Electric Polarization of Br Nuclei in Atomic Br and Molecular LiBr

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An explanation is given for the failure to observe the electric polarization of $Br^{79,81}$ nuclei in atomic Br and molecular LiBr from hfs spectra.

1. Introduction

A nucleus in an atom or molecule is polarized by the field at the nucleus due to electronic charge. The energy of electric polarization contributes to the hfs of the atom[1]. There exists a history of unsuccessful attempts to verify this experimentally[2]. The problem is reviewed at this time for two reasons: (1) Experiments were done recently which provide a sensitivity which is unique up to now for the observation of this polarization[3,4]. (2) A related effect occurs in a muonic-atom and there is cause to believe that its presence will be confirmed soon[5]. Despite a precise measurement of the relevant spectra, recent experiments failed to confirm the polarization of Br nuclei in atomic Br and molecular LiBr. An explanation for this negative result is offered in this work[6]. It is concluded that difficulties associated with observing the effect are not readily overcome. Further, this is the case for other atoms, molecules, and nuclei as well. This confirms the importance of current efforts to observe the related effect in a muonic-atom.

The principal results of this work were given earlier[7].

2. Polarizability and HFS

The electric polarizability of a nucleus is in general a tensor. The time average of the electric field at the nucleus in an atom is zero. This follows from the Hellmann-Feynman theorem[8] and the requirement that the total force on the nucleus be zero. The time average of the square of the electric field is in general not zero. Accordingly, the energy of electric polarization is[1]

$$-\tfrac{1}{2}\,\boldsymbol{\alpha} : (\mathbf{EE}) = -\tfrac{1}{2}\,(\boldsymbol{\alpha} - \alpha\,\mathbf{1}):(\mathbf{EE} - \tfrac{1}{3}E^2\,\mathbf{1}) - \tfrac{1}{2}\,\alpha\,E^2,$$

in which

$$W_{\mathrm{p}} = -\tfrac{1}{2}\,(\boldsymbol{\alpha} - \alpha\,\mathbf{1}):(\mathbf{EE} - \tfrac{1}{3}E^2\,\mathbf{1}). \qquad (1)$$

Equation (1) gives the contribution of the tensor part of the polarizability to the energy. The indicated product is the tensor double-product[9]. The contribution of the scalar part of the polarizability is given by $-(\tfrac{1}{2}\,\alpha\,E^2)$.

This term is not of interest since it has no dependence on the relative orientation of $\boldsymbol{I}$ and $\boldsymbol{J}$, where $\boldsymbol{I}$ is the spin angular momentum of the nucleus and $\boldsymbol{J}$ is the total electronic angular momentum of the atom[10]. The tensors $(\boldsymbol{\alpha} - \alpha\,\mathbf{1})_{ij}$ and $(\mathbf{EE} - \tfrac{1}{3}E^2\,\mathbf{1})_{ij}$ are symmetric and traceless; $\alpha = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$, $E^2 = (E_x^2 + E_y^2 + E_z^2)$, and $\mathbf{1}$ is the unit tensor. Due to the specific properties of $(\boldsymbol{\alpha} - \alpha\,\mathbf{1})_{ij}$, it may be replaced within a constant by $\{\tfrac{3}{2}(I_i\,I_j + I_j\,I_i) - \delta_{ij}\,I^2\}$ for the calculation of matrix elements which are diagonal in I. Similarly, $(\mathbf{EE} - \tfrac{1}{3}E^2\,\mathbf{1})_{ij}$ may be replaced by $\{\tfrac{3}{2}(J_i\,J_j + J_j\,J_i) - \delta_{ij}\,J^2\}$. Further details are omitted since these are identical to those for the evaluation of the electric quadrupole interaction, and the latter procedure is known[11]. The energy W_{p}, after evaluating the double-product, is given by

$$W_{\mathrm{p}} = \frac{(2\,e^2 p_J\,P/3)}{2\,I\,(2\,I - 1)\,J\,(2\,J - 1)} \qquad (2)$$
$$\times\,\{3\,(\boldsymbol{I}\cdot\boldsymbol{J})^2 + \tfrac{3}{2}\,(\boldsymbol{I}\cdot\boldsymbol{J}) - I^2\,J^2\}.$$

In $(2\,e^2 p_J\,P/3)$, e is the electron's charge,

$$p_J = \langle JJ\,|\,(3\cos^2\Theta - 1)/r^4\,|\,JJ\rangle \qquad \text{(see Ref. 12)}$$

and $\qquad P = \tfrac{3}{2}\,\langle II\,|\,(\boldsymbol{\alpha} - \alpha\,\mathbf{1})_{kk}\,|\,II\rangle. \qquad (3)$

The quantities $(e^2 p_J/2)$ and P are the anisotropies of the square of the electric field and the polarizability of the nucleus, respectively. This is more apparent if one elects to be less general and to express these quantities as follows: $(e^2 p_J/2) = \langle JJ\,|\,E_z^2 - \tfrac{1}{2}(E_x^2 + E_y^2)\,|\,JJ\rangle$ and $P = \langle II\,|\,\alpha_{zz} - \tfrac{1}{2}(\alpha_{xx} + \alpha_{yy})\,|\,II\rangle$. The energy W_{p} has the same dependence on $\boldsymbol{I}$ and $\boldsymbol{J}$ as does the energy which describes the electric quadrupole interaction; consequently, for an atom with E2 hfs, one determines in fact the sum $(e^2 q_J\,Q + \tfrac{2}{3}\,e^2 p_J\,P)$, in which $(e^2 q_J\,Q)$ is the constant of the electric quadrupole interaction[13]. For the latter constant, $q_J = \langle JJ\,|\,(3\cos^2\Theta - 1)/r^3\,|\,JJ\rangle$ and Q is the nuclear quadrupole moment. The effect of the polarizability of the nucleus may be sought for by determining the foregoing sum from the hfs of two atoms of differing isotopic species 1 and 2, forming the ratio

$$(e^2 q_J\,Q_1 + \tfrac{2}{3}\,e^2 p_J\,P_1)/(e^2 q_J\,Q_2 + \tfrac{2}{3}\,e^2 p_J\,P_2),$$

and then comparing it with

$$(e^2 q_J' Q_1 + \tfrac{2}{3} e^2 p_J' P_1)/(e^2 q_J' Q_2 + \tfrac{2}{3} e^2 p_J' P_2),$$

determined in a different electronic environment, which may be that of a molecule, for which q_J and p_J have other values q_J' and p_J'. Due to the polarizability, there is a difference in the ratios which is given by

$$d = \tfrac{2}{3} (Q_1/Q_2) (P_1/Q_1) (p_J/q_J) \qquad (4)$$
$$\times \left\{ 1 - \frac{(P_2/Q_2)}{(P_1/Q_1)} \right\} \left\{ 1 - \frac{(p_J'/q_J')}{(p_J/q_J)} \right\}.$$

In order to observe this difference, the individual ratios must be measured precisely. Further, the assumption inherent in the above that q_J' is the same in different isotopic species of a given molecule must be valid in order to relate any difference uniquely to polarizability. Accordingly, spectra obtained by atomic-beam methods are in general of more value than spectra obtained from nuclear quadrupole resonance in solids where variation of q_J' with temperature is known to occur[14]. Finally, the ratios $(P_2/Q_2)/(P_1/Q_1)$ and $(p_J'/q_J')/(p_J/q_J)$ must differ significantly from unity; thus, atoms and molecules are particularly worthy of study for which q_J and q_J' (or $e^2 q_J Q$ and $e^2 q_J' Q$) differ significantly. There exist two measurements which best fulfill the preceding criteria for observing d. These are the measurement $b^{79}/b^{81} = 1.1970568(15)$ in atomic Br done by the atomic-beam magnetic-resonance method[3] and

$$(eq Q)_{79_{Br}}/(eq Q)_{81_{Br}} = 1.197056(6)$$

in molecular LiBr done by the molecular-beam electric-resonance method[4]. The two ratios are equal. The uncertainty associated with the LiBr ratio determines the limit $|d| \leq 6 \times 10^{-6}$. Further, from this limit and Eq. (4), it follows that

$$|(P_{79}/Q_{79}) - (P_{81}/Q_{81})| \leq 10^{-15} \text{ cm}, \qquad (5)$$

where in arriving at Eq. (5), (p_J/q_J) is evaluated explicitly[15] and $(p_J'/q_J')/(p_J/q_J)$ is neglected[16]. The $P_{79, 81}$ are calculated below from a well known nuclear model. The results yield a value for $((P_{79}/Q_{79}) - (P_{81}/Q_{81}))$ which is consistent with Equation (5).

3. Polarizability

For the nuclear model of STEINWEDEL and JENSEN[17], the proton and neutron densities ϱ_p and ϱ_n separately fluctuate but the sum $\varrho = (\varrho_p + \varrho_n)$ is a constant. Hence, the symmetry energy density is $V_s = k \{(\varrho - 2\varrho_p)^2/\varrho\}$, in which k is the constant of this energy in the Weizsäcker semi-empirical formula for nuclear ground-state energies[18]. The charge density in the presence of an electric field is $e \varrho_p = e\varrho_p^{(0)} + e (\varrho_x' x + \varrho_y' y + \varrho_z' z)$, where $e \varrho_p^{(0)}$ is the charge density in the absence of a field and $\varrho_x', \varrho_y',$ and ϱ_z' are constants which describe the

anisotropy of the polarization of the nucleus. The induced dipole-moment in, e.g., the x-direction is $\mu_x = e (\varrho_p - \varrho_p^{(0)}) x = e (\varrho_x' xx + \varrho_y' yx + \varrho_z' zx)$. Hence the polarizability per unit volume is $P_{xy} = (e\varrho_y'/E_y) xy$. The electrostatic energy is $V_e = - (\mu_x E_x + \mu_y E_y + \mu_z E_z)$. It is stated without proof that $\varrho_x' = (e E_x \varrho/8k)$, $\varrho_y' = (e E_y \varrho/8k)$, and $\varrho_z' = (e E_z \varrho/8k)$[19]. Accordingly, the polarizability per unit volume is in general

$$P_{ij} = (e^2 \varrho/8k) x_i x_j \quad \text{(see Ref. }^{20}), \qquad (6a)$$

or $\quad P_{ij} = (e^2 \varrho/8k) \{(x_i x_j - \tfrac{1}{3} \delta_{ij} r^2) + \tfrac{1}{3} \delta_{ij} r^2\} \quad$ (6b)

in which $(e^2 \varrho/8k)(x_i x_j - \tfrac{1}{3} \delta_{ij} r^2)$ and $(e^2 \varrho/8k)(\tfrac{1}{3} \delta_{ij} r^2)$ are $(\alpha - \alpha \mathbf{1})_{ij}$ and $(\alpha \mathbf{1})_{ij}$, respectively; $(\alpha \mathbf{1})_{ij}$ contributes to $- (\tfrac{1}{2} \alpha E^2)$ and, hence, is not relevant. From the foregoing and Eq. (3), the anisotropy of the polarizability is

$$P = \langle II | (e^2 \varrho/16k) (3 z^2 - r^2) | II \rangle. \qquad (7a)$$

Since Eq. (7a) resembles closely the proper expression for the nuclear quadrupole moment Q, the polarizability is expressed in the alternative form $\qquad (7b)$

$$P = (e^2 A/16 kZ) \langle II | \varrho_p (3 z^2 - r^2) | II \rangle \quad \text{(see Ref. }^{21})$$

from which it follows that

$$P = (e^2 A/16 kZ) Q. \qquad (8a)$$

Using the relation

$$Q = Q^{(i)} I (2 I - 1)/(I + 1)(2 I + 3), \qquad \text{(see Ref.}^{22})$$

the polarizability is finally

$$P = (e^2 A/16 kZ) Q^{(i)} I (2 I - 1)/(I + 1)(2 I + 3), \qquad (8b)$$

where A is the atomic mass number, eZ is the nuclear charge, and $Q^{(i)}$ is the intrinsic quadrupole moment of the nucleus. Using Eq. (8b) and the values $k = 18.1$ Mev[23] and $Q_{79}^{(i)} = 1.075 \times 10^{-24}$ cm^2 (see Ref.[24]) one finds that

$$\{(P_{79}/Q_{79}) - (P_{81}/Q_{81})\} = - (10^{-17}) \text{ cm},$$

which is consistent with the corresponding limit from experiment.

4. Discussion

The measurement

$$\{(eqQ)_e\}_{79_{Br}}/\{(eqQ)_e\}_{81_{Br}} = 1.197053(4)$$

in molecular TlBr[25] and $Q_{79}/Q_{81} = 1.197052(5)$ in molecular HBr[26], both done by the molecular-beam electric-resonance method, confirm the equality between atomic Br and molecular LiBr and, hence, the absence of nuclear polarization for the level of precision associated with the latter measurements.

From Eqs. (4) and (8b), there is the difference $d = - (10^{-7})$ between atomic Br and molecular LiBr. Were, however, a precision of 10^{-7} or better achieved, it

would be very difficult to relate any observed difference uniquely to polarizability. There is a second effect which may cause a ratio to vary, and in LiBr it is expected to be observable if one achieves a precision of 2×10^{-6} or better[27].

A precise atomic-beam magnetic-resonance measurement of the hfs of Lu^{175} and Lu^{176m} for both the $^2D_{3/2}$ and $^2D_{5/2}$ electronic states of the atom has been done[28]. The ratios B_{176m}/B_{175} are equal to within 5×10^{-6} for the two states of the atom. The equality of the ratios reflects a small value for $\{(P_{176m}/Q_{176m}) - (P_{175}/Q_{175})\}$ (although the P's for Lu exceed those for Br by an order-of-magnitude); further, the difference between q_J for the $^2D_{3/2}$ and the $^2D_{5/2}$ state is small. For similar reasons the polarization of $Cl^{35,37}$ nuclei in atomic Cl and molecular $TlCl^{29}$ and of $Rb^{85,87}$ nuclei in molecular RbF and $RbCl^{30}$ were not observed.

The expression for P which is given by Eq. (8b) has two properties worthy of mention: (1) P depends through $Q^{(1)}$ explicitly on the extent to which the nucleus is deformed; since P is the anisotropy of the polarizability, this is satisfying. (2) If $I = 0$ or $1/2$, P is zero; this avoids the curiosity which occurs in an earlier work[31] of P having an infinite value for $I = 1/2$.

It is beyond the scope of this work to determine whether as a means of arriving at a result consistent with Eq. (5) the model of STEINWEDEL and JENSEN is unique. However, it may be said that more primitive evaluations of the polarizability from an extreme single-particle model for the nucleus are not correct[30,31]. The polarizabilities are too large and, hence, predict an inequality between ratios when in fact none is observed.

In summary, the electric polarization of a nucleus in an atom or molecule is very difficult to observe since for most atoms, molecules, and nuclei one or both of the quantities $\{1 - (p_J'/q_J')/(p_J/q_J)\}$ and $\{1 - (P_2/Q_2)/(P_1/Q_1)\}$ are small. This difficulty exists even though, e.g., from Ref. 15 and Eq. (8b), one obtains $p_J(Br^{79}) = - (418.39) \times (a_0)^{-4}$ ($a_0 = 0.529 \times 10^{-8}$ cm), $P_{79} = 1.6 \times 10^{-40}$ cm^3, and $(2e^2 p_J P/3)/h = - (800)$ Hz, where the latter frequency is twice (!) the linewidth which is associated with the atomic Br spectra of Reference 3.

Acknowledgments

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