TABLE II. New measurements of the coupling constants.

Substance	Interval	Cl^{35} (Mc)	$eqQ(Cl^{35})$ (Mc)	Cl^{37} (Mc)	$\frac{eqQ(Cl^{35})}{eqQ(Cl^{37})}$
CH_3Cl	$(F=3/2\rightarrow3/2)-(F=3/2\rightarrow5/2)$	18.695	74.77 ±0.015	14.731	1.2691 ±0.0003
$J=0\rightarrow1$ $K=0$	$(F=3/2\rightarrow5/2)-(F=3/2\rightarrow1/2)$	14.952		11.780	
ClCN	$(F_1=1/2\rightarrow3/2)-(F_1=1/2\rightarrow1/2)$	20.843	83.33 ±0.02	16.436	1.2682 ±0.0006
$J=1\rightarrow2$	$(F_1=1/2\rightarrow1/2)-(F_1=3/2\rightarrow3/2)$	16.849		13.333	
GeH_3Cl	$(F=5/2\rightarrow3/2,\ 5/2,\ 7/2)-(F=7/2\rightarrow5/2,\ 7/2,\ 9/2)$	11.734	46.95 ±0.015	9.262	1.2670 ±0.0005
$J=2\rightarrow3$	$(F=5/2\rightarrow5/2,\ 7/2,\ 9/2)-(F=1/2\rightarrow3/2)$	8.418			

outside the limits of the quoted experimental errors. Table I lists the various results obtained hitherto for the ratios of the quadrupole coupling constants, the quoted errors, and the method of measurement.

Probably at least some of the ratios given in Table I are in error. Although the very nice experiment of Dehmelt and Krüger should yield the most accurate ratio, their value is made somewhat doubtful by preliminary results obtained by Wang using the same technique.[1] For the same molecule he obtained 1.2682±0.004. The atomic beam measurement should be rather accurate, but may be questioned because the ratio of magnetic moments of the two Cl isotopes from the same measurement is also distinctly different from the ratio obtained by nuclear induction methods, and this difference is so far unexplained. A recalculation of the theoretical BrCl spectrum and comparison with experimental measurements indicates that perhaps the accuracy of the Cl^{35}/Cl^{37} ratio obtained therefrom has been overestimated.

Because of these uncertainties we have redetermined the ratio $eqQ(Cl^{35})/eqQ(Cl^{37})$ from the microwave spectrum of CH_3Cl, ClCN, and GeH_3Cl. With the very high resolution afforded by a balanced microwave bridge spectrometer,[2] the intervals from which the quadrupole couplings were determined were measured to 8 kc or better, and hence rather accurate values of quadrupole couplings were obtained. The results of these measurements are given in Table II along with the computed quadrupole coupling ratios. These results are averages of as many as five different sets of determinations for a given molecule on as many different days. For no set were values found which would make the quadrupole coupling ratios in GeH_3Cl and CH_3Cl overlap. Although some of the discrepancies shown in Table I are probably due to errors or to the differing types of experiments used, it seems clear from repeated measurements with the same technique on CH_3Cl and GeH_3Cl that the apparent ratio of quadrupole coupling constants of the two Cl isotopes depends slightly on the molecular environment.

The ClCN spectrum is somewhat complex because of the occurrence of two quadrupolar nuclei in the same molecule. The experimental results were fitted to a theoretical calculation which included all known effects of important size except for a possible magnetic coupling between the nitrogen nucleus and the molecular rotation.

The two measured intervals in GeH_3Cl^{35} did not agree exactly with the spacings expected for pure quadrupole coupling. This deviation was attributed to a magnetic coupling of the type $c(\mathbf{I}\cdot\mathbf{J})$ with $c=-4\pm3$ kc. Inserting this very small correction, one obtains for this molecule $\frac{eqQ(Cl^{35})}{eqQ(Cl^{37})}=1.2670\pm0.0005$. Similarly, if a magnetic coupling of the form $c(\mathbf{I}\cdot\mathbf{J})$ is assumed for Cl in CH_3Cl, the constant c would have the very small value, 0.4 ±0.8 kc.

The only other pair of isotopes for which the quadrupole moment ratios have been measured with some accuracy is Br^{79} and Br^{81}, which in BrCN and CH_3Br seem to agree within experimental accuracy of one part in 2500.

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[1] T. C. Wang, Columbia University, private communication.

[2] Columbia Radiation Laboratory Report, June 30, 1949, unpublished.

Polarization of the Nucleus by Electric Fields*

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THE preceding letter[1] shows that the ratio of quadrupole moments of Cl^{35} and Cl^{37} in CH_3Cl appears to be slightly different from that found in GeH_3Cl. It will be shown below that the most reasonable explanation of this difference is a fictitious quadrupole moment due to anisotropic polarization of the Cl nuclei by molecular electric fields.

Two molecular effects which might change the apparent ratio of the quadrupole moments from one molecule to another are the pseudoquadrupole effect discussed by Foley[2] and the variation in zero-point vibration with isotopic mass.

A reasonable estimate of the pseudoquadrupole effect makes it too small to account for the observed change by a factor of 10^4. In order to obtain an effect of the correct magnitude, electronic levels within 1 cm^{-1} of the molecular ground state would need to be assumed.

From measured changes of quadrupole coupling with vibration in several molecules, an upper limit for the expected change in quadrupole coupling due to isotopic mass variation is one part in 2500. If the observed effect were due to zero-point vibrations in GeH_3Cl the change in Cl quadrupole coupling per quantum of vibration energy would need to be -10 percent. Actual rough measurement shows this change to be $+3$ percent ±3 percent. Although the effect of vibration in CH_3Cl has not been measured specifically, the quadrupole coupling change per vibrational excitation would have the ridiculously large value of 20 percent if it is to explain the variation in apparent quadrupole moment ratios, and hence this explanation is ruled out.

Two other effects which can produce a variation in the apparent quadrupole moment ratio are a second-order perturbation of the electronic levels by the nuclear quadrupole coupling and a penetration of the nuclear volume by electronic charge. The variation due to either one of these effects, however, would be much too small to account for the observed discrepancy.

A reasonable explanation of the discrepancy is that a polarization of the Cl nuclei occurs in the molecular electric fields. If the nuclear polarizability depends on the direction of polarization with respect to the spin axis of the nucleus, then the classical energy of polarization can be shown to be

$$W_P=-\frac{1}{6}\left[(\alpha_z+2\alpha_x)\left(\frac{e\rho}{r^4}\right)_{\text{Av}}\right]+\frac{(\alpha_z-\alpha_x)}{12}\times\left[\frac{e\rho(3\cos^2\theta_m-1)}{r^4}\right]_{\text{Av}}P_2(\cos I, J),$$

where α_z=polarizability along the nuclear axis, α_x=polarizability perpendicular to the nuclear axis, ρ=charge density (outside the nucleus considered), r=distance from center of nucleus to charge, θ_m=angle between molecular axis of symmetry and charge, I=nuclear spin, and J=angular momentum of molecule. The quantum-mechanical equivalent of $\alpha_z-\alpha_x$ is

$$\alpha_z-\alpha_x=\frac{2I(I+1)}{2I-1}\sum_n\frac{[|\mu_{on}|_{M=I}]^2-[|\mu_{on}|_{M=I-1}]^2}{E_n-E_0},$$

where E_0 and E_n are the nuclear energies in the ground and excited states, respectively, and $|\mu_{on}|_{M=I}$ is the z-component of the dipole matrix element between these two states for the magnetic quantum number $M=I$.

With the above definition of $\alpha_z-\alpha_x$, the proper expression for the anisotropic part of the polarization energy for a nucleus on the axis of a symmetric molecule is

$$W=\tfrac{2}{3}e(\alpha_z-\alpha_x)\mathrm{p}\left(\frac{3K^2}{J(J+1)}-1\right)\left[\frac{\frac{3}{4}C(C+1)-I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)}\right],$$

where $C=F(F+1)-I(I+1)-J(J+1)$,

$$\mathrm{p}=\left[\frac{\rho(3\cos^2\theta_m-1)}{r^4}\right]_{\text{Av}}=2(E_z^2-E_x^2)_{\text{Av}}.$$

E_z is the electric field at the nucleus parallel to the molecular axis due to all charges outside the nucleus.

Hence the polarization coupling constant $\tfrac{2}{3}e(\alpha_z-\alpha_x)\mathrm{p}$ is equivalent to a quadrupole coupling constant eqQ and distinguishable only because p depends on the inverse fourth power of r, while q depends on the inverse cube. The ratio of apparent quadrupole moments of Cl^{35} and Cl^{37} isotopes will be

$$\frac{Q_{35}+\frac{2}{3}(\alpha_z-\alpha_x)_{35}(\mathrm{p}/q)}{Q_{37}+\frac{2}{3}(\alpha_z-\alpha_x)_{37}(\mathrm{p}/q)},$$

which will vary when p/q varies unless

$$Q_{35}/(\alpha_z-\alpha_x)_{35}=Q_{37}/(\alpha_z-\alpha_x)_{37}.$$

The lowest known energy level of Cl^{35} is 0.6 Mev, while the lowest for Cl^{37} is 2.7 Mev,[3] so that their polarizabilities may be somewhat different. Assuming a single-particle model, the difference of the matrix elements

$$[|\mu_{on}|_{M=I}]^2-[|\mu_{on}|_{M=I-1}]^2$$

will be of the order of $e^2r_n^2$, where r_n is the nuclear radius, and hence $(\alpha_z-\alpha_x)$ for Cl^{35} can be approximated, with $E_1-E_0=0.6$ Mev. Although a number of higher levels may contribute to α_z, they would probably not affect the difference $(\alpha_z-\alpha_x)$ appreciably. From the use of Hartree wave functions[4] for K^+ and K^{++} it is found that for a 3p-electron $\langle 1/r^4\rangle_{\text{Av}}\approx 7.5(\langle 1/r^3\rangle_{\text{Av}})^{4/3}$, so that p can be estimated from the known value of q. Hence $\tfrac{2}{3}e(\alpha_z-\alpha_x)\mathrm{p}$ for Cl^{35} in CH$_3$Cl would be approximately 0.20 Mc, or 1/550 of eqQ. If, therefore, the ratio p/q changes by 90 percent between CH$_3$Cl and GeH$_3$Cl, the observed discrepancy of one part in 600 in the Cl^{35}Cl^{37} quadrupole moment ratio would be produced.

In the particular case of K^+ and K^{++}, Hartree wave functions[4] indicate that p/q for the 3p-electrons changes by only three percent. However, this value may differ considerably from the change between the CH$_3$Cl and the GeH$_3$Cl molecules.

A rather large possible error should be allowed for the above estimate of the size of the polarization effect because of uncertainties, not only in p/q but also in the dipole matrix elements and the nuclear energy levels. The lowest known Cl^{35} level is 0.6 Mev, but investigation might reveal other lower levels in either Cl^{35} or Cl^{37}.

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A Canonical Transformation in the Theory of Particles of Arbitrary Spin

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MUCH of the work in the theory of elementary particles of arbitrary spin[1] is based on the assumption that the relativistic spin operator is of the form

$$t_{\mu\nu}=(\sigma_k,\gamma_k)=\mathrm{const}\cdot i(\beta_\mu\beta_\nu-\beta_\nu\beta_\mu)\qquad k=1,2,3;\quad \mu,\nu=1,2,3,4.\tag{1}$$

It may therefore be of interest to point out a general condition under which this form of the spin operator can be derived as a result. Also, the knowledge of this condition provides a desirable short-cut in the otherwise lengthy derivation of the commutation relations of the β_μ and in work on the solutions of the wave equation, particularly for the higher spins.

The equations expressing the relativistic invariance of the linear first-order wave equation are

$$\begin{aligned}&[\beta_i,\sigma_i]=0,\quad [\beta_i,\sigma_k]=i\beta_l,\quad [\beta_4,\sigma_i]=0,\\ &[\beta_i,\gamma_k]=0,\quad [\beta_k,\gamma_k]=i\beta_4,\quad [\beta_4,\gamma_k]=-i\beta_k,\end{aligned}\tag{2}$$

where $[A,B]=AB-BA$, and (i,k,l) are in cyclic order. On the other hand, the commutation relations between the components of the relativistic (6-vector) spin operators are

$$\begin{aligned}&\text{(a)}\ [\gamma_i,\sigma_i]=0;\quad \text{(b)}\ [\gamma_i,\sigma_k]=i\gamma_l,\\ &\text{(c)}\ [\gamma_i,\gamma_k]=i\sigma_l;\quad \text{(d)}\ [\sigma_i,\sigma_k]=i\sigma_l.\end{aligned}\tag{3}$$

The similarity existing between Eqs. (2a, b) and (3a, b) suggests that the equations can be solved by the following S-transformation

$$\gamma_k=\lambda S\beta_k S^{-1},\tag{4}$$

where

$$S\sigma_k S^{-1}=\sigma_k,\quad S\beta_4 S^{-1}=\beta_4,\tag{4$'$}$$

with λ as a (real) number. It follows from Eqs. (2d, e, f) that

$$[(S^{-1})^2\gamma_k S^2+\gamma_k]\beta_\mu-\beta_\mu[(S^{-1})^2\gamma_k S^2+\gamma_k]=0.\tag{5}$$

The operator $[(S^{-1})^2\gamma_k S^2+\gamma_k]$ thus commutes with the whole complex generated by the β_μ and is, therefore, a multiple of the unit operator. Since from (3b), Spur$(\gamma_k)=0$, it follows that

$$S^2\gamma_k+\gamma_k S^2=0,\tag{6}$$

whence also

$$S^2\beta_k+\beta_k S^2=0,\tag{7}$$

S^4 thus commuting with all of the β_μ. It can be deduced, therefore, that S^2 is a constant multiple of the operator η_4 the existence of which is necessary for the covariance of the wave equation under reflections of the three space axes.

Applying the canonical transformation (4) and (6) to (2f) and (3c), the important expression (1) is now obtained as a result.