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# The Intermediate Spin-Orbit Coupling for Large Rotational Quantum Number

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If a nucleus of spin one-half is cosine-coupled to the molecular rotation, its molecular beam spectrum can be predicted for all values of the magnetic field from the Zeeman to the Paschen-Back region with one, closed expression. This expression is valid for large values of rotational quantum number and small rotational $g$-factor and is averaged over a Boltzmann distribution of rotational states. The special case of spin one-half is simple because the symmetry permits cosine coupling only, and the energy levels are well known for this hamiltonian. A kind of correspondence principle can be developed for this example which does two things. It shows that the other nucleus in a diatomic molecule has little effect on the spectrum of the first because the coupling of the second nucleus due to the rotation. Second, it permits the extension of the calculation to nuclei of spins greater than one-half when the coupling is predominantly cosinelike.

## I. INTRODUCTION

The radiofrequency spectra of diatomic molecules in molecular beams have been very useful in analyzing very fine molecular effects. The classical example is the experiment of Ramsey[1] on the magnetic field and the magnetic moment of the molecule $H_2$ due to its rotation. This field manifests itself in a term $c\mathbf{I}\cdot\mathbf{J}$ in the hamiltonian, where $\mathbf{I}$ is the nuclear spin and $\mathbf{J}$ is the angular momentum of the molecule. All angular momenta will be expressed in units of $\hbar$. The use of this term can been extended to other diatomic molecules.[2] In the special example of fluorine in LiF, the large width of the observed nuclear resonance is explained completely on the basis of the cosine coupling, since the quadripole broadening is not allowed. The observations were performed at very large values of the magnetic field and good agreement with theory was found. At zero field, the experiments were inconclusive because of the large "nonadiabatic" transitions that masked the effect. The magnitude of $c$ for fluorine in LiF was found to be $8.9\times10^{-23}$ erg and this was considered to be too large by an order of magnitude at the time on the basis of the rather naive picture of a diatomic molecule as a revolving rigid dumbbell.

A theory for the magnitude of $c$ in $H_2$ had been worked out by Wick[3] in an early paper; and the discussions were carried forward in later papers by Wick[4] and Foley[5] with the conclusion that, while the observed interaction was large, it was not incompatible with the calculations. This interaction has since been observed by other investigators in other molecules.[6–8]

The expected line shape for a nucleus of spin one-half, cosine coupled to $\mathbf{J}$, in a magnetic field strong enough to Paschen-Back the coupling was calculated in reference 2 and compared with experiment. However, neither the experiments nor the line shape were done for intermediate and weak values of the field. The purpose of this paper is to obtain a closed expression for the line shape for spin one-half for all values of the magnetic field. As a corollary, a useful kind of correspondence method is justified which extends the result to any value of nuclear spin and gives a good physical picture of the motion of the spin vectors.

## II. QUANTUM-MECHANICAL TREATMENT OF SPIN ONE-HALF

The starting point of the calculation is the hamiltonian. If only terms involving the nucleus of spin one-half are included (the justification for ignoring the other nucleus is based on the large value of $J$ and will be discussed in a later paragraph), then the hamiltonian is

$$\mathcal{H}=-\mu_N g_I\mathbf{I}\cdot\mathbf{H}-\mu_N g_J\mathbf{J}\cdot\mathbf{H}-c\mathbf{I}\cdot\mathbf{J},\tag{1}$$

$\mu_N$ is the nuclear magneton, and $g_I$ and $g_J$ are the $g$-factors corresponding to $\mathbf{I}$ and $\mathbf{J}$, respectively. The energy levels when $I=\frac{1}{2}$ are well known and are given by the Breit-Rabi formula:[9]

$$\begin{aligned}W_{J+\frac{1}{2},m}&=-(\Delta W/2I+1)-g_J\mu_N Hm\\&\qquad-\tfrac{1}{2}\Delta W[1+(4mx/2J+1)+x^2]^{\frac{1}{2}},\\W_{J-\frac{1}{2},m}&=-(\Delta W/2I+1)-g_J\mu_N Hm\\&\qquad+\tfrac{1}{2}\Delta W[1+(4mx/2J+1)+x^2]^{\frac{1}{2}}.\end{aligned}\tag{2}$$

$\Delta W=c(J+\frac{1}{2})$, $x=(g_I-g_J)\mu_N H/\Delta W$, $m$ is the total magnetic quantum number and $J+\frac{1}{2}$, $J-\frac{1}{2}$ are the values of the total angular momentum for very weak fields. The selection rules are $\Delta F=\pm1$, 0 and $\Delta m=\pm1$, 0 in weak fields and $\Delta m_I=\pm1$, 0, $\Delta m_J=\pm1$, 0, $\Delta m=\pm1$, 0 in strong fields. Not all these transitions are observable, however. Transitions which result in changes of $m_J$ only in the strong deflecting fields are not observable in present apparatus. ($H_2$ is an exceptional case because of its large $g_J$.) The only important transitions are those for which $\Delta m_I=\pm1$. Therefore, we need consider only transitions where the total angular momentum goes from $J+\frac{1}{2}$ to $J-\frac{1}{2}$. There is

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[1] N. F. Ramsey, Jr., Phys. Rev. **58**, 226 (1940).

[2] W. A. Nierenberg and N. F. Ramsey, Phys. Rev. **72**, 1075 (1947).

[3] G. C. Wick, Z. Physik **85**, 25 (1933).

[4] G. C. Wick, Phys. Rev. **73**, 51 (1948).

[5] H. M. Foley, Phys. Rev. **72**, 504 (1947).

[6] J. W. Trischka, Phys. Rev. **74**, 718 (1948).

[7] A. Roberts, Phys. Rev. **76**, 1723 (1949).

[8] L. Grabner and V. Hughes, Phys. Rev. **79**, 819 (1950).

[9] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).

one exception. In the transitions

$$(J+\tfrac{1}{2},\, J-\tfrac{1}{2}) \leftrightarrows (J+\tfrac{1}{2},\, J+\tfrac{1}{2})$$

or

$$(J+\tfrac{1}{2},\, -J+\tfrac{1}{2}) \leftrightarrows (J+\tfrac{1}{2},\, -J-\tfrac{1}{2})$$

there is a difference in that a large change in magnetic moment occurs. In the present analysis $\bar{J}\sim 50$. Therefore, this exceptional transition is statistically negligible. It follows that the observable frequencies are

$$\nu=(\Delta W/h)(1+2zx+x^2)^{\frac{1}{2}}. \qquad (3)$$

The approximations $|g_J|\ll|g_I|$ and $J\gg 1$ are used, and $z=m/J$. Thus, for each value of $z$, $-1\leqslant z\leqslant 1$, there is a corresponding resonance; and, therefore, a spectrum is observed for a range of frequencies corresponding to $-1\leqslant z\leqslant 1$. If the method of Feld and Lamb[10] is followed, the density of states is calculated from $dz/d\nu$, since it is assumed that all values of $m$ are equally probable in the beam. The number of states per unit frequency interval is

$$dN/d\nu=|dz/d\nu|=\tfrac{1}{2}(\nu/\nu_I)(h/cJ), \qquad -1\leqslant z\leqslant 1, \qquad (4)$$

where $\nu_I=cJx/h=g_I\mu_N H/h$, the Larmor frequency for the uncoupled nucleus. The factor $\frac{1}{2}$ is to normalize the range of $z$. Therefore, for a given (large) value of $J$, the spectrum is a trapezoid centering about $\nu_I$ if $x>1$ and centering about $cJ/h$ if $x<1$. (See Fig. 1.) This is the line shape for a given value of $J$. In the molecular beam apparatus there is no separation of different $J$ states; and, therefore, the contributions from all states $J$ to a given frequency are summed with a weight $2a^2J\exp(-a^2J^2)dJ$ for each interval $dJ$, $a^2=h^2/8\pi^2KT$, where $K$ is the moment of inertia of the molecule. There are two regions of $\nu$ for which the summation is different. First, consider $\nu\leqslant\nu_I$:

$$\frac{dN}{d\nu}=\int_{h(\nu_I-\nu)/c}^{h(\nu+\nu_I)/c}\frac{1}{2}\frac{\nu}{\nu_I}\frac{1}{(cJ/h)}2a^2J\exp(-a^2J^2)dJ. \qquad (5)$$

Second, consider $\nu\geqslant\nu_I$:

$$\frac{dN}{d\nu}=\int_{h(\nu-\nu_I)/c}^{h(\nu+\nu_I)/c}\frac{1}{2}\frac{\nu}{\nu_I}\frac{1}{(cJ/h)}2a^2J\exp(-a^2J^2)dJ. \qquad (6)$$

By an appropriate change of variables and the use of an absolute value bracket, the two cases can be combined into a single expression for the spectrum:

$$dN/dy=\tfrac{1}{2}\pi^{\frac{1}{2}}(y/y_I)[\operatorname{erf}(y+y_I)-\operatorname{erf}|y-y_I|], \qquad (7)$$

where

$$y=(ha/c)\nu, \quad y_I=(ha/c)\nu_I$$

and

$$\operatorname{erf} y=(2/\pi^{\frac{1}{2}})\int_0^y\exp(-\xi^2)d\xi.$$

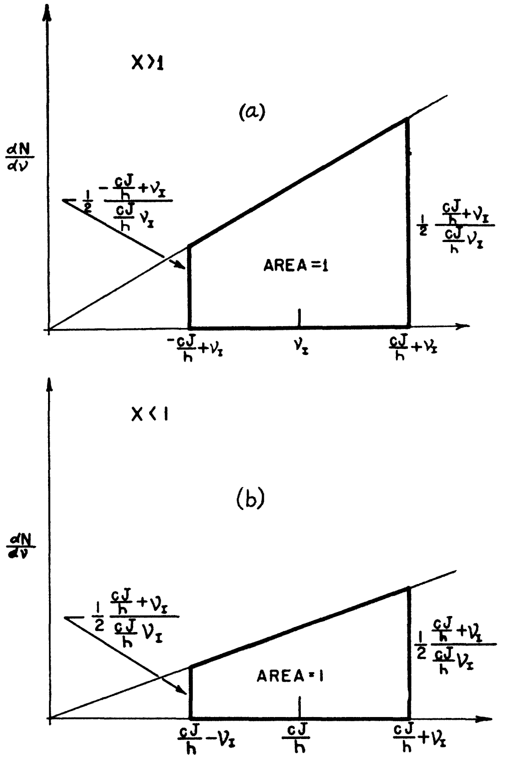

FIG. 1(a and b). The density of states for a fixed value of $J$ *versus* the reduced frequency.

In the limits of large field ($\nu_I\rightarrow\infty$) and zero field ($\nu_I\rightarrow 0$) the expression (7) reduces to those previously found.[2] Figure 2 displays the calculated spectral curves for different values of the parameter $y_I$ which may be used as a measure of the cosine coupling. The largest value of $y_I$ used, $y_I=5$, is equivalent to $\infty$, in so far as the term $\operatorname{erf}(y+y_I)=1.00$ over the range where the spectrum is appreciably different from zero but an appreciable asymmetry still exists because of the factor $y/y_I$. The transition of the spectrum between the two limits is clearly exhibited.

## III. SEMICLASSICAL APPROXIMATION AND EXTENSION TO HIGHER SPIN

Within the range of validity of the result, $|g_J|\ll|g_I|$ and $J\gg 1$, the same result can be obtained from a more classical picture which gives some insight to the motion of the angular momentum vectors. If $|g_J|\ll|g_I|$ and

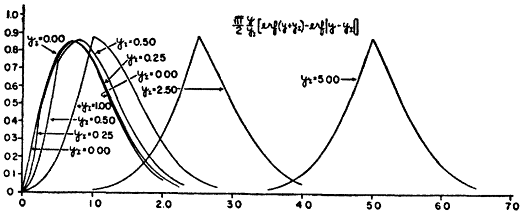

FIG. 2. The complete spectrum for different values of magnetic field. The parameter $y_I$ is proportional to the magnetic field.

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[10] B. T. Feld and W. E. Lamb, Jr., Phys. Rev. **67**, 15 (1945).

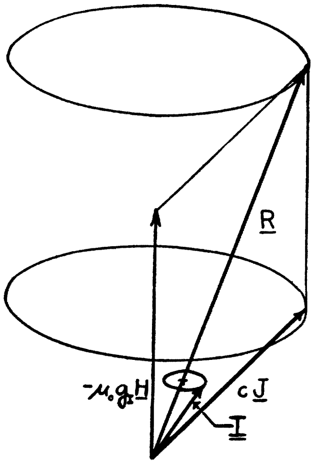

FIG. 3. The vector model of the motion of the angular vectors.

$J \gg 1$, then, to a first approximation under the existing torques, **I** is the only vector that will move, **J** can be considered stationary. This is equivalent to the statement that the precessional frequency of **I** is much greater than that of **J**. To this approximation, the hamiltonian is

$$\mathcal{H} = -\mu_N g_I \mathbf{I}\cdot\mathbf{H} - c\mathbf{I}\cdot\mathbf{J} = \mathbf{I}\cdot(-\mu_N g_I \mathbf{H} - c\mathbf{J}), \tag{8}$$

where **J** is now understood to be a *fixed* vector of magnitude $J$. The problem has therefore been reduced to the space quantization of the spin vector **I** with respect to the vector resultant **R**:

$$\mathbf{R} = -\mu_N g_I \mathbf{H} - c\mathbf{J}, \tag{9}$$

whose magnitude is

$$R = [(\mu_N g_I H)^2 + (cJ)^2 + 2\mu_N g_I H c J \cos\vartheta]^{\frac{1}{2}} \tag{10}$$

and $\theta$ is the angle between **J** and **H**. The energy levels are

$$W_{m_I} = -m_I R, \quad m_I = -I, -I+1, \cdots, I, \tag{11}$$

and the Larmor frequency of precession of $I$ about **R** is

$$\nu = R/h; \tag{12}$$

and this agrees with Eq. (3) if $z = \cos\theta$, an obvious correspondence. A good physical picture can be obtained (Fig. 3), by picturing **I** processing rapidly about **R** with frequency $R/h$ and **R** itself precessing slowly about **H**. Therefore, the motion of **I** can be approximately described as conical with the axis of the cone itself moving in a cone. This answer, to this approximation, is valid for all values of $I$. As a result of this picture, it can be easily understood why the second nucleus of the diatomic molecule can have very little influence on the spectrum of the first nucleus. Aside from the small dipole-dipole term, the two nuclei interact only because they are both coupled to $J$. Since this approximation sees $J$ as fixed the couplings cannot be transmitted through $J$. This argument holds for the most general form of the coupling function as well as for cosine coupling, and for all values of the magnetic field.

## IV. APPARATUS RESOLVING POWER AND TRANSITION PROBABILITIES

The spectrum, to this point, has only included the density of states factor. A complete calculation should include the transition probability as a factor in Eq. (4) before summing contributions from all $J$. In addition, the natural line width of the apparatus has to be "folded in" to get the true spectrum.

In any practical application, the line width is $\sim$5000–25,000 sec$^{-1}$ and is much smaller than the width of the spectrum. Therefore, the shape will not be appreciably changed but an estimate can be made of the expected intensity. The resolution function can be chosen rectangular,[2]

$$F(\nu', \nu) = K_1 K_2, \quad \nu - \Delta\nu \leqslant \nu' \leqslant \nu + \Delta\nu; \tag{13}$$

$K_1$ and $K_2$ are constant apparatus factors less than unity and $\Delta\nu$ is the effective half-width of the natural line. For all other $\nu'$, $F(\nu', \nu) = 0$. Then the true spectrum is given by the total number of transitions per resolution interval of frequency:

$$N(\nu) = \int_0^\infty F(\nu', \nu)(dN/d\nu')d\nu'; \tag{14}$$

$dN/d\nu$ is considered a function of $\nu'$ in the integrand. Since $F(\nu', \nu)$ is a narrow function, $dN/d\nu'$ may be taken from the integrand as a constant factor with $\nu = \nu'$. The integration is performed with the result that

$$N(\nu) = \Delta\nu K_1 K_2 (ha/c)\pi^{\frac{1}{2}}(y/y_I) \times [\mathrm{erf}(y+y_I) - \mathrm{erf}|y-y_I|]. \tag{15}$$

Referring to Fig. 2, it is clear that the greatest fractional reduction of the beam is approximately equal to $2\Delta\nu K_1 K_2(ha/c)$ and is roughly constant for all fields.

The transition probability factor is more complicated, and no calculation will be made chiefly because the oscillating magnetic field is always set at a high value when observing broad spectra. By a high value is meant a value such that the average molecule undergoes several transitions while in the field. This would, at first sight, seem to make matters worse; but then the temperature distribution of velocities of the beam molecules prevents complete transition for the average molecule, and the reduction in beam intensity can be taken as a constant factor $K_2$. It can be argued that this factor, despite the large perturbing field can still depend slightly on frequency and therefore should be included before summing over $J$. That this is not so can be understood by considering the first-order transition probabilities which will give a maximum estimate of the effect. On one hand, the transition probability is independent of $z$ for strong fields; and for weak fields where the transition probability varies rapidly with $z$ the trapezoid of Fig. 1 is very narrow, and the line shape is determined primarily by the variation in $J$ and is again unaffected. Therefore, it is concluded the Eq. (13) should describe the observed line shape quite well.

### IV. CONCLUSION

As a result of the calculation, a closed expression is given for the line shape for all values of the magnetic field. This suggests the experiment of following the fluorine resonance structure in LiF and CsF down in field to nearly zero field to corroborate the existence of the assumed cosine interaction. As for spins greater than one-half, the omission of a quadrupole coupling makes the calculation less useful. There still exist spectra, however, which have not yet been interpreted, particularly $Cl^{35}$ and $Cl^{37}$ in the alkali chlorides; and the possibility exists that large cosine coupling might explain the shape of the resonance.

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# The Mobility of Electrons in Silver Chloride

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Techniques are described which utilize the "print out effect" to obtain both the direction and velocity of photoelectrons in silver chloride crystals in an electric field. Hall mobility of the electrons is calculated from their change in direction produced by crossed electric and magnetic fields. Drift mobility of the electrons is obtained by measurement of their velocity in known electric fields. The value obtained for the Hall mobility ($R\sigma$) multiplied by $8/3\pi$ is 51 cm²/volt sec at 25°C. The values obtained for the drift mobility are shown to be a function of temperature. A value of 49.5 cm²/volt sec was obtained at 25°C, which is within experimental error of $(8/3\pi)R\sigma$, indicating that acoustical scattering is the principal mechanism and that temporary trapping is unimportant. A summary of the behavior of conduction electrons in silver chloride, calculated from the results of these experiments, is included.

## I. INTRODUCTION

THE measurements of the mobility of electrons in silver chloride described in this paper are a continuation of earlier experiments which were originally undertaken to furnish definite evidence of the role of electrons in certain photographic processes in this material. Not only were these early experiments successful in their primary objective, but they have also led to the development of new techniques for the study of the motion and trapping of electrons in silver halides.

The results of the early experiments, dealing largely with the trapping of electrons in silver chloride, were published by the authors in the Report of a Conference on the Strength of Solids.[1] The present paper presents later studies of mobility.

## II. THEORY OF THE "PRINT OUT EFFECT"[2]

The original object of this investigation was to establish the mechanism of the "print out effect," which is very closely related to latent image formation (see Mott and Gurney[3] for a general discussion on this topic). It is observed that if a photographic emulsion is exposed to strong light for a long time, it becomes dark. Microscopic examination of the small ($10^{-4}$–$10^{-5}$ cm in diameter) single crystals of the salt in the emulsion shows that the darkening is localized in the form of a number of small specks within the grain. Further research has shown that these specks are colloidal metallic silver[4] and that the total amount of metallic silver produced in the grain is approximately that which would be expected if every photon absorbed added one atom of silver to the colloidal specks.[5] Since the photons are absorbed in all parts of the grain, there must, therefore, be a transport mechanism by which the absorbed energy is made effective at the silver speck.

The transport mechanism proposed by Mott and Gurney involves the fact that silver chloride is an ionic conductor at room temperature and that its conductivity is due to the motion of silver ions. An illustration of how this conductivity occurs is shown in Fig. 1. Thermal agitation causes some silver ions to move from normal sites to interstitial positions $B$, thus leaving a vacant lattice point $C$ in the normal lattice. A series of exhaustive experiments by Koch and Wagner[6] and by Tubandt and Eggert[7] has shown that both the vacant lattice points and positive interstitial silver ions are mobile and both contribute significantly to the conductivity, the negative chlorine ions making a negligible contribution.[7a]

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[1] Conference on Strength of Solids, University of Bristol, July, 1947 (The Physical Society, London, England, 1948), pp. 151, 157.

[2] The following description of the "print out effect" is largely reproduced from the original article.

[3] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 122. For a recent review article see J. H. Webb, Phys. Today 3, No. 5, 8 (1950).

[4] R. Hilsch and R. W. Pohl, Z. Physik **77**, 421 (1932).

[5] J. Eggert and W. Noddack, Z. Physik **20**, 299 (1923); Handb. Wissenschaftlichen Angewandten Photographie **5**, 132 (1932).

[6] E. Koch and C. Wagner, Z. physik. Chem. **B38**, 295 (1937).

[7] C. Tubandt and S. Eggert, Z. anorg. Chem. **110**, 196 (1920).

[7a] It has been proposed by J. W. Mitchell that conduction by chlorine vacancies plays an important role in the photographic