

Search for parity- and time-and-parity-violation effects in lead monofluoride (PbF): *Ab initio* molecular study

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The relativistic coupled-clusters method combined with the generalized relativistic effective core potential approach and nonvariational one-center restoration technique is applied to evaluation of parameters of the spin-rotational effective Hamiltonian in lead monofluoride to study the effects of violation of time-reversal invariance (T) and space parity (P) in PbF. The obtained hyperfine structure constants, $A_{\parallel} = 9942$ MHz and $A_{\perp} = -7174$ MHz, are stable with respect to the improvement of the correlation treatment, and they are in very good agreement with the experimental data, $A_{\parallel} = 10\,147$ MHz and $A_{\perp} = -7264$ MHz [R. J. Mawhorter, B. S. Murphy, A. L. Baum, T. J. Sears, T. Yang, P. M. Rupasinghe, C. P. McRaven, N. E. Shafer-Ray, L. D. Alpei, and J.-U. Grabow, *Phys. Rev. A* **84**, 022508 (2011); A. N. Petrov, L. V. Skripnikov, A. V. Titov, and R. J. Mawhorter, *ibid.* **88**, 010501(R) (2013)]. This is essential to the important task of verifying the value of effective electric field $E_{\text{eff}} = 40$ GV/cm, the parameter of P -odd interaction $W_p = -1213$ Hz, and the parameter of T, P -odd pseudoscalar-scalar electron-nucleus interaction $W_{T,P} = 91$ kHz, which are of primary interest in the Brief Report.

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I. INTRODUCTION

Theoretical study of PbF is primarily motivated by the proposed experiments to search for the effects of simultaneous violation of time-reversal invariance (T) and space parity (P) (T, P -parity nonconservation or PNC effects below) such as electron electric dipole moment (e EDM) [1–6]. An experiment using PbF to measure the P -odd anapole moment has also been recently suggested [7]. The hyperfine structure (HFS) constants for the ground state of PbF are known with high accuracy [6,8].

First, the PbF molecule was theoretically studied in Refs. [1,2] in order to evaluate the parameters of P - and T, P -odd effects in heavy-atom molecules. Then a number of new studies were performed in Refs. [5,9,10]. However, even the most recent results [5,10] display a significant disagreement for the parameter of P -odd interaction [see Eq. (8) below]. It can be considered rather surprising, especially, if one takes into account that PbF, unlike other systems actively considered for PNC experiments to date (HfF⁺ [11], YbF [12], ThO [13], ThF⁺ [14], WC [15], etc.), is not a compound of a transition d element or lanthanide/actinide f element. Nevertheless, the main feature of the electronic structure of the PbF $\Pi_{1/2}$ ground state is that the valence unpaired electron is occupying the π state (which is derived from the $6p$ state of Pb), as opposed to the majority of other systems, taken into consideration over the years, having an unpaired σ electron (that is derived from the valence s state of a heavy atom). These unpaired electrons provide the leading contribution to the HFS constant [16] and PNC parameters of interest. However, the leading (one-configuration) contribution is somewhat suppressed for the systems with unpaired π state(s) due to their weaker asymptotic behavior on the heavy nucleus, making the relative influence of correlation effects, etc., more important. This

means that the PbF results should be sensitive to the quality of calculation, i.e., accounting for correlation effects and their interplay with spin-orbit interaction.

A revival of interest in PbF during recent years [7] was initiated by the discovery of coincidental near degeneracy for levels of opposite parity in the ground rotational state $J = 1/2$ for ²⁰⁷PbF [4], caused by the near cancellation between the shifts in the energies of these levels due to omega-type doubling and the magnetic hyperfine interaction. This degeneracy had contradicted the previous theoretical studies and was resolved in Ref. [5]. This leads to improved sensitivity of PbF to the PNC effects, as it was earlier expected. Also, the molecule was suggested to be sensitive to variation of the fundamental constants [17]. So, a reliable theoretical study of the parameters of the P - and T, P -odd effective spin-rotational Hamiltonian is of considerable interest for experiment.

II. THEORY

Following Refs. [1,2], we represent the effective spin-rotational Hamiltonian as

$$\mathbf{H}_{\text{eff}} = B\mathbf{J}^2 + \Delta\mathbf{J} \cdot \mathbf{S}' + \mathbf{I} \cdot \hat{\mathbf{A}} \cdot \mathbf{S}' + \mu_B \mathbf{B} \cdot \hat{\mathbf{G}} \cdot \mathbf{S}' + DE \cdot \mathbf{n} \\ \times (W_p \kappa_p) \mathbf{n} \times \mathbf{S}' \cdot \mathbf{I} + (W_{T,P} \kappa_{T,P} + W_d d_e) \mathbf{S}' \cdot \mathbf{n}. \quad (1)$$

The first line in Eq. (1) corresponds to the rotational and hyperfine structure. The second line describes the interaction with the external magnetic (\mathbf{B}) and electric (\mathbf{E}) fields. The last line corresponds to P - and T, P -odd interactions. B is the rotational constant, Δ is the Ω -doubling constant, \mathbf{n} is the unit vector directed from the heavy nucleus to the light one, and \mathbf{S}' is effective spin [1,2]. In the molecular frame, the tensor contractions

$$\mathbf{I} \cdot \hat{\mathbf{A}} \cdot \mathbf{S}' = A_{\parallel} \mathbf{I}_0 \mathbf{S}'_0 - A_{\perp} (\mathbf{I}_1 \mathbf{S}'_{-1} + \mathbf{I}_{-1} \mathbf{S}'_1) \quad (2)$$

are determined by the hyperfine parameters A_{\parallel} and A_{\perp} . Equations for the parameters of the effective spin-rotational Hamiltonian Eq. (1) are given below.

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To obtain the W_d parameter one can evaluate the expectation value of the following T, P -odd operator (discussed in Refs. [1,18,19]):

$$W_d = \frac{1}{\Omega} \langle \Psi_{2\Pi_{\pm 1/2}} | \sum_i \frac{H_d(i)}{d_e} | \Psi_{2\Pi_{\pm 1/2}} \rangle, \quad (3)$$

where d_e is the value of e EDM, Ψ is the wave function of the considered state of the PbF molecule, $\Omega = \langle \Psi_{2\Pi_{\pm 1/2}} | \mathbf{J} \cdot \mathbf{n} | \Psi_{2\Pi_{\pm 1/2}} \rangle$, \mathbf{J} is the total electronic momentum, \mathbf{n} is the unit vector along the molecular axis directed from Pb to F ($\Omega = \pm 1/2$ for the considered ${}^2\Pi_{\pm 1/2}$ state of PbF),

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \sigma \mathbf{E} \end{pmatrix}, \quad (4)$$

\mathbf{E} is the inner molecular electric field, and σ are the Pauli matrices. In these designations a widely used parameter known as the effective electric field acting on unpaired electrons is $E_{\text{eff}} = W_d |\Omega|$.

The T, P -odd pseudoscalar-scalar electron-nucleus interaction with a characteristic dimensionless constant $k_{T,P}$ is given by the following operator (see Ref. [20]):

$$H_{T,P} = i \frac{G_F}{\sqrt{2}} Z k_{T,P} \gamma_0 \gamma_5 n(\mathbf{r}), \quad (5)$$

where G_F is the Fermi-coupling constant, γ_0 and γ_5 are the Dirac matrices, and $n(\mathbf{r})$ is the nuclear density normalized to unity. To extract the fundamental $k_{T,P}$ constant from an experiment one needs to know the factor $W_{T,P}$ that is determined by the electronic structure of a studied molecular state on a given nucleus:

$$W_{T,P} = \frac{1}{\Omega} \langle \Psi_{2\Pi_{\pm 1/2}} | \sum_i \frac{H_{T,P}(i)}{k_{T,P}} | \Psi_{2\Pi_{\pm 1/2}} \rangle. \quad (6)$$

The P -odd electron-nucleus interaction is characterized by the dimensionless constant k_P , which is given by

$$H_P = k_P \frac{G_F}{\sqrt{2}} \boldsymbol{\alpha} \cdot \mathbf{I} n(\mathbf{r}). \quad (7)$$

To extract the fundamental k_P constant from an experiment one needs to know the electronic parameter W_P , which can be written as

$$W_P = \frac{G_F}{\sqrt{2}} \langle \Psi_{2\Pi_{1/2}} | n(\mathbf{r}) \alpha_+ | \Psi_{2\Pi_{-1/2}} \rangle, \quad (8)$$

where α_+ is defined as

$$\alpha_+ = \alpha_x + i\alpha_y = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} + i \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix}.$$

To compute A_{\parallel} and A_{\perp} on Pb in the ground electronic ${}^2\Pi_{1/2}$ state of the PbF molecule the following matrix element can be evaluated:

$$A_{\parallel} = \frac{\mu_{\text{Pb}}}{I\Omega} \langle \Psi_{2\Pi_{\pm 1/2}} | \sum_i \left(\frac{\boldsymbol{\alpha}_i \times \mathbf{r}_i}{r_i^3} \right)_z | \Psi_{2\Pi_{\pm 1/2}} \rangle, \quad (9)$$

$$A_{\perp} = \frac{\mu_{\text{Pb}}}{I} \langle \Psi_{2\Pi_{1/2}} | \sum_i \left(\frac{\boldsymbol{\alpha}_i \times \mathbf{r}_i}{r_i^3} \right)_+ | \Psi_{2\Pi_{-1/2}} \rangle, \quad (10)$$

where μ_{Pb} is the nuclear magnetic moment of a Pb isotope with spin I , $\boldsymbol{\alpha} = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}$.

III. RESULTS AND DISCUSSIONS

The matrix elements (3,6,8,9,10) are examples of the so-called atom in a compound or AIC properties [21]. They are mean values of operators heavily concentrated in the atomic core of Pb and are sensitive to variation of core-region spin densities of the valence electrons. The matrix elements were computed using a scheme which combines the generalized relativistic effective core potential (GRECP) approach [22,23] with the nonvariational restoration procedure [19]. Compared to direct all-electron Dirac-Coulomb four-component methods, the GRECP approach has an advantage of naturally combining the fully relativistic and scalar-relativistic treatment. Within the latter it is possible in many cases to take account of high-order correlation effects and effects of an extended basis set. Moreover, Breit interaction (as well as quantum electrodynamic and other important effects) can be effectively included into the GRECP operator [22,24,25]. Although the GRECP approximation and the nonvariational restoration procedures introduce a certain theoretical uncertainty, contemporary full-electron studies have not yet been able to unambiguously surpass our approach when it comes to AIC and spectroscopic properties of interest, as one can see from the recent comparative study of ThO [26].

The single-reference two-component relativistic coupled-clusters method with single, double, and perturbative treatment of triple cluster amplitudes, $2c$ -CCSD(T), was used to take account of both the relativistic and correlation effects for valence electrons. For calculation of off-diagonal matrix elements (8,10) the linear-response two-component coupled-clusters method with single and double cluster amplitudes [27] was used. The $1s$ - $4f$ inner-core electrons of Pb were excluded from the molecular correlation calculations using the ‘‘valence’’ semilocal version of the GRECP operator [22]. Thus, 31 electrons [$5s^2 5p^6 5d^{10} 6s^2 6p^2$ (Pb) and $1s^2 2s^2 2p^5$ (F)] were treated explicitly in our correlation calculations. A basis set consisting of 13s, 12p, 8d, 3f, and 1g ([13,12,8,3,1]) contracted Gaussian basis functions on Pb and 6s, 5p, 4d, 3f ([6,5,4,3]) functions on F were used. The basis set on Pb was reoptimized from a previous paper [28], while for F the aug-ccpVQZ basis set [29] with two removed g -type basis functions was employed. In the present calculation we used a Pb-F internuclear distance of 3.9 a.u., which is close to the experimental datum 3.89 a.u. [30]. The coupled-clusters calculations were performed using the DIRAC12 [31] and MRCC [32] codes. The nonvariational restoration code developed in Refs. [33–35] and interfaced to these codes was used to restore the four-component electronic structure near the Pb nucleus.

Results of calculations, as well as the results of previous studies, are given in Table I. According to our analysis the main cause of difference between values of E_{eff} obtained in Ref. [5] and in the present Brief Report is the contribution of outer-core electrons that was not considered in Ref. [5] within 13-electron calculations.

Taking into account the results from Table I and our earlier studies within the two-step procedure and the coupled-clusters approach (e.g., see [26,36]) of E_{eff} , $W_{T,P}$, and A_{\parallel} we expect that the theoretical uncertainty for our final values is smaller than 7%.

TABLE I. Calculated values of the molecule-frame dipole moment (d), effective electric field (E_{eff}), parameter of the T, P -odd pseudoscalar-scalar electron-nucleus neutral currents interaction ($W_{T,P}$), hyperfine structure constants (A_{\parallel}, A_{\perp}), and parameter of the P -odd electron-nucleus interaction (W_P) of the $^2\Pi$ state of PbF.

Method	d (D)	E_{eff} (GV/cm)	$W_{T,P}$ (kHz)	A_{\parallel} (MHz)	A_{\perp} (MHz)	W_P (Hz)
SCF ^a [1]	6.1	29 ± 8	75 ± 24	9120 ± 430	-7850 ± 390	950 ± 300
SCF ^a [2]	4.62	29	55	10 990	-8990	-720
Semiempirical [9]		31				
13 e -SODCI ^b [5]	4.26	33	75	9727	-6860	-990
13 e -SODCI + OC correction ^c [37]	5.00	37	83	10 262		
DHF + CP ^d [10]						-1269
31 e -2 c -CCSD	3.97	41	93	10 265	-7174	-1213
31 e -2 c -CCSD(T)	3.87	40	91	9942		
(Final)						
Experiment [6,8]	3.5 ± 0.3			10 147	-7264	

^aSCF, self-consistent field.

^bThirteen-electron SODCI, spin-orbit direct configuration interaction [5].

^cThirteen-electron SODCI plus correction on correlation of the outer-core electrons. The calculation was aimed at AIC properties.

^dDHF + CP, Dirac-Hartree-Fock plus core polarization [10].

IV. CONCLUSIONS

The relativistic coupled-clusters method combined with the generalized relativistic effective core potential approach and nonvariational one-center restoration technique is applied to evaluate parameters of the spin-rotational effective Hamiltonian in lead monofluoride, which can be used to study the effects of T and P symmetries' violation in molecular-beam or Stark trap [7] experiments. Our results are rather stable with respect to the improvement of the correlation treatment. Also, hyperfine structure constants (A_{\parallel}, A_{\perp}) and the molecule-frame dipole moment are in very good agreement with the available experimental data. This is an essential improvement of the

present calculation compared to the previous one [5] in light of the importance of verifying the values of $E_{\text{eff}}, W_{T,P}$, and W_P , which is of primary interest here.

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