Progress toward the electron electric-dipole-moment search: Theoretical study of the PbF molecule

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We report *ab initio* relativistic correlation calculations of potential curves and spectroscopic constants for the four lowest-lying electronic states of lead monofluoride. We also calculated parameters of the spin-rotational Hamiltonian for the ground $^2\Pi_{1/2}$ and the first excited $A\ ^2\Sigma_{1/2}^+$ states including P,T-odd and P-odd terms. In particular, we have obtained hyperfine constants of the ^{207}Pb nucleus. For the $^2\Pi_{1/2}$ state, $A_\perp = -6859.6$ MHz, $A_\parallel = 9726.9$ MHz and for the $A\ ^2\Sigma_{1/2}^+$ state, $A_\perp = 1720.8$ MHz, $A_\parallel = 3073.3$ MHz. Our values of the ground-state hyperfine constants are in good agreement with previous theoretical studies. We discuss and explain seeming disagreement with the recent experimental data of the sign of the constant $A_\perp$. The effective electric field on the electron E_{eff}, which is important in the planned experiment for searching for the electric dipole moment of the electron, is found to be 3.3×10^{10} V/cm.

Planned experiments to search for the simultaneous violation of the time-reversal invariance (T) and space parity (P) have motivated interest in the theoretical study of the PbF molecule [1–4]. Such P,T violation may be caused either by a P,T-odd electron-nucleus interaction or by an electric dipole moment of the electron (eEDM or d_e), which can exist only as a result of fundamental P,T-odd interactions [5]. Possible experiments to search for P,T-odd interactions were discussed in several books and reviews [6–12].

An experiment to search for an eEDM using the PbF molecule is currently under preparation by the group of Shafer-Ray [3]. The experimentally measured eEDM frequency shifts of a molecule are determined by the effective electric field E_{eff}. The PbF molecule has one of the strongest values of E_{eff} [1,2], making the experiment a good place to test for "new Physics" beyond the standard model, including different supersymmetric models. Many such models predict an eEDM in a range between 10^{-28} and $10^{-29}e$ cm, within reach of a new generation of molecular eEDM experiments [12,13].

Recently, McRaven *et al.* [4] measured hyperfine structure parameters for the ground and first excited states of ^{207}PbF and found them to be in disagreement with previous predictions [1,2]. Taking into account that theoretical studies of lead monofluoride took place decades ago within rather simple theoretical models, we recalculate spectroscopic constants and parameters of the spin-rotational Hamiltonian, H_{sr}, for the PbF molecule. In particular, we focus on the calculations of the effective electric field on the electron E_{eff} and the hyperfine structure constants for the lead nucleus. Our new results are in reasonable agreement with previous calculations [1,2]. We discuss the discrepancy between theory and experiment [4] and argue that it is caused by the incorrect phase factor in the spin-rotational wave function rather than the difference in the sign of the hyperfine constant $A_\perp$.

The Hamiltonian H_{sr} can be written as [2]

$$H_{sr} = B'\mathbf{J}^2 + \Delta\mathbf{S}' \cdot \mathbf{J} + \mathbf{S}'\mathbf{AI} + \mu_0\mathbf{S}'\mathbf{GB} - D\mathbf{n} \cdot \mathbf{E} + W_P\kappa_P\mathbf{n} \times \mathbf{S}' \cdot \mathbf{I} + (W_{P,T}\kappa_{P,T} + W_d d_e)\mathbf{S}' \cdot \mathbf{n}, \quad (1)$$

where the first three terms in the first line correspond to the rotational structure with Ω-doubling and the hyperfine interaction of the effective electron spin $\mathbf{S}', S' = \frac{1}{2}$, with the spin of the nucleus $\mathbf{I}$; B' is the rotational constant, $\mathbf{J}$ is the electron-rotational angular momentum, Δ is the Ω-doubling constant, and $\mathbf{A}$ is the hyperfine structure tensor. Other two terms in the first line describe the interaction of the molecule with the external fields $\mathbf{B}$ and $\mathbf{E}$, $\mathbf{n}$ is the unit vector along the molecular axis, ζ, directed from Pb to F, and $\mathbf{G}$ is the g-factor tensor. The last line corresponds to the interaction with the P-forbidden anapole moment of the nucleus, the P,T-odd weak interactions of the electrons with the heavy nucleus, and the interaction of eEDM with the internal electric field of the molecule; κ_P and $\kappa_{P,T}$ are the anapole constant and the P,T-odd neutral current constant, respectively, for Pb nucleus.

Parameters W_i in (1) cannot be measured experimentally and have to be obtained from the molecular electronic structure calculations. Their accurate knowledge is crucial for extracting the constants κ_P, $\kappa_{P,T}$, and d_e from the experiment. Expressions for calculating parameters W_i can be found in Refs. [1,6,11]. In the literature the effective electric field seen by the unpaired electron is usually used instead of the parameter W_d. It is defined as $E_{\text{eff}} = W_d|\Omega|$, where $\Omega = \langle\Psi_\Omega^e|\mathbf{S}' \cdot \mathbf{n}|\Psi_\Omega^e\rangle = \pm 1/2$ and Ψ_Ω^e is the electronic wave function for the $^2\Pi_{1/2}$ or $^2\Sigma_{1/2}^+$ states.

We use the generalized relativistic effective core potential (GRECP) [14] to simulate the interaction of valence electrons with 68 core electrons of Pb ($1s$ to $4f$). The valence space includes the 4 outermost electrons of lead and all electrons of fluorine. In addition, the $5s$, $5p$, and $5d$ shells of Pb are frozen. The resulting configurations are $6s^2 6p^2$ for Pb and $1s^2 2s^2 2p^5$ for F. For Pb we use the generalized correlation atomic basis set [15,16] ($15s16p12d9f$)/[$5s7p4d2f$] and the GRECP from Ref. [16]. For F we use the ANO-I ($14s9p4d3f$)/[$4s3p2d1f$] atomic basis from the MOLCAS 4.1 library [17].

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Molecular orbitals are obtained by means of the complete active-space self-consistent field method. We use a C_{2v} point group classification scheme to account for molecular symmetry. The next step is to apply the spin-orbit direct configuration interaction (SODCI) approach [18–20] (modified in [21] to account for spin-orbit interaction in the configuration selection procedures). The main idea of this method is to use selected singly and doubly excited configurations with respect to some multiconfigurational reference states within the second-order perturbation theory. Only the most important configurations which give contribution to the energy greater than some chosen threshold T_i are selected. Typically, we do calculations for two thresholds, $T_1 = 5 \times 10^{-10}$ and $T_2 = 5 \times 10^{-11}$ a.u. After that, the SODCI approach is employed in the space of all the selected configurations.

In the present work we calculate the four lowest states, which belong to the configurations $[\ldots]\sigma^2\pi_{1/2}$ $(^2\Pi_{1/2})$, $[\ldots]\sigma^2\pi_{3/2}$ $(^2\Pi_{3/2})$, $[\ldots]\sigma^2\sigma'$ $(A\,^2\Sigma^+_{1/2})$, and $[\ldots]\sigma^2\sigma''$ $(B\,^2\Sigma^+_{1/2})$. Here σ is mainly formed from the $6s$ basis function of Pb, $\pi_{1/2}$ and $\pi_{3/2}$ are close to $6p_x$ and $6p_y$ functions of Pb. The orbitals σ' and σ'' are formed from the $6p_z$ and $7s$ functions of Pb, respectively.

One of the main goals of the present article is to draw potential curves for the ground and three lowest excited states. Therefore, we make calculations for several internuclear distances (from 3.8 to 4.2 a.u.) near the ground-state equilibrium distance ($R_e = 2.0575$ Å ≈ 4.0 a.u.).

Equilibrium internuclear distances, R_e, vibrational constants, w_e, excitation energy, T_e, and dipole moments D for the four lowest states of PbF molecule can be found in Table I. Dipole moments were calculated with threshold T_2 for internuclear distance $R = 4.0$ a.u. Other parameters were calculated for thresholds T_1 and T_2. After that, we applied linear $T = 0$ correction [22] and generalized Davidson correction [23].

TABLE I. Internuclear distances, vibrational constants, T_e, and the dipole moment D (1 D = 0.3934 a.u.) for four lowest states of PbF molecule.

	Reference	R_e (A)	w_e (cm^{-1})	T_e (cm^{-1})	D (D)
$^2\Pi_{1/2}$	[2]	2.06	489		4.62
	[29]	2.0575	503	0	
	[30]				3.5 ± 0.3
	This work	2.08	494	0	4.26
$^2\Pi_{3/2}$	[29]	2.0342	529	8264	
	This work	2.07	522	8259	
$A\,^2\Sigma^+_{1/2}$	[2]	2.18	418		5.5
	[29]	2.1597	395	22 557	
	[30]				2.8 ± 0.2
	This work	2.18	389	23 380	2.51[a]
$B\,^2\Sigma^+_{1/2}$	[29]	1.97	606	35 644	
	This work	1.99	598	36 584	

[a]This value was obtained before experimental result [30] became available.

In this article we are interested in the parameters of the Hamiltonian H_{sr}, which have a rather different nature. Most of them are calculated for the ground and first excited states at $R = 4.0$ a.u., which is close to the equilibrium distance. The components of the g-factor tensor, the molecular dipole moment D, and the Ω-doubling constant, Δ, depend on the wave functions of the valence electrons at large distances, where the chemical bond is formed. On the other hand, such properties as $E_{\text{eff}}, A_\perp, A_\parallel$, the anapole moment constant W_P, and the P,T-odd interaction constant $W_{P,T}$ depend on the wave function of the unpaired electron at short distances inside the lead core. An accurate calculation of such properties can be done only with the four-component relativistic molecular orbitals. However, we have performed calculations on two-component orbitals by means of the pseudopotential. Therefore, at the next stage we need to restore four-component orbitals from the two-component ones. For this purpose we use the nonvariational one-center restoration method developed in Refs. [14,24–28].

One can find calculated parameters of the spin-rotational Hamiltonian H_{sr} for the $^2\Pi_{1/2}$ and $A\,^2\Sigma^+_{1/2}$ states in Table II. Finally, for the internuclear distance $R = 4.0$ a.u. we made a calculation for Ω-doubling constant. Respective results divided by $2B' = 2/MR^2$ for the $^2\Pi_{1/2}$ and $A\,^2\Sigma^+_{1/2}$ states are -0.361 and 1.46 compared to -0.303 and 1.49 in Ref. [4].

According to Table I, the calculated values of T_e are in good agreement with the experimental data. The equilibrium distance, R_e, has slightly higher value than in the experiment. Present values of the vibrational constants are in much better agreement with the experiment than in previous calculation [2].

Note that our value of the ground-state dipole moment is almost the same, as in [2], but the dipole moment of the excited state decreased approximately two times.

Let us look closer at the results for the ground state in Table II. The first point to note is that all theoretical values for $A_\parallel$ are close to each other and are in good agreement with the experimental result [4]. A very different situation takes place for g-factors. Our present value for $G_\parallel$ is two times bigger than the one from Ref. [2]. Our values of the W_i parameters are also significantly bigger than in the previous *ab initio* calculation [2]; for the anapole moment constant W_P and P,T-odd interaction constant $W_{P,T}$ the difference is almost 40%. It is interesting that most of the values obtained here lie between the semiempirical results from Ref. [1].

The most intriguing situation takes place for the hyperfine structure constant $A_\perp$. Here all the theoretical calculations give negative values, while recent experiment [4] gives positive value. Theoretical values for the constants $A_\perp$, $G_\perp$, and the Ω-doubling constant Δ are determined by the off-diagonal matrix elements of the respective electronic operators. The signs of all these parameters depend on the consistent phase conventions for *the electronic wave functions*. In our present calculations electronic phases are the same as in Eq. (14) of Ref. [1]. When we calculate experimental spin-rotational spectrum of the Hamiltonian (1) we need to control phases of *the spin-rotational functions*. The hyperfine energy level structure in

TABLE II. Parameters of the spin-rotational Hamiltonian H_{sr} for $^2\Pi_{1/2}$ and $A\,^2\Sigma_{1/2}^+$ states of PbF molecule. In Ref. [1] calculations were made for small and large spin-orbital mixing. Respective results are marked with (a) and (b).

State	Reference	$A_\perp$ (MHz)	$A_\parallel$ (MHz)	$G_\perp$	$G_\parallel$	$W_d(10^{25}\,\mathrm{Hz}/e\,\mathrm{cm})$	$W_{P,T}$ (kHz)	W_P (kHz)
$^2\Pi_{1/2}$	[2]	-8990	10 990	-0.326	0.040	1.4	55	-0.72
	[4]	7200 ± 150	$10\,300 \pm 800$					
	[30]	-7264	10 147	-0.380 ± 0.020	0.120 ± 0.010			
	[31]					1.5		
	[1] (a)	-7460	8690	-0.269	0.034	1.0	51	-0.65
	[1] (b)	-8240	9550	-0.438	0.114	1.8	99	-1.25
	This work	-6860	9727	-0.319	0.082	1.6	75	-0.99
$A\,^2\Sigma_{1/2}^+$	[4]	-1200 ± 300	3000 ± 2500					
	[32]	1460	2800					
	This work	1721[a]	3073[a]	2.42	1.92	2.5	124	-1.59

[a]This value was obtained before experimental result [32] became available.

Ref. [4] is determined correctly, but the analysis is based on the spin-rotational functions given by Eq. (23) of Ref. [1]. In what follows we argue that the phase factor $(-1)^{J+1/2}$ in this expression is incorrect and should be replaced by $(-1)^{J-1/2}$ [33]. This changes the relation between $A_\perp$ and experimentally observed hyperfine intervals in the spectrum and resolves the discrepancy between theory and experiment for the constant $A_\perp$. The preceding corrected sign convention for $A_\perp$ is already taken into account in [30,32,34].

Let us consider symmetry properties of the wave function of a diatomic molecule at the space inversion operation. Let x,y,z be a laboratory frame and ξ,η,ζ be a molecular body frame. The Euler angles α and β are defined so that the ζ axis coincides with the molecular axis and a third angle $\gamma = 0$. The vibrational wave function is not important here, and the electronic-rotational wave function within the adiabatic approximation in the Hund case c is written as

$$\Psi_\Omega^e(\ldots,\xi_a,\eta_a,\zeta_a,\tilde{\sigma}_a,\ldots,R)\,\theta_{M,\Omega}^J(\alpha,\beta), \qquad (2)$$

where M is the projection of the total angular momentum, J, on the z axis, subscript a enumerates electrons, $\tilde{\sigma}_a = \pm 1$ is the spin variable which corresponds to the projection of the spin of the ath electron on the ζ axis, R is the internuclear distance, and $\theta_{M,\Omega}^J(\alpha,\beta) = \sqrt{(2J+1)/4\pi}\,D_{M,\Omega}^J(\alpha,\beta,\gamma=0)$ is the rotational wave function.

We can express the electronic wave function Ψ_Ω^e in (2) as a unitary transformation of the wave function $\tilde{\Psi}_\Omega^e$ defined in the laboratory frame, $\Psi_\Omega^e = \hat{U}\tilde{\Psi}_\Omega^e$, where unitary operator $\hat{U}$ has the form $\hat{U} = \exp(i\beta J_2^e)\exp(i\alpha J_3^e)$.

Inversion operation in the laboratory frame $\hat{P}$ has clear meaning:

$$\hat{P}\tilde{\Psi}_\Omega^e(\ldots,x_a,y_a,z_a,\sigma_a\ldots,R,\alpha,\beta)\,\theta_{M,\Omega}^J(\alpha,\beta)$$
$$= \tilde{\Psi}_\Omega^e(\ldots,-x_a,-y_a,-z_a,\sigma_a\ldots,R,\alpha+\pi,\pi-\beta)$$
$$\times\theta_{M,\Omega}^J(\alpha+\pi,\pi-\beta).$$

Now we can define inversion operation in the body frame as $\hat{\tilde{P}} = \hat{U}\hat{P}\hat{U}^+$ and apply it to the wave function (2):

$$\hat{\tilde{P}}\Psi_\Omega^e(\ldots,\xi_a,\eta_a,\zeta_a,\tilde{\sigma}_a,\ldots,R)\,\theta_{M,\Omega}^J(\alpha,\beta)$$
$$= i^N\Psi_\Omega^e(\ldots,-\xi_a,\eta_a,\zeta_a,-\tilde{\sigma}_a,\ldots,R)$$
$$\times\theta_{M,\Omega}^J(\alpha+\pi,\pi-\beta), \qquad (3)$$

where $i = \sqrt{-1}$ and N is the number of electrons.

The preceding transformation of the electronic wave function corresponds to the reflection in the $\eta\zeta$ plane. Note that this reflection changes the sign of Ω (as ζ projection of the axial vector **J**) and, therefore, $\Psi_\Omega^e \to \Psi_{-\Omega}^e$. Obviously, the electronic wave function with $\Omega = 0$ should remain unchanged under such transformation up to the phase ± 1. The rotational wave functions are also transformed into each other with changing sign of Ω [35]:

$$\theta_{M,\Omega}^J(\alpha+\pi,\pi-\beta) = (-1)^{J+2\Omega}\theta_{M,-\Omega}^J(\alpha,\beta). \qquad (4)$$

The total electronic rotational wave function (2) has no definite parity, except for the case $\Omega = 0$. Two wave functions (2) with quantum numbers Ω and $-\Omega$ are transformed into each other. Thus, we can form two linear combinations with parity $p = \pm 1$. Let us construct such combinations for the case $\Omega = \pm 1/2$. This case includes $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}^+$ states, which are important for us here. Since the closed electronic shells are invariant under reflection, we can consider transformation only of the valence spinor $\varphi_\omega^e(\xi_a,\eta_a,\zeta_a,\tilde{\sigma})$, where $\omega = \pm 1/2$ is projection of the total angular momentum of the valence electron j_ζ. One can verify that for phase factors accepted in Eq. (14) of Ref. [1] we get

$$\hat{\tilde{P}}\varphi_{1/2}^e(\xi_a,\eta_a,\zeta_a,\tilde{\sigma}) = i\varphi_{1/2}^e(-\xi_a,\eta_a,\zeta_a,-\tilde{\sigma})$$
$$= i\varphi_{-1/2}^e(\xi_a,\eta_a,\zeta_a,\tilde{\sigma}). \qquad (5)$$

Taking into account Eqs. (4) and (5), we can write the wave function of definite parity $|J,M,p\rangle$ as

$$|J,M,p\rangle = \left[\Psi_{1/2}^e\theta_{M,1/2}^J + (-1)^{J-1/2}p\Psi_{-1/2}^e\theta_{M,-1/2}^J\right]/\sqrt{2}. \qquad (6)$$

This wave function differs from Eq. (23) of Ref. [1] by the phase of the second term: $(-1)^{J+1/2} \rightarrow (-1)^{J-1/2}$. As we mentioned earlier, this change resolves the discrepancy between theoretical and experimental values of $A_\perp$ for $^2\Pi_{1/2}$ and $A\,^2\Sigma^+_{1/2}$ in Table II. Equation (6) is in agreement with [36]. We note, however, that Eq. (6) is correct only when the relative phase of the electronic wave function is chosen as in Eq. (14) of Ref. [1]. For different relative phase factors, Eq. (6) will not hold. See also a discussion of this subject in [30].

In conclusion, we note that we have performed a highly accurate electronic structure calculation of the lowest states of PbF. As a result, we have obtained more reliable values of the ground-state spin-rotational Hamiltonian. Our calculated spectroscopic constants are in a better agreement with the existing experimental data. Our value of the effective electric field on the electron is 14% bigger than in previous calculations [2]. In addition, we have proposed a solution to the sign problem for the hyperfine structure constant $A_\perp$.

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