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Addendum to "Possibility of 0-g-factor paramagnetic molecules for measurement of the electron's electric dipole moment"

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Recent experimentation has revealed a discrepancy between the calculated and actual hyperfine structure of the $^{207}Pb^{19}F$ molecule. This discrepancy has been attributed to a misrepresentation of the parity for the ground-state PbF molecule. In a previously published work [Shafer-Ray, Phys. Rev. A **73**, 034102 (2006)], we derived a formula for the electric-field-dependent g factor of the ground-state PbF molecule with the misassigned parity. In this Addendum, we reformulate that work and derive the g factor based on the corrected ground state. We discuss the impact of the corrected g factor of the PbF molecule and conclude that the PbF molecule has a g factor which can be small enough to perform an experiment sensitive to the electron's electric dipole moment.

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There has been extensive experimental [1–14] and theoretical [15–20] work done to understand the detailed rotational and hyperfine structure of the PbF molecule. The recent experimental studies [8–14] and the theoretical studies [16–20] have been motivated by the recognition of PbF as an important molecule sensitive to the electron's electric dipole moment (e-EDM). In Ref. [20], we recognized that the PbF molecule has a zero g factor at a critical value of the externally applied electric field. The high-resolution spectroscopy by McRaven *et al.* [9] resolved the hyperfine structure of the $^{207}Pb^{19}F$ molecule caused by the magnetic moment of the ^{207}Pb nucleus; however, this work revealed a hyperfine-rotational structure markedly different from the prediction of the theory [16]. This disagreement was actually due to a phase error in the rotational wave function and resulted in the misassignment of the parity of the ground state [19]. Soon after the discovery of the phase error, detailed microwave studies of all common isotopologs of PbF [13,14] confirmed the energy level structure of $^{207}Pb^{19}F$ found by McRaven *et al.* [9] and provided spectroscopic constants completely consistent with those of the theory [19].

The history of this phase error in the rotational wave function and its resolution has an impact on the possibility of a molecule for which the g factor of the molecule vanishes at a critical value of the applied electric field. To model such an occurrence, the effective Hamiltonian was used [18]:

$$\mathbf{H}_E = \beta \mathbf{J}^2 + \Delta \mathbf{S}' \cdot \mathbf{J} - D\mathbf{n} \cdot \mathbf{E}. \tag{1}$$

To motivate the work with an analytic solution, it is first assumed that J-state mixing is minimal and the appropriate secular equation is given by

$$\begin{aligned}\langle J'M'\Omega'|H_E|JM\Omega\rangle &= \delta_{JJ'}\delta_{MM'}\left[\left(\beta J(J+1) + \frac{\pm\Delta}{4}\right)\delta_{\Omega\Omega'} \right.\\ &\left. + \frac{\pm\Delta}{4}(2J+1)\delta_{\Omega,-\Omega'}\right] + DE(-1)^{J+\Omega}\sqrt{(2J+1)(2J'+1)}\\ &\times \begin{pmatrix} J' & 1 & J \\ \Omega' & 0 & -\Omega \end{pmatrix}(-1)^{J'-M'}\begin{pmatrix} J' & 1 & J \\ -M' & 0 & M \end{pmatrix}. \end{aligned} \tag{2}$$

Although Eq. (1) is exactly adopted from the original publication, Eq. (2) has Δ replaced with $\pm\Delta$. This ambiguity in the sign allows for the possibility that the true ground state of the molecule is of even $(+\Delta)$ or odd $(-\Delta)$ parity. The sign in the original work was not taken arbitrarily. Given the lack (at the time) of the Zeeman and Stark spectroscopy, the sign was taken so that the addition of the hyperfine structure due to the nuclear spin of the fluorine would be in agreement with the theoretical prediction [16]. Unfortunately this mimicked the sign error that caused the first hyperfine-resolved spectra of the ground state of $^{207}Pb^{19}F$ to be in disagreement with theory.

The incorrect sign of the true ground parity state goes on to alter many conclusions in the previously published literatures [19]. Most importantly, the qualitative picture of the field-dependent g factor of the true ground $J = 1/2$, Ω-doublet state of the $^{208}Pb^{19}F$ molecule should have a g factor which is given by replacing Δ with $-\Delta$ in the original publication:

$$g \approx \frac{1}{3}G_{||} + \frac{2\Delta}{\sqrt{9\Delta^2 + 4D^2E^2}}G_{\perp}. \tag{3}$$

If the $^{208}Pb^{19}F$ molecule can satisfy both the inequality

$$G_{\perp}G_{||}\Delta < 0, \tag{4}$$

and $|G_{\perp}| > \frac{1}{2}|G_{||}|$, the ground-state g factor will vanish at the critical field:

$$E_o \approx \frac{3}{2}\frac{|\Delta|}{D}\sqrt{4\left(\frac{G_{\perp}}{G_{||}}\right)^2 - 1}. \tag{5}$$

Unfortunately, the spectroscopic parameters of $^{208}Pb^{19}F$ do not meet these requirements [14].

Two important points must be made. The first is that, in the presence of a strong electric field, the g factor of the molecule approaches $\frac{1}{3}G_{||}$, a number of the order of $g_e - 2$. Thus, even without the exact zero crossing of the molecular g factor, the g factor becomes small, approaching 0.04. This low value along with quality magnetic shielding allows for great reduction in sensitivity to stray magnetic field effects. Finally, this analysis does not preclude the existence of an e-EDM sensitive molecule with no magnetic moment. For example, careful analysis of the hyperfine substructure of $^{207}Pb^{19}F$ reveals several electric fields for which the g factor does vanish. Unfortunately these states are not overly sensitive to an e-EDM experiment at the critical electric field for which the g factor vanishes.

In summary, a sign error appearing in the rotational wave function led to a disagreement between the theory and the first observed hyperfine energy level structure of the $^{207}Pb^{19}F$ molecule. Failure to catch this sign error also led the author of the paper we are commenting on to falsely predict the existence of a vanishing magnetic moment of the ground state of the $^{208}Pb^{19}F$ molecule. We emphasize that although the magnetic moment of the ground-state $^{208}Pb^{19}F$ does not vanish at a critical value of the applied electric field, it does become very small in the strong fields, approaching a value of 0.04, which is low enough to perform a competitive *e*-EDM experiment.

[1] G. D. Rochester, Proc. R. Soc. London, Sect. A **153**, 407 (1936).
[2] G. D. Rochester, Proc. R. Soc. London, Sect. A **167**, 567 (1938).
[3] S. P. Singh, Indian J. Pure Appl. Phys. **5**, 292 (1967).
[4] D. J. W. Lumley and R. F. Barrow, J. Phys. B **10**, 1537 (1977).
[5] O. Shestakov, A. M. Pravilov, H. Demes, and E. H. Fink, Chem. Phys. **165**, 415 (1992).
[6] J. Chen and P. J. Dagdigian, J. Chem. Phys. **96**, 1030 (1992).
[7] K. Ziebarth, K. D. Setzer, O. Shestakov, and E. H. Fink, J. Mol. Spectrosc. **191**, 108 (1998).
[8] C. P. McRaven, P. Sivakumar, and N. E. Shafer-Ray, Phys. Rev. A **75**, 024502 (2007).
[9] C. P. McRaven, P. Sivakumar, and N. E. Shafer-Ray, Phys. Rev. A **78**, 054502 (2008).
[10] P. Sivakumar, C. P. McRaven, D. Combs, N. E. Shafer-Ray, and V. Ezhov, Phys. Rev. A **77**, 062508 (2008).
[11] P. Sivakumar, C. P. McRaven, P. M. Rupasinghe, T. Z. Yang, N. E. Shafer-Ray, T. J. Sears, and G. E. Hall, Mol. Phys. **108**, 927 (2010).
[12] C. P. McRaven, P. Sivakumar, N. E. Shafer-Ray, G. E. Hall, and T. J. Sears, J. Mol. Spectrosc. **262**, 89 (2010).
[13] L. D. Alphei, J.-U. Grabow, A. N. Petrov, R. Mawhorter, B. Murphy, A. Baum, T. J. Sears, T. Z. Yang, P. M. Rupasinghe, C. P. McRaven, and N. E. Shafer-Ray, Phys. Rev. A **83**, 040501 (2011).
[14] 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. Alphei, and J.-U. Grabow, Phys. Rev. A **84**, 022508 (2011).
[15] K. Balasubramanian, J. Chem. Phys. **83**, 2311 (1985).
[16] M. G. Kozlov, V. I. Fomichev, Y. Y. Dmitriev, L. N. Labzovsky, and A. V. Titov, J. Phys. B **20**, 4939 (1987).
[17] Y. Y. Dmitriev, Y. G. Khait, M. G. Kozlov, L. N. Labzovsky, A. O. Mitrushenkov, A. V. Shtoff, and A. V. Titov, Phys. Lett. A **167**, 280 (1992).
[18] M. G. Kozlov and L. N. Labzowsky, J. Phys. B **28**, 1933 (1995).
[19] K. I. Baklanov, A. N. Petrov, A. V. Titov, and M. G. Kozlov, Phys. Rev. A **82**, 060501 (2010).
[20] N. E. Shafer-Ray, Phys. Rev. A **73**, 034102 (2006).