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Explanation of Nuclear Quadrupole Interaction in ^{14}N "Spherical" Atomic Ground State

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The explicit incorporation of the Breit interaction in relativistic many-body perturbation theory provides an explanation of the recent experimental value of 1.27 ± 0.10 Hz for the nuclear quadrupole interaction constant in the spherical ^{14}N atom. The theoretical value including the Breit and other mechanisms is 1.7 Hz.

Recently, through the advent of new experimental techniques capable of remarkable precision, hyperfine interactions have been measured in systems in which they were believed to be vanishingly small if not exactly zero. The most noteworthy of such measurements is the quadrupole interaction in half-filled S-state atoms[1-3] in free state, and similar ions in solids at sites of cubic symmetry.[4] The origin of these interactions poses a formidable challenge to qualitative and quantitative theoretical analysis. Of the S-state atoms, nitrogen has remained refractory[1,2] for about a decade. The latest value of the quadrupole coupling constant of ^{14}N was measured by Hirsch, Zimmerman, Larson, and Ramsey,[1] in its ground state, to be 1.27 ± 0.10 Hz with an ingenious technique involving spin exchange between hydrogen and nitrogen atoms.

Sandars and Beck[5] have proposed two mechanisms referred to in the literature as Casimir and breakdown of LS coupling (BDLSC) in order to explain the origin of quadrupole interaction in relatively heavy S-state atoms and ions such as manganese and europium, and an approximate treatment[5] of these mechanisms provided a reasonable explanation of the experimental data. A detailed treatment of these mechanisms including many-body effects has been carried out recently[6] for Gd^{3+}. In contrast to this encouraging situation in transition-metal and rare-earth systems the net contribution from Casimir and BDLSC mechanisms for nitrogen[7] is in sharp disagreement with experiment yielding a contribution of -19.1 Hz, compared with the very small positive experimental value.

In the present work, we demonstrate that the influence of the Breit interaction[8] between the electrons is critical for the problem at hand and that its incorporation within the framework of relativistic many-body perturbation theory (RMBPT) is necessary to provide the balance to reach satisfactory agreement with the experimental ^{14}N quadrupole coupling constant.[1] While the influence of the Breit interaction on two-electron systems has been considered before,[9] to our knowledge this is the first treatment of its influence on the ground state of a multi-electron system in many-body theory.

Before discussing the procedure and results for the Breit-interaction contribution to the quadrupole coupling, we shall briefly discuss the contribution from the Casimir and BDLSC mechanisms as well as from the small pseudo quadrupole interaction. These mechanisms can also be handled in the framework of RMBPT, as has been done in earlier work in Gd^{3+} ion. Thus, the relativistic ls coupling[6] used for the one-electron rls states occurring in the zeroth-order (unperturbed) many-electron wave function Φ_0 of RMBPT preserves the nonrelativistic LS composition of the configuration, ^4S in the present problem of the nitrogen atom. The expectation value of the quadrupole Hamiltonian with respect to Φ_0, referred to later as the $(0,0)$ term in RMBPT, gives a zero result. The finite contributions from the Casimir and BDLSC mechanisms depend on the admixture of other multiplets ^2D and ^2P of the $2p^3$ configuration of the nitrogen atom to Φ_0. These admixtures can be incorporated conveniently with the spin-orbit interaction as a perturbation. This procedure leads to the same expression for the Casimir contribution B_{Cas} derived earlier by the effective operator technique,[7] namely,

$$hB_{\text{Cas}} = -\left(\frac{8e^2Q\zeta}{15E_P}\right)(\langle r^{-3}\rangle_{++} - \langle r^{-3}\rangle_{+-}). \tag{1}$$

With values[10] of the spin-orbit constant $\zeta = 74.2$ cm^{-1}, the $^4S_{3/2}$-$^2P_{3/2}$ multiplet separation $E_P = 28\,840$ cm^{-1}, the quadrupole moment[11] $Q = 0.015$ b and $\Delta = \langle r^{-3}\rangle_{++} - \langle r^{-3}\rangle_{+-} = -0.0046$ a.u. from our relativistic radial functions, we have obtained $B_{\text{Cas}} = -22.3$ Hz. This is about 4 Hz smaller in magnitude than the earlier value which was based on a different choice of ζ and an approximate value of Δ. For the contributions from the BDLSC effect within the $2p$ shell and from the pseudo quadrupole interaction (which, like the quadrupole interaction, involves an I_z^2 dependence on the nuclear spin components and arises[2] out of second-order effects of the magnetic dipole hyperfine interaction), we have adopted the values obtained earlier[2,7] in the literature, namely, $B_{\text{pseudo}} = 2.0$ Hz and $B_{\text{BDLSC}} = 3.2$ Hz, because they are relatively small. Thus, the net theoretical value due to the contributions, B_{pseudo}, B_{Cas}, and B_{BDLSC} from within the $2p^3$ configuration is seen to be $B(2p^3) = 2.0 + 3.2 - 22.3 = -17.1$ Hz, which is about an order of magnitude larger and of opposite sign relative to the experimental value.[1]

We turn next to the treatment of the influence of the Breit interaction which will be shown to bridge the gap with experiment.

The formalism for handling the influence of electron-electron interaction in RMBPT has been described extensively in our earlier work on hyperfine interactions.[6] Although the Breit interaction[8] is somewhat more complicated in form, in principle the same general techniques[12] as were used for handling the $1/r_{12}$ interaction can be used here. We sketch here the most essential aspects of the RMBPT procedure[6] that are pertinent to the influence of the Breit interaction on electron-nuclear quadrupole coupling. The mathematical techniques for handling the matrix elements associated with the Breit interaction have been discussed by Grant and Pyper.[12]

The relativistic Hamiltonian, $\mathcal{H}$, for the many-electron atom can be written as

$$\mathcal{H} = \sum_{i=1}^{N} h_i + \sum_{i>j} v_{ij}, \tag{2}$$

where h_i represents the one-electron term in the usual notation and

$$v_{ij} = \frac{e^2}{r_{ij}} + \mathcal{H}_{\text{Breit}}, \tag{3}$$

with

$$\mathcal{H}_{\text{Breit}} = -e^2[\vec{\alpha}_i \cdot \vec{\alpha}_j / r_{ij} + \tfrac{1}{2}(\vec{\alpha}_i \cdot \nabla_i)(\vec{\alpha}_j \cdot \nabla_j) r_{ij}], \tag{4}$$

represents the two-electron terms in $\mathcal{H}$. We write, as is usual in many-body theory,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \tag{5}$$

where the zeroth-order term $\mathcal{H}_0 = \sum_i (h_i + V_i)$ and the perturbation term $\mathcal{H}' = \sum_{i>j} v_{ij} - \sum_i V_i$. The bound- and continuum-state eigenfunctions of the equation

$$(h_i + V_i)\varphi_i = \epsilon_i \varphi_i, \tag{6}$$

form a complete set of one-electron wave functions. The choice of V_i and the construction of Φ_0 with the rls prescription[6] have been discussed in the earlier literature. We follow the same prescription and construct the ground-state relativistic atomic wave function Φ_0 appropriate for the ^4S multiplet state of the half-filled $2p^3$ configuration of nitrogen. The contribution from the combined effect of the Breit and electrostatic electron-electron interactions to the quadrupole coupling constant is evaluated with the linked-cluster perturbation expression:

$$\tfrac{1}{4}hB_{\text{el-el}} = \sum_{m,n=0}^{\infty} \left\langle \Phi_0 \left| \left(\frac{\mathcal{H}'}{\epsilon_0 - \mathcal{H}_0}\right)^m \mathcal{H}_Q \left(\frac{\mathcal{H}'}{\epsilon_0 - \mathcal{H}_0}\right)^n \right| \Phi_0 \right\rangle, \tag{7}$$

where

$$\mathcal{H}_Q = -\frac{1}{4}e^2Q\sum_i \frac{3\cos^2\theta_i - 1}{r_i^3}$$

is the electron-nuclear quadrupole interaction. The contribution from $(m+n)$-th order is labeled by the pair of indices (m, n) so that

$$B_{\text{el-el}} \sum_{m,n=0}^{\infty} B_{\text{el-el}}^{(m,n)}.$$

Since the form of the Breit interaction given above is not admissible[8] in orders higher than the first, care must be exercised in evaluating the many-body diagrams arising from Eq. (7).

We have to restrict ourselves to those diagrams which involve $\mathcal{H}_{\rm Breit}$ just once while the electrostatic interaction $1/r_{12}$ can be considered to any order.

From the lowest order (0, 0) $B_{\rm el\text{-}el}^{(0,0)} = 0$, as remarked earlier, since Φ_0 leads to a spherically symmetric charge distribution. The various terms that contribute in the next higher order, $B_{\rm el\text{-}el}^{(0,1)}$, can be represented by the perturbation diagrams in Figs. 1(a) and 1(b) involving the Breit component of the electron-electron interaction once and no $1/r_{12}$. The particle states k in these diagrams are pure (jm) orbitals referring to excited $p_{1/2}$, $p_{3/2}$, $f_{5/2}$, or $f_{7/2}$ states. Of these the $p_{1/2}$ and $p_{3/2}$ excited states make the most important contributions and these are listed in Table I.

In Table I, the *rls* notation[6] is used for the states p and q, for instance, 1^+ represents the ls state with $m_l = 1$ and $m_s = \frac{1}{2}$ expressed as a linear combination of the relativistic jm orbitals. The contributions listed refer to the net Breit term consisting of the sum of the magnetic and retardation terms.[8, 12] The retardation term gives vanishing contribution in Fig. 1(a). Through the exchange term [Fig. 1(b)], it gives a contribution of the order of 0.1 Hz, three orders of magnitude smaller than the net contribution from the magnetic term. Thus, the Breit contribution in order (0, 1) arises almost completely from the magnetic term composed of substantially canceling contributions of direct and exchange effects which had to be evaluated accurately. The (0, 1) contribution from the f excited states was found to be − 1.6 Hz so that we obtain for the net (0, 1) contribution, $B_{\rm el\text{-}el}^{(0,1)}$, a value of 13.4 Hz.

It should be mentioned that Sandars[7] has studied in nonrelativistic theory the influence of configuration interaction caused by spin-spin interaction, obtaining a substantially smaller contribution to the nuclear quadrupole interaction than our result, possibly because the Breit interaction in relativistic theory contains, besides the spin-spin interaction, the important spin-other-orbit interaction.

Of the second-order terms, that is, (1, 1) and (0, 2), only the effect represented by Fig. 2, which can be considered as the influence of consistency effect on the Breit interaction, was found to be significant. From this diagram we obtained $B_{\rm el\text{-}el}^{(0,2)} = 3.2$ Hz.

In addition to this second-order–consistency effect involving the Breit and $1/r_{12}$ interactions, one can also have another consistency-type effect from the influence of electron-electron interaction on the Casimir mechanism. This influence is best described as the shielding by the core electrons of the field gradient induced in the $2p$ shell through the Casimir effect. By comparison with the corresponding shielding effect on the field gradient due to the anisotropic electron distribution from the single $2p$ electron in beryllium[13] and boron,[14] we have estimated this shielding contribution to be approximately 10% of that due to the Casimir mechanism, so that $B_{\rm Sternheimer} = 2.2$ Hz. The various contributions we have discussed are listed together in Table II, leading to a net result of

$$B_{\rm theory} = 1.7 \text{ Hz}, \tag{8}$$

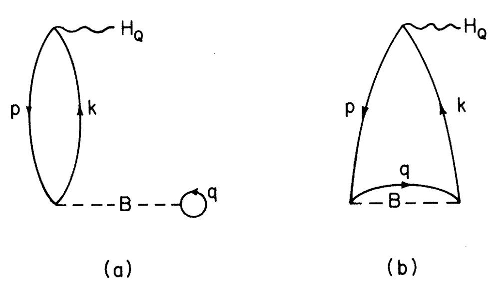

FIG. 1. Lowest-order, (0, 1) diagrams representing the Breit-interaction contribution to the ^{14}N nuclear quadrupole interaction: (a) The direct contribution and (b) the exchange contribution.

TABLE I. The contributions (in hertz) to the quadrupole coupling constant in the ground state of ^{14}N from the (0, 1) order of perturbation due to the Breit interaction.

			Contributing diagram	
p	q	k	Fig. 1(a)	Fig. 1(b)
1+	0+	$p_{3/2}$	106.07	−104.70
1+	−1+		−130.42	−93.51
0+	1+		−127.30	202.07
−1+	1+		−0.97	0.90
0+	−1+		87.00	213.58
−1+	0+		−9.59	−103.97
0+	1+	$p_{1/2}$	−83.64	−31.28
−1+	1+		−22.70	−15.89
0+	−1+		61.07	126.46
−1+	0+		−11.39	−46.75
		Total	−131.87	+ 146.91 = 15.03 Hz

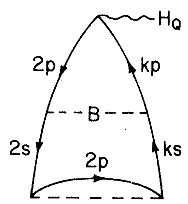

FIG. 2. Typical (0, 2)-order diagram representing influence of the electrostatic interaction on the Breit contribution to the ^{14}N nuclear quadrupole interaction.

TABLE II. Summary of contributions (in hertz) to the quadrupole coupling constant in the ground state of ^{14}N atom, yielding a net theoretical value of 1.7 Hz.

Casimir mechanism	−22.3
BDLSC	3.2
Pseudo quadrupole interaction	2.0
Breit electron-electron interaction (0, 1)	13.2
Consistency effect on electron-electron interaction (0, 2)	3.4
Shielding of Casimir mechanism	2.2

as compared to the experimental value 1.27 ± 0.10 Hz.

Besides these mechanisms summarized in Table II we have also examined some higher order processes as well as the counterparts of diagrams in Figs. 1(a) and 1(b) with the unoccupied *rls* 2*p* orbitals for the particle states (which were not included in obtaining the results listed in Table I). We found the contributions from these latter diagrams and higher-order diagrams associated with the Breit as well as Casimir and BDLSC mechanisms to be all less than 1 Hz in magnitude and of differing signs, so that we expect substantial mutual cancellations among them. From this analysis and a consideration of the accuracy of the computational procedures, ± 0.5 Hz appears to be a reasonable confidence limit for our theoretical result.

In summary, theory has been able to meet the challenge of explaining the result of accurate measurement[1] of nuclear quadrupole coupling in the ground state of ^{14}N atom. What we have demonstrated is the occurrence of an unusual instance in atomic hyperfine interaction that requires explicit incorporation of the Breit interaction in the relativistic framework of the many-body theory. Thus, in nitrogen atom, in contrast to heavier half-filled shell *S*-state systems such as, for example, the rare-earth Gd^{3+} ion, the Breit-interaction contribution has turned out to be comparable in magnitude and opposite in sign to the Casimir contribution. In heavier atoms, due to the preponderance of the spin-orbit interaction, the Casimir mechanism was very substantial[5,6] relative to the Breit-interaction contribution. It would be interesting to study how the relative importance of the various mechanisms contributing to the nuclear quadrupole interaction in *S*-state atoms changes as one proceeds successively along the half-filled *p*-shell series, arsenic, antimony, and bismuth.

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