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* NRL Postdoctoral Fellow.
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A Method of Synthesis of the Statistical and Impact Theories of Pressure Broadening

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TWO types of theories of pressure broadening have been current in the literature: the "statistical" theory of Kuhn[1] and Margenau,[2] and the "impact" theory of Weisskopf,[3] Lenz,[4] and others. Spitzer[5] and Holstein[6] have indicated the limits of validity of the two types of theory: At low pressures the statistical theory is certainly valid on the wings of the line, the impact theory in the center, while at high pressures the statistical theory is valid if its fundamental assumption that the frequency perturbation for a given atom is the sum of that due to all others in the gas,

$$\nu = \sum_{j=1}^{N} \nu(R_j),\tag{1}$$

is not too seriously incorrect. Most of these discussions and this note are confined to the "adiabatic" or nondegenerate case in which the perturbations due to the atoms in the gas may be expressed simply as frequency perturbations.

Lindholm[7] carried out a complete study of the transition between the two theories for a frequency perturbation proportional to $1/R^6$. Unfortunately, he used a simplified model of the collision in which the frequency was constant during the collision and thus the perturbation started and stopped abruptly; some of his results seem to be in error because of this fact.

This note presents a more general and more workable technique for synthesizing the two theories and studying the transition between them. The spectral intensity which is desired is given by the Fourier integral

$$I(\omega) = \left| \int_{-\infty}^{\infty} \exp\left[i\left(\omega t - \int_{-\infty}^{t} \nu(t')dt' \right) \right] dt \right|^2,\tag{2}$$

where $\nu(t')$ is the frequency at the time t', given by (1) with the R_j assuming the correct values for this time. Now we transform (2) by the standard correlation-function transformation[8] and obtain

$$I(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau} \varphi(\tau);\tag{3a}$$

$$\varphi(\tau) = \int_{-\infty}^{\infty} dt \exp\left[i \int_{t}^{t+\tau} \nu(t')dt' \right]$$
$$= \left\langle \exp\left[i \int_{0}^{\tau} \nu(t')dt' \right] \right\rangle_{Av}.\tag{3b}$$

We now use (1) and obtain

$$\varphi(\tau) = \left\langle \prod_{j} \exp\left[i \int_{0}^{\tau} \nu(R_j)dt \right] \right\rangle_{Av}.$$

To an approximation more than adequate for our purposes the motions of the molecules in the gas are independent, so that

$$\varphi(\tau) = \left\{ \left\langle \exp\left[i \int_{0}^{\tau} \nu(R)dt \right] \right\rangle_{Av} \right\}^N.\tag{4}$$

More general methods of averaging are possible than the following, in case the situation is more complicated, but this should

suffice to show the method: Suppose that the paths of atoms are straight relative to each other; then the parameters to be averaged over are b, the impact parameter, and x_0, the position of the atom at the start of the time-interval 0 to τ along the straight line of impact parameter b. Now

$$2\pi \int b\,db \int dx_0 = V,\tag{5}$$

where V is the volume available to the N atoms of the gas. Then

$$\varphi(\tau) = \left(1 - \frac{2\pi}{V} \int_0^{\infty} b\,db \int_{-\infty}^{\infty} dx_0 \right.$$
$$\left. \times \left\{ 1 - \exp\left[i \int_0^{\tau} \nu([(x_0+vt)^2+b^2]^{\frac{1}{2}})dt \right] \right\} \right)^N$$
$$= \exp[-nV'(\tau)].\tag{6}$$

Here $n = N/V =$ density of atoms per cc, and

$$V'(\tau) = 2\pi \int_0^{\infty} b\,db \int_{-\infty}^{\infty} dx_0$$
$$\times \left\{ 1 - \exp\left[i \int_0^{\tau} \nu([(x_0+vt)^2+b^2]^{\frac{1}{2}})dt \right] \right\}.\tag{7}$$

It is an easy matter, for which we have no space here, to show that (6) and (7), with (3a), lead to the impact and statistical theories in the proper limits. The criteria for validity of the two theories are easily derived, being the same as those given in references 5 and 6; in particular, these hold even for $\nu \sim 1/R^3$, a case in which there had been some question as to the validity of the impact theory in the low-pressure limit. Analytical methods can be applied to give first corrections to the two types of theories, while V', which is a function only of one variable for a given form of $\nu(R)$, can be approximated numerically for any given $\nu(R)$ without much difficulty. The numerical calculation of the line shape for various densities, from (3a), should then be fairly easy.

Further details, and some computations using the above method, will be given in a later publication.

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Quadrupole Coupling Ratio of the Chlorine Isotopes*

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THE ratio of the nuclear quadrupole coupling constants, eqQ, for the chlorine isotopes has been found to depend to about 0.02 percent on the molecular environment. Radio frequency transitions were measured for several chlorine compounds in the solid state.

A variation in the ratio $(eqQ)_{35}/(eqQ)_{37}$ with molecular species is to be expected because of nuclear polarization and certain kinds of molecular vibrations.[1] A change as large as 0.1 percent has previously been reported in microwave spectra,[2] but measurements of direct quadrupole transitions[3] with an accuracy of the order of 0.01 percent had failed to show conclusively any such variation.

The lines are narrow enough to permit considerably better accuracy, and were hence measured to an accuracy of about 0.001 percent. At Columbia University this degree of precision was obtained by using a Signal Corps type BC221 frequency meter to measure differences between the line frequency and a nearby harmonic of a standard crystal oscillator. At Bell Telephone

Substance		Temp. °C	Resonance frequency Mc(Cl³⁵)	$(eqQ)_{35}/(eqQ)_{37}$	Obs.
$p\text{C}_6\text{H}_4\text{Cl}_2$		26	34.262	1.268860 ±0.00001	B
		20.6	34.282	1.268861 ±0.00001	C
		0.2	34.349	1.268859 ±0.00001	C
		−195	34.780	1.268800 ±0.00001	C
		−195	34.780	1.268806 ±0.00001	B
	(high temp. phase)ᵃ	27	34.235	1.268856 ±0.00001	B
SbCl₃	Strong lines	25.5	19.175	1.268920 ±0.00002	C
	Strong lines	0.6	19.199	1.268898 ±0.00002	C
	Strong lines	−195	19.305	1.268774 ±0.00002	C
	Weak lines	25.5	20.407	1.269001 ±0.00002	C
	Weak lines	0.6	20.474	1.268973 ±0.00002	C
	Weak lines	−195	20.908	1.268831 ±0.00002	C
NaClO₃		26	29.920	1.268754 ±0.00001	B
		0.4	30.025	1.268739 ±0.00002	C
		−195	30.632	1.268736 ±0.00001	B
KClO₃		25.2	28.086	1.268758 ±0.00001	B
		−195	28.953	1.268734 ±0.00001	B
CH₂Cl₂		−195	35.993	1.268790 ±0.00001	B

ᵃ C. Dean and R. V. Pound, J. Chem. Phys. 20, 195 (1952).

Laboratories harmonics of a General Radio Type 1110A Interpolating Frequency Standard were used. At both laboratories the nuclear quadrupole resonances were observed with frequency modulated oscillating detectors using triodes but differing in circuit details.

The results listed in Table I show that the ratio of $(eqQ)_{35}/(eqQ)_{37}$ depends on the compound and also on the temperature (see $p\text{C}_6\text{H}_4\text{Cl}_2$ and SbCl₃). In SbCl₃ there are two nonequivalent sites for Cl in the crystal lattice giving different resonant frequencies, different variations with temperature, and different ratios $(eqQ)_{35}/(eqQ)_{37}$. The variations are within the reasonable upper limit of one part in 2500 for the effect of nuclear mass on zeropoint vibrations.[1] Moreover, the dependence on temperature of the ratio confirms the effect of molecular vibrations on this ratio. It is very probably the higher frequency vibrations of the crystal lattice which are most important in changing the coupling ratio.

Some of the variation may be the result of nonisotropic polarization of the nucleus by the valence electrons. However, Table I shows that this effect does not produce variations much larger than 0.02 percent in these cases and is difficult to distinguish from the effects of lattice vibrations.

¹ Gunther-Mohr, Geschwind, and Townes, Phys. Rev. 81, 289 (1951).
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Hyperfine Structure of $p_{\frac{1}{2}}$ States*

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FOLEY[1] has considered the discrepancies between values of the nuclear moments of gallium and indium measured by atomic beam methods and the values obtained from magnetic resonance experiments. By using a nonrelativistic wave function he finds that a second-order perturbation term resulting from the atomic $p_{3/2}$ state modifies the apparent value of the nuclear moment factor g_I in the $p_{1/2}$ state by the factor

$$1/R = 1 - (\Delta\nu)/[6(2I+1)g_I\delta].$$

Here $\Delta\nu$ is the zero field hyperfine splitting and δ is the fine structure interval between $p_{1/2}$ and $p_{3/2}$ states.

It seemed desirable to see how this expression might be modified by the use of relativistic wave functions. For this purpose Dirac central field functions were employed for the electron in the $p_{1/2}$ and $p_{3/2}$ states. The terms arising from Dirac's equation resulting from the vector potentials $[\mathfrak{IC} \times \mathbf{r}_e]/2$ of the applied field $\mathfrak{IC}$ and

$[\mathbf{\mu}_I \times \mathbf{r}_e]/r_e^3$ of the nuclear moment $\mathbf{\mu}_I$, together with the energy $-(\mathbf{\mu}_I \cdot \mathfrak{IC})$ of the nucleus in an external field, were treated as perturbations. Matrix elements were computed between states of definite F, M_F and the secular determinant was solved to order $1/\delta$. The displacement of $p_{1/2}$ energy levels due to the perturbations was found to be

$$\epsilon = -\frac{\Delta\nu}{2(2I+1)} - g_I'\mu_0\mathfrak{IC}M \pm \frac{\Delta\nu}{2}\left(1 + \frac{4Mx}{2I+1} + x^2\right)^{\frac{1}{2}}$$
$$- \frac{2(a''')^2}{\delta}I(I+1) - \frac{2\mu_0{}^2\mathfrak{IC}^2N^2}{9\delta}. \quad (1)$$

Here $x = (g_J' + g_I')\mu_0\mathfrak{IC}/\Delta\nu$, where g_J' is the Landé g-factor multiplied by the relativistic correction $(1 - \alpha^2\bar{T}/\text{Ry})$.[2] The zero separation $\Delta\nu$ and apparent nuclear moment factor g_I' are given by

$$\Delta\nu = \frac{1}{2}(2I+1)[a'' - 2(a''')^2/\delta],$$
$$g_I' = g_I(1 + 4Na'''/3g_I\delta),$$

where

$$a'' = -\frac{8}{3}eg_I\mu_0 \int_0^\infty F_{1/2}G_{1/2}dr_e,$$

$$a''' = \frac{1}{3}eg_I\mu_0 \int_0^\infty (F_{1/2}G_{3/2} + F_{3/2}G_{1/2})dr_e,$$

$$N = \int_0^\infty G_{1/2}G_{3/2}r_e^2dr_e.$$

Here F_J and G_J are solutions for particular J of Dirac's radial equations in the form used by Darwin[3] with the normalization condition

$$\int_0^\infty (F_J^2 + G_J^2)r_e^2dr_e = 1.$$

Equation (1) is seen to have the same form as the Breit-Rabi equation except for the addition of terms in $(a''')^2/\delta$ and $\mathfrak{IC}^2/\delta$ which are the same for all sublevels of the $p_{1/2}$ state and cancel out in transitions within this state as in the experiments of Becker and Kusch.[4] Thus the only apparent effect of perturbation by the $p_{3/2}$ state is in the substitution of g_I' for g_I.

Expressions for a'' and a''' employing approximations to the radial functions valid near the nucleus, where the integrands are large, have been obtained by Breit and Wills.[5] Using these, one finds that the ratio a'''/a'' is $-(1/16)\lambda$, where λ is the ratio G/F of the relativistic correction factors G and F of Eq. (29) of their paper and is given by

$$\lambda = 1 - 1.396Z^2\alpha^2 - 0.121Z^4\alpha^4 + \cdots.$$

To a good approximation $\Delta\nu \cong (2I+1)a''/2$, since the correction term in $(a''')^2/\delta$ is small, of the order of $10^{-6} a''$ for gallium. With this value of $\Delta\nu$ and assuming N to be approximately unity one obtains

$$g_I' \cong g_I\{1 - (\Delta\nu)\lambda/[6(2I+1)\delta]\}.$$

Thus Foley's correction to g_I is multiplied by λ. For gallium this makes the fractional change in apparent g_I -0.0058 and for indium one has -0.0035. The gallium value is somewhat lower than that found experimentally (see reference 1) which may, as Foley suggests, be indicative of configuration interaction in the $p_{3/2}$ state. It should be pointed out that the calculated value of the ratio a'/a'' of the hyperfine coupling constant a' for the $p_{3/2}$ state to that for the $p_{1/2}$ state differs from the value found experimentally for gallium by about 30 percent. A different and lower value of the correction to g_I is obtained by using a'''/a' instead of a'''/a'' as above.

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³ C. G. Darwin, Proc. Roy. Soc. (London) A118, 654 (1928). The notation is the same as that used in reference 5.
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⁵ G. Breit and L. A. Wills, Phys. Rev. 44, 470 (1933).