

Further investigation of g factors for the lead monofluoride ground state

L. V. Skripnikov,^{1,2,*} A. N. Petrov,^{1,2,†} A. V. Titov,^{1,2,‡} R. J. Mawhorter,^{3,4} A. L. Baum,³ T. J. Sears,⁵ and J.-U. Grabow⁴

¹National Research Centre “Kurchatov Institute” B. P. Konstantinov Petersburg Nuclear Physics Institute, Gatchina, Leningrad District, 188300 Russia

²Saint-Petersburg University, Saint Petersburg State University, SPbSU, SPbU, 7/9 Universitetskaya nab., Saint Petersburg, 199034 Russia

³Department of Physics and Astronomy, Pomona College, Claremont, California 91711-6359, USA

⁴Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie and Elektrochemie, Lehrgebiet A, Hannover, D-30167 Germany

⁵Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

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We report the results of our theoretical study and analysis of earlier experimental data for the g -factor tensor components of the ground $^2\Pi_{1/2}$ state of the free PbF radical. The values were obtained both within the relativistic coupled-cluster method combined with the generalized relativistic effective core potential approach and with our fit of the experimental data from [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. L. Baum, B.A. thesis, Pomona College, 2011]. The obtained results agree very well with each other but contradict the previous fit performed in the cited works. Our final prediction for g factors is $G_{\parallel} = 0.081(5)$, $G_{\perp} = -0.27(1)$.

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I. INTRODUCTION

With a ground state sensitive to T, P -parity-violating effects, the lead monofluoride molecule PbF has long been a promising candidate in the quest to quantify the electron electric dipole moment (e EDM). It has been studied and discussed during three decades in many papers including [1–6]. It is also predicted to have a very large and negative P -odd nuclear anapole moment [7]. It was recently shown in [8] that some “enhanced” (coincidental) near degeneracy for the levels of opposite parity in the ground rotational state $J = 1/2$ for ^{207}PbF of the ground electronic state $^2\Pi_{1/2}$ [4] takes place that is caused by the near cancellation between the shifts in the energies of these levels due to omega-type doubling and the magnetic hyperfine interaction. One further consequence of this is a very favorable sensitivity to temporal variation of the fundamental constants [9]. From an experimental point of view, this near degeneracy and the small g factors of the $^2\Pi_{1/2}$ ground state both lead to a significant suppression of systematic errors.

In [10] we have calculated the PbF parameters (more generally, the characteristics of atoms in compounds [11–13]) required to interpret the experimental energy shift in terms of the e EDM and other effects of simultaneous violation of space parity (P) and/or time-reversal invariance (T) including the P -odd anapole moment [8] and the T, P -odd pseudoscalar-scalar electron-nucleus neutral current interaction for the ground $^2\Pi_{1/2}$ state. For instance, the effective electric field in PbF was found to be greater than or equal to those in the other transition element and actinide compounds considered (1.7 times larger than in HfF^+ [14,15], 1.4 larger than in PtH^+ [16], and 1.1 larger than in WC [17] and TaN [18] and ThF^+ [13,19]).

In a similar manner to the study of the Zeeman interaction in ThO [20], in the present paper our aim is to study the PbF g factor for the $^2\Pi_{1/2}$ term which is required for preparation of experiments on the molecule [3,21]. Up to now the g factors have been measured in [22,23] only. Previous theoretical estimations and calculations of g factors have been performed in [1,2,5].

II. MOLECULAR HAMILTONIAN

We represent the molecular Hamiltonian for ^{208}PbF as [6]

$$\mathbf{H}_{\text{mol}} = \mathbf{H}_{\text{rot}} + \mathbf{H}_{\text{hfs}} + \mathbf{H}_1 + \mathbf{H}_{\text{ext}}. \quad (1)$$

Here \mathbf{H}_{rot} is the rotational Hamiltonian and \mathbf{H}_{hfs} is the hyperfine interaction between electrons and nuclei. \mathbf{H}_1 includes the nuclear spin-rotational interaction and also effectively takes into account the rotational and hyperfine interactions between $^2\Pi_{1/2}$ and other electronic states. \mathbf{H}_{ext} describes the interaction of the molecule with an external magnetic field \mathbf{B} . Parameters for \mathbf{H}_{rot} , \mathbf{H}_{hfs} , and \mathbf{H}_1 are taken from [6]. For \mathbf{H}_{ext} we have

$$\mathbf{H}_{\text{ext}} = \mu_B \mathbf{B} \cdot \hat{\mathbf{G}} \cdot \mathbf{S}' - g_1 \mu_N \mathbf{B} \cdot \mathbf{I}_1. \quad (2)$$

Here \mathbf{S}' is effective spin defined by the following equations: $\mathbf{S}'_{\hat{n}}|\Omega\rangle = \Omega|\Omega\rangle$, $\mathbf{S}'_{\pm}|\Omega = \mp 1/2\rangle = |\Omega = \pm 1/2\rangle$, $\mathbf{S}'_{\pm}|\Omega = \pm 1/2\rangle = 0$ [1,2]; \mathbf{I}_1 is the angular-momentum operator of the fluorine nucleus; μ_B and μ_N are Bohr and nuclear magnetons, respectively; and $g_1 = 5.25773$ is the ^{19}F nuclear g factor.

In the molecular frame coordinate system the tensor contractions

$$\mathbf{B} \cdot \hat{\mathbf{G}} \cdot \mathbf{S}' = G_{\parallel} \mathbf{B}_0 \mathbf{S}'_0 - G_{\perp} (\mathbf{B}_1 \mathbf{S}'_{-1} + \mathbf{B}_{-1} \mathbf{S}'_1) \quad (3)$$

are determined by the body-fixed g factors:

$$G_{\parallel} = \frac{1}{\Omega} \langle \Psi_{2\Pi_{1/2}} | \hat{L}_{\hat{n}}^e - g_S \hat{S}_{\hat{n}}^e | \Psi_{2\Pi_{1/2}} \rangle, \quad (4)$$

$$G_{\perp} = \langle \Psi_{2\Pi_{1/2}} | \hat{L}_{+}^e - g_S \hat{S}_{+}^e | \Psi_{2\Pi_{-1/2}} \rangle, \quad (5)$$

*leonidos239@gmail.com

†alexandernp@gmail.com

‡http://www.qchem.pnpi.spb.ru

TABLE I. Calculated values of g factors (G_{\parallel} , G_{\perp}) of the $^2\Pi$ state of PbF.

Method	G_{\parallel}	G_{\perp}
SCF ^a [1]	0.034 < G_{\parallel} < 0.114	-0.438 < G_{\perp} < -0.269
SCF ^a [2]	0.114	-0.438
13e-SODCI ^b [5]	0.082	-0.319
31e-CCSD, this work	0.081	-0.274
31e-CCSD(T), this work	0.081	
Experiment [22]	0.12	-0.38
Experiment + fit 1, this work	0.081	-0.269
Experiment + fit 2, this work	0.085	-0.271

^aSCF, self-consistent field.

^bThirteen-electron SODCI, spin-orbit direct configuration interaction [5]. Outer-core electrons $5s^25p^65d^{10}$ of Pb are excluded from the correlation treatment.

where \vec{L}^e and \vec{S}^e are the electronic orbital and electronic spin momentum operators, respectively; $g_S = -2.0023$ is a free-electron g factor; \hat{n} is the unit vector along the molecular axis directed from Pb to F.

In this paper the parameters G_{\parallel} and G_{\perp} are obtained (i) by using Eqs. (4) and (5) from calculation of the *electronic* wave function $\Psi_{2\Pi_{1/2}}$ and (ii) by fitting the experimentally observed transitions reported in [23].

TABLE II. Observed Zeeman shifts $(\Delta U/B)_{\text{obs}}$ (MHz/G) of the $J = 1/2$ to $3/2$ transitions for $^{208}\text{Pb}^{19}\text{F}$ [23]. The number in parentheses gives a two standard deviation error of the final digits of precision. The subscripts U and L refer to the upper and lower energy level of the transition, respectively. F is the total angular momentum of PbF, and MF is its projection on the laboratory axis. The deviation of the n th fit is given by $\delta_n = (\Delta U/B)_{\text{fit}} - (\Delta U/B)_{\text{obs}}$ in units of the last digit of precision.

Unsplit line (MHz)	F_L	F_U	MF_L	MF_U	$(\Delta U/B)_{\text{obs}}$ [23]	δ_1	δ_2
18414.588	1	2	-1	-1	0.0665(13)	-40	-30
			0	0	-0.00050(93)	107	50
			1	1	-0.0635(13)	9	0
			0	0	0.00032(90)	-89	-32
18462.193	0	1	0	0	-0.1369(30)	-4	5
			0	1	0.1363(29)	-2	11
			-1	-1	0.00766(86)	-150	-70
			1	1	-0.00729(92)	119	33
18497.136	1	1	1	0	-0.1428(17)	0	-15
			0	-1	-0.1328(21)	-33	-46
			0	1	0.1345(13)	29	29
			-1	0	0.1427(9)	2	16
			-1	-1	-0.03864(29)	28	100
			0	0	-0.00005(11)	2	5
22574.934	1	2	1	1	0.03851(9)	-14	-87
			1	0	0.1023(36)	64	62
			0	-1	0.07296(25)	-264	-207
			-1	-2	0.03411(60)	-211	-85
			1	2	-0.03406(49)	206	80
			0	1	-0.07267(52)	229	178
			-1	0	-0.10323(79)	-546	-529
			0	-1	0.11139(48)	346	408
22691.931	0	1	0	-1	-0.11133(41)	-346	-414
			0	1			

III. METHODS

The matrix elements (4) and (5) were calculated using a computational scheme similar to that used by us in [10]. The basis set for Pb was taken from [10]. For F the aug-ccpVQZ basis set [24] with two removed g -type basis functions was employed [25]. The Pb-F internuclear distance was set to 3.9 a.u., which is close to the experimental datum 3.8881(4) a.u. [26], which was later confirmed by [27]. Inner core $1s$ - $4f$ electrons of lead were excluded from the correlation calculation using the “valence” semilocal version of the generalized relativistic effective core potential approach [28,29]. Note that the approach allows one to account for the Breit interaction very effectively [28,30,31]. All the other 31 electrons were included into the calculation. Electron correlation effects were considered within the relativistic two-component coupled-cluster approach with accounting for single and double cluster amplitudes, CCSD, as well as single, double, and perturbative triple cluster amplitudes, CCSD(T). Note that the matrix element (5) is off-diagonal. Therefore, it was calculated within the multireference (the active space included $\sigma_{1/2}$ and $\sigma_{-1/2}$ orbitals) linear-response two-component coupled-cluster method with single and double cluster amplitudes [32]. The coupled-cluster calculations were performed using the DIRAC12 [33] and MRCC [34] codes. Matrix elements of the operators corresponding to Eqs. (4) and (5) over the molecular spinors were calculated with the code developed in [13,20,35–38].

To obtain the experimental values for G_{\parallel} and G_{\perp} we have performed two fits using the data from [23]. In “fit 1” the

Zeeman shifts of $J = 1/2$ to $3/2$ transitions for the ground vibrational level of the $^2\Pi_{1/2}$ electronic state are obtained by numerical diagonalization of the molecular Hamiltonian (\mathbf{H}_{mol}) on the basis set of the electronic-rotational wave functions. The scheme of the calculation is similar to that employed in [6,17,39]. Only the G_{\parallel} and G_{\perp} parameters were optimized. The other parameters of \mathbf{H}_{mol} were taken from [6]. In “fit 2” we have reimplemented the scheme described in [22].

IV. RESULTS AND DISCUSSION

The results of our calculations of g factors for the PbF ground state together with the results of previous studies are given in Table I. One can see that the value of G_{\parallel} is stable with respect to improvement of the electron correlation treatment in the present study from CCSD to CCSD(T) level.

G_{\parallel} and G_{\perp} values obtained by fit 1 and fit 2 (see Methods section) are also given in Table I. The deviations of our fits from the observed Zeeman shifts are given in Table II. For the last seven transitions the shifts are reproduced with deviations which are much larger than the declared experimental accuracy. One is inclined to suspect that the experimental accuracy is overestimated for these transitions. We note, however, that the experimental $(\Delta U/B)_{\text{obs}}$ values for Zeeman components that only differ (model independent) in sign (e.g., $F_L, MF_L \rightarrow F_U, MF_U = 1, 0 \rightarrow 2, 1$ versus $1, 0 \rightarrow 2, -1$; $1, 1 \rightarrow 2, 2$ versus $1, -1 \rightarrow 2, -2$; $1, 1 \rightarrow 2, 0$ versus $1, -1 \rightarrow 2, 0$; $0, 0 \rightarrow 1, 1$ versus $0, 0 \rightarrow 1, -1$) agree within their error bars, which indicates correct accuracy estimations. It is also the case that the deviations for those pairs are systematic and not statistical. It seems that the $F_L \rightarrow F_U = 1 \rightarrow 2$ pattern is predicted to be somewhat too narrow while the $F_L \rightarrow F_U = 0 \rightarrow 1$ pattern is somewhat too wide.

We also note that the $G_{\parallel} = 0.085$, $G_{\perp} = -0.271$ parameters obtained in fit 2 differ substantially from the $G_{\parallel} = 0.12$, $G_{\perp} = -0.38$ values obtained by the same method and reported in [22]. While the fit 2 results do demonstrate the tendency of the first-order perturbation theory used in this method

to produce larger values, this and the other assumptions mentioned in [22] should not be large enough to fully explain the difference. As the difference is a common factor of 1.4–1.5, it seems likely that this is due to a missing or misplaced factor of $\sqrt{2}$ (or possibly $3/2$) in the earlier work. Our results here show good agreement between G_{\parallel} and G_{\perp} obtained in fit 1, fit 2, and the *ab initio* calculation. As discussed above in “fit 2” we have followed the scheme described in [22] and obtained a good agreement with “fit 1” and calculations. These combined results are thus strongly in favor of the correctness of the consistent set of values presented here.

Our final values for the g factors are $G_{\parallel} = 0.081(5)$ and $G_{\perp} = -0.27(1)$. It should be noted that these smaller g -factor values and their improved accuracy together favor the aforementioned experimental search for the electron electric dipole moment and other parity-violating and related effects [7,9] in PbF due to the additional suppression of systematic errors. Beyond these several applications, this will be especially important when it comes time to verify the e EDM results of the best current molecular system, ThO.

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