MEASURABILITY OF THE PROTON ELECTRIC DIPOLE MOMENT

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Calculations are presented which suggest that a suitable molecular-beam resonance experiment can form a sensitive test for the existence of an electric dipole moment on the proton.

In this Letter we report calculations which suggest that a suitable molecular-beam resonance experiment can provide a sensitive test for the existence of an electric dipole moment (edm) on the proton. The detection of such a moment would provide unambiguous evidence for the violation of time-reversal invariance. While this violation is suggested by the CP-nonconserving $K_L^0 \to 2\pi$ decays,[1] there is as yet no direct evidence available.

The size of the edm on the nucleon to be expected on the basis of the observed $K_L^0 \to 2\pi$ decay has been the subject of a number of calculations.[2] The results are highly dependent on the model of CP-invariance violation chosen and range from $e\times10^{-19}$ cm to $e\times10^{-26}$ cm. However, many different models predict a value in the range of $e\times10^{-22}$ cm, and this is clearly a region of considerable interest.

This situation has stimulated a number of experiments[3-5] on the electric dipole moment of the neutron. The long-standing limit of 2×10^{-20} $e\times$cm has been considerably improved. Ramsey and his co-workers[3] find from a beam resonance experiment $d_n = (-2\pm3)\times10^{-22}$ $e\times$ cm. Shull and Nathans, using a neutron-scattering method, obtain a result of very similar precision, $d_n = (2.4\times3.9)\times10^{-22}$ $e\times$cm.

The situation for the edm of the proton is very different. Because it is charged, the beam and scattering methods used on the neutron are not applicable. The best published value[6] appears to be $d_p \lesssim 1.3\times10^{-13}$ $e\times$cm, which was obtained from a calculation of the effect of an edm on the Lamb shift in hydrogen. It is probable that a limit several orders of magnitude better than this can be obtained from current experiments[7] on the edm of alkali atoms. Even so, the limit on the proton edm is clearly much worse than that on the neutron and is not yet in the region of experimental interest. We suggest here that a precision beam resonance experiment on TlF in the presence of parallel electric and magnetic fields can form a test for the proton edm of sensitivity comparable with the neutron experiments quoted above.

At first sight, the search for an edm in a molecule would seem unprofitable. The electric dipole moment of each particle interacts with the electric field acting on it. But the particles which make up the molecule are charged and are in equilibrium under their mutual electrostatic forces. Each particle must therefore experience an electric field which averages to zero, and one would not expect any first-order edm interactions.

Several authors[8-11] have shown that this argument is not exact and that there can be linear edm effects in atoms and molecules. Schiff[10] has considered the measurability of edm's on nuclei. He showed that there can be a term in the energy linear in the nuclear edm either if the nucleus is subject to nonelectrostatic forces such as the magnetic hyperfine interaction, or if the nucleus has finite size or structure. In the systems to be considered here, the finite-size effect is dominant. Schiff[10] has shown that the residual edm interaction due to the finite size of the nucleus can be expressed in terms of the Hamiltonian

$$H_{\mathrm{edm}} = \sum_{N,i} e\vec{\mathrm{d}}_N \times \int \frac{(\vec{\mathrm{r}}_{iN} - \vec{\mathrm{r}}_{nN})}{(|\vec{\mathrm{r}}_{iN} - \vec{\mathrm{r}}_{nN}|)^3} \rho_N(\vec{\mathrm{r}}_{nN}) d^3 r_{nN}. \quad (1)$$

The sum over N and i spans the nuclei and the electrons in the system under consideration. d_N is the operator representing the nuclear edm and is the difference between the normalized distributions of charge and edm in the Nth nucleus. The radius vectors $\vec{\mathrm{r}}_{iN}$ and $\vec{\mathrm{r}}_{nN}$ are taken from the center of mass of the nucleus N.

In free atoms or molecules which have inversion symmetry in the absence of external fields, the expectation value of the Hamiltonian (1) must vanish as it is an odd-parity operator. But when the particle is placed in an external

field, the inversion symmetry can be destroyed, and the expectation value of (1) need not be zero. This is the basis of the determination of a limit on the nuclear edm from the atomic-beam experiments mentioned above. The point that we wish to make in this paper is that such effects can be much larger in a suitable polar molecule since a polar molecule can be almost completely polarized in attainable laboratory electric fields, whereas the polarization that can be induced in an atom is extremely small.

The detection of edm effects in a molecule is somewhat more difficult than in an atom because the molecule already possesses a linear Stark effect. One can get around this difficulty by using a magnetic resonance involving the nuclear spin. If this resonance is excited in parallel electric and magnetic fields, the edm interaction (1) will produce a slight dependence of the resonance frequency on the relative sense of the two fields. Thus, an edm effect will show up through a slight shift of the resonance as one field is reversed with respect to the other.

The choice of the best type of molecule to use is determined by the requirements that it be suitable for beam work, that it contain as heavy an atom as possible, and that the nucleus of this atom have an unpaired proton. The second condition is very important since the edm interaction (1) increases extremely rapidly with atomic number. The outstanding choice appears to be TlF. It is convenient for beam work, its properties are known, Tl is very heavy, and the nuclei contain unpaired protons.

To relate experimental sensitivity to the edm of the Tl nucleus, and hence to that of the proton, we have to take the expectation value of (1) over the appropriate molecular wave functions. Unfortunately, no wave function is available for a molecule as heavy as TlF, and the calculation of one would be a major computational problem.

However, self-consistent field functions are available for the lighter but electronically similar molecules BF,[12] AlF,[13] and GaF.[13] These functions are expressed in the familiar LCAO form in terms of spherical harmonics and radial functions centered on the two nuclei. It is easy to show that with a wave function of this form, the expectation value of the edm Hamiltonian (1) can be factorized into nuclear and electronic parts. The result is most conveniently expressed in terms of the effective electric field at the nuclear edm. By symmetry, this must lie along the internuclear axis and will average to zero in the absence of an external field. When the molecule is polarized by a field, the effective field at the nucleus will no longer average to zero but will be parallel to the external field. Its magnitude is given by

$$E_{\text{eff}} = R_0^2 \chi = R_0^2 \sum_i \frac{1}{\sqrt{3}} \left\{ \frac{R_p^i(r) R_s^i(r)}{r^3} \right\}_{r \to 0} . \quad (2)$$

R_0^2 is a quantity introduced by Schiff[10] which is essentially the mean-square radius of the difference between the normalized charge and edm distributions in the nucleus. The sum over i is taken over the single-particle functions which make up the molecular wave function. $R_s^i(r)$ and $R_p^i(r)$ are the radial parts of the s and p components centered on the nucleus of interest in the ith single-particle function.

We have evaluated χ for the three molecules BF, AlF, and GaF, and the results are displayed in Table I. There are two important features of these calculations: First, the value of χ increases rapidly with Z. Second, the only appreciable contribution to χ comes from the highly polarized outer orbitals of the molecule.

In order to extrapolate these results to TlF, we make three plausible assumptions: (a) that χ can be factorized into an outer part which expresses the relative admixtures of s and p functions in the molecular wave function, and an inner part which depends on the magnitude of the radial functions $R_s^i(r)$ and $R_p^i(r)$ near the nucleus; (b) that these s and p admixtures do not vary very much along a series of electronically similar molecules; (c) that the behavior of the radial wave functions near the nucleus can be adequately represented by the outer-shell wave functions of the appropriate free atom.

If these assumptions are good then the ratio

Table I. Calculated values of χ and β for BF, AlF, and GaF. All values in atomic units.

Molecule	χ	β
BF	3.15	0.093
AlF	16.4	0.095
GaF	97	0.075

$\beta = \chi/\{R_p{}^a(r)R_S{}^a(r)/r^3\}_{r\to 0}$ should be approximately constant over a range of molecules. To check this we have made calculations of β for B, Al, and Ga using our calculated values of χ and the atomic functions of Herman and Skillman.[14] The results are displayed in column 3 of Table I. We see that the ratio is indeed remarkably constant over the series of molecules for which χ has a range of 30.

We now use these results of our calculations to estimate the value of the effective electric field seen by the Tl nucleus in TlF. We do this by assuming that the constancy of β extends to TlF. From the wave functions of Herman and Skillman,[14] we find $\{R_S{}^a(r)R_p{}^a(r)/r^3\}_{r\to 0} = 7500$ a.u. for Tl which, combined with the value $\beta \approx 0.08$ from Table I, yields $\chi \approx 600$ a.u.

In order to calculate the effective field we also need a value for $R_0{}^2$. We have made an estimate of this by assuming that the nucleus is a uniformly charged sphere of radius $R = 1.3A^{1/3} \times 10^{-13}$ cm and that the edm distribution is that of the unpaired $s_{1/2}$ proton moving in a three-dimensional, infinite potential well of this radius. We find with this assumption $R_0{}^2 = (4/15)R^2$. On substituting these values for χ and $R_0{}^2$ into (2), we obtain

$$E_{\text{eff}} \approx 20\,000 \text{ V/cm}$$

as our estimate of the effective field at the Tl nucleus.

From this value of the effective electric field, we can estimate the sensitivity of a beam experiment to the edm of the proton. We assume that we can detect a resonance shift as small as 10^{-3} Hz. This figure is based on experience with atoms and assumes a 100-Hz-wide resonance line and a total resonance signal of greater than 10^{10} molecules during the course of the experiment. With this sensitivity, it should be possible to detect an edm on the Tl nucleus of the order of $1\times10^{-22}e\times$cm. The sensitivity to the edm of the proton is essentially the same since the two isotopes of Tl have $s_{1/2}$ proton states with projection factor unity.

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[1]J. H. Christenson, J. W. Cronin, V. L. Fitch, and R. Turlay, Phys. Rev. Letters 13, 138 (1964).

[2]For a summary, see P. D. Miller, W. B. Dress, J. K. Baird, and N. F. Ramsey, Phys. Rev. Letters 19, 381 (1967).

[3]See Miller et al., Ref. 2.

[4]C. G. Shull and R. Nathans, Phys. Rev. Letters 19, 384 (1967).

[5]V. W. Cohen, E. Lipworth, N. F. Ramsey, and H. B. Silsbee, private communication; K. F. Smith, private communication.

[6]R. M. Sternheimer, Phys. Rev. 113, 828 (1959).

[7]T. Stein, J. P. Carrico, E. Lipworth, and M. C. Weisskopf, Phys. Rev. Letters, 19, 741 (1967); J. R. P. Angel, P. G. H. Sanders, and M. H. Tinker, Phys. Letters 25A, 160 (1967).

[8]E. E. Salpeter, Phys. Rev. 112, 1642 (1958).

[9]M. Sachs and S. L. Schwebel, Ann. Phys. (N.Y.) 6, 244 (1959), and 8, 475 (1959).

[10]L. I. Schiff, Phys. Rev. 132, 2194 (1963).

[11]P. G. H. Sandars, Phys. Letters 14, 194 (1965), and 22, 290 (1966).

[12]R. K. Nesbet, J. Chem. Phys. 40, 3619 (1964).

[13]C. Moser, private communication.

[14]F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).