \frac{2\gamma + 1}{3} \left( \frac{a_B}{2Zr_0A^{1/3}} \right)^{2-2\gamma} \frac{4}{[\Gamma(2\gamma + 1)]^2},$$ (10)

where $\gamma = [1 - (Z\alpha)^2]^{1/2}$.

In Eq. (10), $a_B$ is the Bohr radius, $r_0 = 1.2 \times 10^{-15}$ m, and $\alpha$ is the fine-structure constant. The $R_w$ parameters are shown in Table III for each of the metal atoms. In Fig. 1 we plot log $R_w$ as a function of log($Z$) for both groups of dimers. For group-13 fluorides the scaling
is, indeed, $Z^2$. In the case of group 15 fluorides, however, the ground state is $^2\Pi_{1/2}$, for which the $W_A$ parameter vanishes in the non-relativistic limit, since in this limit it does not contain the $s$-wave electronic orbital and can not provide the matrix element $\langle s_{1/2} | \alpha \rho(r) | p_{1/2} \rangle$. The effect appears due to the mixing of $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ electronic states by the spin-orbit interaction, and gives an extra factor of $Z^2 \alpha^2$ in the $Z$-dependence of $W_A$, as seen in Fig. 1.

To summarize, here we have performed calculations of the $P$-odd interaction constant $W_A$ in singly-ionized group-13 and group-15 fluorides as well as other select singly-ionized diatomic systems. To the best of our knowledge, this is the first investigation of nuclear spin-dependent parity violation effects in molecular ions and it is motivated by progress in the cooling and trapping of such systems.

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Fig. 1. (color online) Log-log plot illustrating the scaling of $W_A$ with relativistic parameter $R_W$ and atomic number $Z$ for group-13 and -15 singly-ionized fluorides.

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