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

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The electric-field-dependent g factor of the ground state of $^2\Pi_{1/2}$ molecules is predicted cross zero at a specific value of electric field. Furthermore, Edg/dE evaluated at this field is expected to be small, allowing for extremely precise zeroing of the molecular magnetic moment. For the PbF molecule, we estimate this field to be 68 kV/cm. If this prediction is correct, PbF could provide a uniquely sensitive probe of the electric dipole moment of the electron.

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It is immediately obvious that a videotape of a window breaking played in reverse is not physical: Shards of glass do not spontaneously reassemble to form a perfect window. The discovery of a more subtle form of time-reversal asymmetry in 1964, namely the observation of a T-forbidden decay channel of the K-long meson [1], expanded our understanding of the direction of time beyond the ever increasing entropy of a closed system and led to the 1980 Nobel Prize in Physics. A third and completely different form of time-reversal asymmetry was first proposed by Purcell and Ramsey in 1950 [2]. Here the dynamics of a single particle moving in a combined electric and magnetic field may itself depend on the direction of time. Such T-forbidden dynamics would be the result of a nonzero permanent electric dipole moment (EDM) parallel to the particle's intrinsic spin $\vec{S}$. This dynamics would be governed by an energy $(\mu\vec{B}+p\vec{E})\cdot\vec{S}$ which changes value upon time reversal because $\vec{B}$ is T-odd and $\vec{E}$ is T-even. Such time-asymmetric dynamics has not been observed because, although all particles with nonzero spin have a nonzero magnetic moment μ, no nonzero value of p has ever been measured. If $p\neq 0$ were to be measured, a new arrow pointing to the direction of time would be found.

Purcell and Ramsey's realization [2] of the possibility of a nonzero permanent electric dipole moment of a particle initiated a search for the electric dipole moment of the electron that is now in its 54th year. Limits placed on the value of the electric dipole moment [2–17] have culminated with the value $p_e < 1.6\times 10^{-27}$ e cm resulting from precise resonant spectroscopy of the Tl atom [9,14,15,17]. The significance of this limit on the value of p_e goes beyond the philosophical implications of dynamics that are sensitive to the direction of time, bearing directly on our search for a fundamental theory of all physical forces. An often-quoted Standard Model value of p_e is $p_{e,\mathrm{SM}} \leqslant 10^{-38}$ e cm [18]. This dipole moment is beyond current experimental reach. Supersymmetric models, on the other hand, predict electronic EDM's in the range 10^{-30} e cm $< d_{e,\mathrm{SUSY}} < 10^{-25}$ e cm [19]. It is of little wonder that measuring electric dipole moments has sparked widespread popular interest among physicists [20,21]. In this paper, we discuss a new system for probing the electron's electric dipole moment with a seven-order-of-magnitude suppression in sensitivity to background magnetic fields.

For any system of total angular momentum F in a pure electric field, states that only differ in the sign of the projection M_F along the electric field axis are expected to be degenerate. A nonzero electronic electric dipole moment would split this degeneracy. Modern atomic and molecular searches for a permanent electric dipole moment probe for such a splitting. It was established long ago [22] that the splitting between two such states of a relativistic atom is much greater than the energy difference $\Delta u_e = 2p_eE$ expected from a single free electron. The Berkeley investigation of the Tl atom responsible for the current limit [15,17] benefited from a calculated [23] enhancement of $-585\Delta u_e$.

The large internal fields of relativistic paramagnetic molecules led to an exaggerated sensitivity to electron electric dipole moments [24]. Thus a given electron electric dipole moment causes a much bigger energy split between the $\pm M_F$ levels of a molecule than it does for an atom. In addition to enhanced sensitivity to an electric dipole moment, the large tensor splitting of a molecule makes it immune to $\vec{v}\times\vec{E}$ effects that limit measurements of atomic systems [16]. For this reason, the next limit is likely to come from studies of molecules, or by the recently initiated work in the solid state by Lamoreaux and co-workers [25,26].

As a $^2\Pi_{1/2}$ molecule, PbF provides an additional advantage over other heavy paramagnetic molecules, namely the existence of an electric field at which the magnetic moment is zero. This occurs when the small magnetic moment along the diatomic axis is canceled by the larger but rotationally averaged magnetic moment perpendicular to the diatomic axis. Consideration of the spin rotational Hamiltonian $\mathbf{H}_E$ allows one to predict the field at which this occurs,

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

Here $\mathbf{H}_E$ is simplified from the spin rotational Hamiltonian of Kozlov and Labzowsky [27] to neglect hyperfine structure. (A full analysis including hyperfine interaction changes the value of the electric field at which the magnetic moment is zero by roughly 1% and therefore may be ignored for the discussion that follows.) The first term of Eq. (1) gives the usual rotational energy. The second gives the Ω-doubling energy and is written in terms of a pseudospin that gives the projection of total electronic angular momentum on the in-

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ternuclear axis. In this way both $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ molecules may be considered, provided that for the latter case we let $\Delta=-2\beta+\gamma$, where $\gamma \ll \beta$ is the spin-rotational constant [27]. The final term gives the Stark interaction where D is the dipole moment of the molecule, $\mathbf{n}$ is the internuclear axis, and $\mathbf{E}$ is the electric field.

The Stark energies and electric-field-dependent spin rotational wave functions may be found by solving a secular equation in a basis described by quantum numbers $|J,M,\Omega\rangle$ where J gives the total angular momentum, M the projection of total angular momentum on the electric field axis, and $\Omega=\pm\frac{1}{2}$ the projection of angular momentum on the internuclear axis. The matrix elements of H_E then become

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

The interaction with a weak background field may be treated as a perturbation. Thus we need only find the expectation of the Zeeman interaction

$$H_B=\mu_B\mathbf{S}'\cdot\hat{G}\cdot\mathbf{B}. \tag{3}$$

Here the tensor $\hat{G}$ gives the strength of the Zeeman interaction and is diagonal in the molecular frame. The elements of H_B in our chosen basis can be shown to be given by

$$\begin{aligned}\langle J'M'\Omega'|H_B|JM\Omega\rangle &= \sum_{q,r}\mu_B B^1_{-r}\sqrt{\frac{3}{2}(2J+1)(2J'+1)}\\ &\quad\times G_q(-1)^{r+J-(1/2)}\\ &\quad\times\begin{pmatrix}\frac{1}{2} & 1 & \frac{1}{2}\\ \Omega' & q & -\Omega\end{pmatrix}\times\begin{pmatrix} J' & 1 & J\\ \Omega' & q & -\Omega\end{pmatrix}\end{aligned} \tag{4}$$

$$\times(-1)^{J'-M'}\begin{pmatrix} J' & 1 & J\\ -M' & r & M\end{pmatrix}. \tag{5}$$

Here the ranges of r and q in the sum are from -1 to 1, $G_0=G_\parallel$, $G_{\pm1}=G_\perp$, $B^1_0=B_z$, and $B^1_{\pm1}=\mp(B_x\pm iB_y)/2^{1/2}$. In the presence of a strong electric field, the hyperfine interaction leads to a large tensor splitting, causing $B_\pm$ not to contribute to the first-order Zeeman effect [16]. For this reason, we need only consider $r=0$.

We are interested in the electric field at which the ground-state magnetic moment goes to zero. If we ignore the effect of the upper rotational levels on the ground state, then we need only solve a 2×2 secular equation. For this case, the g factor can be found by determining the lowest-energy eigenvector of $\langle J'M'\Omega'|H_E|JM\Omega\rangle$ and then dividing the expectation value of H_B by $\mu_B B_z$. The result is

$$g\approx\frac{1}{3}G_\parallel-\frac{2\Delta}{\sqrt{9\Delta^2+4D^2E^2}}G_\perp. \tag{6}$$

Provided the molecule provides the positive product

$$G_\perp G_\parallel\Delta>0, \tag{7}$$

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

$$E_o\approx\frac{3}{2}\frac{|\Delta|}{D}\sqrt{4\left(\frac{G_\perp}{G_\parallel}\right)^2-1}. \tag{8}$$

The values of g and E_o are approximate because the result considers the interaction of only the $\pm\Omega$ states of the lowest $J=\frac{1}{2}$ state. Further analysis shows that six rotational states must be included to obtain 1% convergence to the value of E_o. For $J>\frac{1}{2}$, the limitations of this simple two-state model are more dramatic, with the two-state model predicting an electric field magnitude for which $g=0$, but numerical inclusion of a large number of rotational states showing no such magnitude at any field that could be reasonably achieved in a laboratory setting.

For a $^2\Sigma_{1/2}$ molecule, one expects $\Delta=-2\beta+\gamma$ to be less than zero. For the electronic-EDM sensitive molecules YbF and HgF, the electronic spin is not strongly coupled to the internuclear axis. Thus both $G_\parallel$ and $G_\perp$ are both roughly 2 and the product of Eq. (7) is less than zero. This implies the ground state g factor will not vanish, but does not necessarily imply the g factor of an excited state will not vanish. However, an analysis of the electric-field-dependent-g factor of HgF for fields up to 500 kV/cm and rotational states as high as $J=\frac{11}{2}$ showed no situation for which $|g|$ becomes less than 0.5. The YbF molecule has similar values of Δ, $G_\parallel$, and $G_\perp$ and is therefore unlikely to behave differently.

The magnetic moment of the $^2\Pi_{1/2}$ ground state of PbF is influenced not only by electronic spin, but also by electronic orbital angular momentum and strong spin-orbit interactions. Thus one does not expect $G_\parallel$ and $G_\perp$ to be the same. The only reported values of $G_\parallel$ and $G_\perp$ are calculations consistent with this picture, giving $G_\perp=-0.326$ and $G_\parallel=0.034$ [28]. With $\Delta=-0.138\ \text{cm}^{-1}$, $\beta=0.231\ \text{cm}^{-1}$ [29,30], and $D=4.62D$ [31,32], Eq. (8) predicts $g=0$ at a field $E_o=51.0$ kV/cm. A more careful analysis considering the interaction of J levels up to 11/2 gives $E_o=67.7$ kV/cm, whereas inclusion of the hyperfine interaction gives $E_o=67.4$ kV/cm.

For an experiment carried out at the electric field E_o, the effective moment of the molecule will depend on the range of electric fields observed by the molecule. Specifically

$$\Delta g=\left.E_o\frac{dg}{dE}\right|_{E_o}f_E \tag{9}$$

$$\approx\frac{8D^2E_o^2}{3(9\Delta^2+4D^2E_o^2)}G_\parallel f_E \tag{10}$$

$$=0.022 f_E \text{ for } X_1{}^2\Pi_{1/2}\text{PbF}. \quad (11)$$

Here f_E is the fractional variation in the electric field. For an experiment designed to be done in a uniform electric field, f_E could be as low as 10^{-5}, corresponding to an energy difference between the $J=\frac{1}{2}$, $M=\pm\frac{1}{2}$ states to be $\mu_B \Delta g = 0.3\ \mu\text{Hz}/\mu\text{G}$. The electronic EDM induced energy split is expected to be $12\ \text{mHz}/(10^{-27}\ e\ \text{cm})$) [28]. Thus, in an optical resonance molecular beam experiment for which the magnetic field is shielded to 1.0 μG, one would expect background magnetic fields parallel to the electric field to contribute at the $2.5\times 10^{-32}\ e$ cm level. Background fields perpendicular to the electric field are expected to contribute at a much smaller level [16]. This zeroing of the g factor corresponds to a roughly seven-order-of-magnitude improvement in tolerance to background magnetic fields as compared to other molecular electronic EDM experiments and a roughly ten-order-of-magnitude improvement compared to atomic electronic EDM experiments.

There are many ways in which the possibility described here could falter. One is that the condition of Eq. (7) is not met. However, in a personal communication just before submitting this manuscript, Mikhail Kozolov argued that the parameters η and ξ which describe the relative Σ and Π character of PbF [28] will not allow for a negative value product $G_\perp G_\parallel \Delta$. Another failing might be that $G_\parallel$ is much smaller than predicted, causing the critical field to be too great to be achieved in the laboratory. It is also important to note that background magnetic fields are only one of many sources of error in electronic EDM experiments. One must still overcome problems including limited statistics and geometric phase effects. That said, if measured values of $G_\parallel$ and $G_\perp$ give a critical field E_o that is accessible in the laboratory, ground state $g=0$ PbF molecules may provide a uniquely sensitive probe of the electron's electric dipole moment.

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[1] J. H. Christenson, J. W. Cronin, V. L. Fitch, and R. Turlay, Phys. Rev. Lett. **13**, 138 (1964).
[2] E. Purcell and N. Ramsey, Phys. Rev. **78**, 807 (1950).
[3] E. Salpter, Phys. Rev. **112**, 1642 (1958).
[4] E. S. Ensberg, Bull. Am. Phys. Soc. **7**, 534 (1962).
[5] P. Sandars and E. Lipworth, Phys. Rev. Lett. **13**, 718 (1964).
[6] R. Rand, Phys. Rev. **140**, B1605 (1965).
[7] E. S. Ensberg, Phys. Rev. **153**, 36 (1967).
[8] M. Weisskopf, Phys. Rev. Lett. **21**, 1645 (1968).
[9] H. Gould, Phys. Rev. Lett. **24**, 1091 (1970).
[10] M. Player and P. Sandars, J. Phys. B **3**, 1620 (1970).
[11] B. Vasil'iev and E. Kolycheva, Zh. Eksp. Teor. Fiz. **74**, 466 (1978).
[12] F. Huang-Hellinger, Ph.D. thesis, University of Washington (1987).
[13] S. A. Murthy, D. Krause, Z. L. Li, and L. R. Hunter, Phys. Rev. Lett. **63**, 965 (1989).
[14] K. Abdullah, C. Carlberg, E. D. Commins, H. Gould, and S. B. Ross, Phys. Rev. Lett. **65**, 2347 (1990).
[15] E. D. Commins, S. B. Ross, D. DeMille, and B. C. Regan, Phys. Rev. A **50**, 2960 (1994).
[16] J. J. Hudson, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, Phys. Rev. Lett. **89**, 023003 (2002).
[17] B. Regan, E. D. Commins, C. J. Schmidt, and D. DeMille, Phys. Rev. Lett. **88**, 071805 (2002).
[18] F. Hoogeveen, Nucl. Phys. B **341**, 322 (1990).
[19] R. Arnowitt, B. Dutta, and Y. Santoso, Phys. Rev. D **64**, 113010 (2001).
[20] E. Hinds, Phys. Scr., T **T70**, 34 (1997).
[21] N. Fortson, P. Sandars, and S. Barr, Phys. Today **5**(6), 33 (2003).
[22] P. Sandars, Phys. Lett. **14**, 194 (1965).
[23] Z. W. Liu and H. P. Kelly, Phys. Rev. A **45**, R4210 (1992).
[24] P. Sandars, At. Phys. **14**, 71 (1975).
[25] S. K. Lamoreaux, Phys. Rev. A **66**, 022109 (2002).
[26] C. Yu-Lu and S. Lamoreaux, Lepton Moments International Symposium, Yarmouthport, Cape Cod, MA (2003).
[27] M. Kozlov and L. Labzowsky, J. Phys. B **28**, 1933 (1995).
[28] M. Kozlov, V. Fomichev, Y. Y. Dmitriev, L. Labzovsky, and A. Titov, J. Phys. B **20**, 4939 (1987).
[29] D. Lumley and R. Barrow, J. Phys. B **10**, 1537 (1977).
[30] K. Ziebarth, K. Setzer, O. Shestakov, and E. Fink, J. Mol. Spectrosc. **191**, 108 (1998).
[31] C. T. Munger, Phys. Rev. A **72**, 012506 (2005).
[32] Y. Y. Dmitriev, Y. G. Khait, M. Kozlov, L. Labzovsky, A. Mitrushenkov, A. Shtoff, and A. Titov, Phys. Lett. A **167**, 280 (1992).