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POLARIZATION OF NUCLEAR SPINS

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Date Received: 5/27/48

Date Issued: 6/9/48

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## POLARIZATION OF NUCLEAR SPINS

M. E. Rose

The purpose of the following is to discuss some of the elementary aspects of the theory underlying the problem of polarization of nuclear spins. In addition, a detailed description of the role of hyperfine structure (hfs) coupling will be given. It turns out that in certain special cases, viz: atoms with incompletely filled inner shells, one may utilize the hfs coupling between nuclear and electronic spins to produce appreciable alignment of nuclear spins at low temperatures but without the necessity of applying very strong magnetic fields. In the case of solids which have the aforementioned property this will always exist and, except for very low temperatures ( $\sim 10^{-3}$  °K) or very strong magnetic fields ( $\sim 10^5$  gauss) it will be the main mechanism for producing what may be called nuclear paramagnetism or diamagnetism.<sup>1)</sup>

### (1) Case of Direct Coupling

Consider first a solid in which the nuclear spins are coupled only to an external magnetic field  $H$ . Interactions between spins of different nuclei are entirely negligible and we assume no hfs coupling. The energy  $W$  of the system of  $N$  nuclei will in general depend on the quantum numbers describing the magnetic state of each nucleus. The nuclear spin of the  $n^{\text{th}}$  nucleus is  $I_n$  and the component of  $I_n$  in the direction of the field will be  $m_{I_n}$  so that  $W$  is a function of all the  $m_{I_n}$ . The probability that the system of  $N$  nuclei be in a state designated by the set of quantum numbers  $m_{I_n}$  is simply the Boltzmann factor  $e^{-W/kT}$ .

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<sup>1)</sup> Whether the nuclei show paramagnetic or diamagnetic behavior as a result of hfs coupling will depend on whether the hfs multiplet is normal or inverted, i.e., whether the ground state is the one with lowest total electronic angular momentum  $J$  or the state with maximum  $J$ , and also on the sign of the nuclear magnetic moment. This point is discussed below.

Then the component in the field direction of the total spin of the N nuclei is

$$I_T = \frac{\sum_{m_{11}} \dots \sum_{m_{1N}} \sum_n m_{1n} e^{-W/kT}}{\sum_{m_{11}} \dots \sum_{m_{1N}} e^{-W/kT}} \quad (1)$$

where the limits on the sum over  $m_{1n}$  are  $-I_n$  and  $I_n$ . Similarly, the total magnetic moment in the field direction is

$$M = \frac{\sum_{m_{1n}} \sum_n g_n m_{1n} e^{-W/kT}}{\sum_{m_{1n}} e^{-W/kT}} \quad (2)$$

where  $g_n$  is the Landé  $g$ -factor of the  $n^{\text{th}}$  nucleus, and the symbol  $\sum$  is an abbreviation indicating an  $n$ -fold sum over the  $m_i$  quantum numbers.

In the absence of magnetic coupling between nuclei the energy  $W$  is simply the sum of magnetic energies of each nucleus and is simply

$$W = \sum_{n=1}^N W_n \quad (3)$$

where each  $W_n$  depends only on  $m_{1n}$ . Then the denominator in (1) or (2) which is, of course, the partition function, is

$$\begin{aligned} Z &= \sum_{m_{1n}} e^{-\sum W_n/kT} = \prod_n \sum_{m_{1n}} e^{-W_n/kT} \\ &= \prod_n Z_n \end{aligned} \quad (4)$$

where  $Z_n$  is the partition function for the  $n^{\text{th}}$  nucleus.

It is clear that we need to consider only the magnetic energy since any term  $E_n$  added to  $W_n$  will factor out from each partition function as

$e^{-E_n/kT}$  and a similar factor enters from the numerator. The magnetic energy is simply

$$W_n = -\mu_n \cdot H = -\frac{m_1 n}{I_n} \mu_n H = -m_1 n g_n H \quad (5)$$

where  $\mu_n$  is the nuclear magnetic moment. It follows then that

$$\begin{aligned} M &= kT \frac{\partial}{\partial H} \log Z \\ &= kT \sum_n \frac{\partial}{\partial H} \log Z_n \end{aligned} \quad (6)$$

As expected, the magnetic moment is the sum of contributions from each nucleus.

The fraction of nuclei lined up with the field is

$$f_N = \frac{M}{\sum_n \mu_n} \quad (7)$$

For a mononuclear lattice, which we consider henceforth, each partition function has the same value which we designate by  $Z_0$  so that

$$M = NkT \frac{\partial}{\partial H} \log Z_0 \quad (8)$$

and since  $Z_0$  will depend only on  $\alpha = \mu H / kT$  we have

$$f_N = \frac{M}{\mu H} = \frac{1}{I} \frac{\partial}{\partial \alpha} \log Z_0 \quad (9)$$

With the energy given by (5) we have

$$\begin{aligned} Z_0 &= \sum_{-I}^I e^{\alpha m_1} = -1 + \frac{e^{\alpha(I+1)} - 1}{e^{\alpha} - 1} + \frac{1 - e^{-\alpha(I+1)}}{1 - e^{-\alpha}} \\ &= \frac{\sinh \alpha(I + \frac{1}{2})}{\sinh \frac{\alpha}{2}} \end{aligned}$$

Therefore we find directly for the degree of polarization the well-known Brillouin formula

$$f_N = \phi(\alpha) \equiv \frac{2I+1}{2I} \coth \frac{(2I+1)}{2} \alpha - \frac{1}{2I} \coth \frac{\alpha}{2} \quad (10)$$

For large spin I this reduces to the classical Langevin formula.

For  $\alpha \ll 1$  as will generally be the case, we have

$$f_N \approx \frac{1}{3} \frac{I+1}{I} \frac{\mu H}{kT} \quad (11)$$

The numerical factor varies between  $\frac{1}{3}$  and 1. To get a 20% polarization we therefore require

$$\frac{\mu H}{T} = 0.5 \text{ to } 1.5 \times 10^4 \text{ kilogauss/deg}$$

where  $\mu$  is the nuclear moment in nuclear magnetons and H is here in kilogauss. Thus for protons,  $\mu = 2.79$  and  $I = \frac{1}{2}$ , we require

$$\frac{H}{T} = 1900 \text{ kg/deg}$$

Thus a temperature of  $10^{-2}$  °K and a field of 20 kg would suffice. Since the spin factor does not vary over a wide range and the nuclear magnetic are similarly all of the same order of magnitude, the required values of H/T for other nuclei will be about the same or somewhat larger than that quoted above. A few typical cases of interest are:

	H <sup>2</sup>	Li <sup>6</sup>	Li <sup>7</sup>	Co <sup>59</sup>	In <sup>115</sup>
I	1	1	3/2	7/2	9/2
$\mu$	.856	.82	3.25	2.3	5.49
H/T	9200	9600	2900	5400	2350

(2) Case of hfs Coupling

Although low temperature techniques may allow one to produce appreciable polarization with reasonable magnetic fields for most nuclei with spin, it is of interest to inquire whether one can produce the same polarization without using strong fields. Alternatively, one may even hope to produce larger polarizations for a given temperature by using the fact that the magnetic moment of the orbital electrons produces a stronger field at the nucleus than one may expect to produce by external means. Of course, it is not implied that no external field is required since it is necessary to align the electronic moments. But due to the fact that the electronic moments are much larger than that possessed by nuclei, only a comparatively weak field need be used. Moreover, in one case at least,  $\text{Co}^{59}$ , it may be sufficient to use the permanent moment to align the electrons and, provided sufficient hfs coupling is present, one can then expect appreciable nuclear alignment.

It is first of all necessary to recognize that the utilization of hfs coupling is severely restricted insofar as it is impossible to produce any appreciable electron alignment in a solid unless there are incompletely filled inner shells. In the case of the large majority of crystalline solids those electrons which, in the isolated atom are in incompletely filled shells, valence electrons, are not localized in the vicinity of any particular nucleus but instead are in the quasi-continuous spectrum where their wave function is spread over the entire crystal. These electrons, which from the point of view of energy space belong to the bands characteristic of the periodic lattice, also belong, from the point of view of positional space, to each nucleus with equal probability. As a consequence one must consider now that the exclusion principle and the consequent Fermi statistics must apply. Therefore in a strong field it is not possible to make all the electrons occupy the lowest

level in which each spin is parallel to the field. In fact one must apply a field such that  $\mu H$  is of order of the Fermi energy  $\xi$ ,  $\mu$  being the electronic moment. Since  $\xi \sim$  a few e.v. such fields are completely out of the question.

Thus, alignment of only bound electrons is possible in the solid phase and for this it is necessary that the bound electrons have a net angular momentum. This will be the case only for incompletely filled inner shells whose electrons are screened by surrounding closed shells and therefore remain more or less unperturbed by the forces introduced when many atoms are brought together to form a crystal.

We are therefore restricted to solids containing elements in the iron, palladium, rare earth and platinum groups where respectively sub-shells of ten 3d, ten 4d, fourteen 4f and ten 5d electrons have not been completely filled. In addition, it seems that one may add the interesting case of the transuranic elements where, beginning with Pa, the 5f shell is presumably in the process of being filled. Of the Fe group only cobalt is of interest since all stable isotopes of Fe and Ni are even-even nuclei and presumably have zero spin. The following table shows the pertinent data for the elements in the Pd group for which there are stable isotopes with nuclear spin. The column headed A gives the mass number of the nucleus and the numbers in parentheses give the isotopic abundances. The last column gives the slow neutron cross section in barns.

<u>Pd Group</u>			
Symbol	Z	A	$\sigma$ -(barns)
Y	39	89 (100)	1.1
Zr	40	91 (11.5)	
Nb	41	93 (100)	0.0099
Mo	42	95 (16.1)	
		97 (9.65)	
Ru	44	99 (12.81)	
		101 (16.98)	
Rh	45	103 (100)	12.8

In the case of the rare earths one usually uses the salts, and the ion which is generally trivalent must be considered. According to Meggers<sup>2)</sup> the neutron atom has a configuration of the form  $4f^n 6s^2$  in most cases and it is to be expected that successive ionizations remove the s electrons and one f electron. In any case one will still be left with an incomplete inner shell in the ion in almost every case. The following table shows which rare earth nuclei come under consideration. Values of nuclear moment and spin, as well as slow neutron cross sections as given by Segré's chart, have been included.

Rare Earth Group

Symbol	Z	A	$\mu^1$	I	$\sigma$ (barns)
Pr	59	141 (100)			
Nd	60	143 (13.0)			
		145 (9.2)			
Sm	62	147 (16.1)			
		149 (15.5)			
Eu	63	151 (49.1)	3.4	5/2	53000
		153 (50.9)	1.3	5/2	530
Gd	64	155 (18.4)			
		157 (18.9)			
Tb	65	159 (100)			
Dy	66	161 (21.1)			
		163 (24.8)			
Ho	67	165 (100)			
Er	68	167 (24.4)			
Tm	69	169 (100)			100
Yb	70	171 (14.26)	0.45	1/2	
		173 (17.02)	-0.65	5/2	

Pt Group

Hf	72	177 (18.47)			
		179 (13.85)			
Ta	73	181 (100)		7/2	22.5
W	74	183 (17.3)			
Re	75	185 (38.2)	3.3	5/2	109
		187 (61.8)	3.3	5/2	82
Os	76	189 (16.1)			
Ir	77	191 (38.5)			
		193 (61.5)			
Pt	78	195 (35.3)	0.6	1/2	

<sup>2)</sup> W. F. Meggers, Science 105, 514 (1947).

The spectroscopic term designations have not been given since the electron configuration in the solid state is entirely uncertain. In fact, in the Pd and Pt groups the incompletely filled shells are surrounded by one or two 5s electrons in the former case and one or two 6s electrons in the latter. In the solid these electrons would presumably go into broad bands. In addition some of the 4f and 5d electrons may be no longer in bound states. In the rare earth group the unfilled 4f shell is surrounded by the 8 electrons in the 5s, 5p levels of the O shell and by a completely filled 6s level so that the 4f shell is fairly well shielded. Nevertheless, one cannot deduce any useful information from spectroscopic data referring to the neutral atom. One might guess, however, that for the ion the angular momenta J and L as well would be large since values of J and L up to 10 occur in the case of the neutral atom.<sup>3)</sup>

Although these J values are uncertain rather large L and large S values are deduced by Meggers from the spectroscopic evidence. The bearing of these facts on the present problem will be made clear below.

We now consider in detail the manner in which hfs coupling can align nuclear spins. For the case considered, ions with incomplete inner shells, the crystal can be treated as a system of non-interacting ions so that again  $W = \sum_n W_n$ . For a mono-isotopic lattice each of the magnetic ions have the same energy so that the fraction of nuclei lined up is again

$$f_N = \frac{M}{\mu_N N} = \frac{\sum n_i e^{-E/kT}}{I \sum e^{-E/kT}} \quad (12)$$

where the sum goes over all magnetic numbers of a single ion and E is the energy of a single ion. In (12)  $\mu_N$  is the nuclear magnetic moment and  $g_N$  is

(3) According to Pauling and Goudsmit, Structure of Line Spectra, p. 149

the nuclear g-factor.

With hfs coupling in a strong magnetic field the magnetic energy of the system of nucleus plus electrons is

$$E(m_I, m_J) = -m_I g_N H - m_J g_e H + A I \cdot J \quad (13)$$

where  $g_e$  is the electronic g-factor and A is a constant related to the hfs splitting:

$$A = \frac{\Delta E}{J(2I+1)} \quad I \geq J$$

$$A = \frac{\Delta E}{I(2J+1)} \quad I \leq J \quad (14)$$

where  $\Delta E$  is the overall hfs splitting

$$\Delta E = E_{F=I+J} - E_{F=|I-J|}$$

so that  $A > 0$  for the normal multiplets and  $A < 0$  for the inverted case.

In a strong field the nuclear and electron momenta are decoupled, i.e., precess about the field independently (complete Paschen-Beck effect) so that  $I \cdot J = m_I m_J$ . Thus E depends only on the quantum numbers  $m_I$  and  $m_J$ .

It is of interest to see qualitatively how the various factors in (13) effect the polarization direction. In general the states for which  $E < 0$  are most strongly populated. Consider first the direct coupling. For  $g_N > 0$  we get a negative contribution to E if  $m_I$  is positive so that the spins are aligned parallel to the field. For  $g_N < 0$  the antiparallel alignment will occur. For electrons  $g_e < 0$  so that the most favored states have  $m_J < 0$ . Therefore the hfs term tends to populate states for which  $m_I > 0$  when  $A > 0$  and  $m_I < 0$  when  $A < 0$ . Thus we have the following situation

with regard to the cooperation of the direct and hfs coupling.

	A		
$\epsilon_N$		+	-
+		add	oppose
-		oppose	add

Here the entries indicate that when A and  $\epsilon_N$  have the same sign the effect of the two types of coupling are of the same sign, and when  $A/\epsilon_N < 0$  the effects of the two couplings partially cancel.

We may now inquire under what conditions the hfs coupling is more effective than the direct coupling. Evidently this coupling produces an effective field equal to

$$H_{\text{eff}} = \frac{A \bar{m}_J}{\epsilon_N} \sim \frac{\Delta \epsilon}{2} \frac{f_e}{\mu_N}$$

where  $f_e = \bar{m}_J/J$  is the fraction of electronic moments lined up and the bar indicates an average over the Boltzmann distribution. Expressing  $\Delta \epsilon$  in  $\text{cm}^{-1}$  as  $\Delta \nu$  this gives

$$H_{\text{eff}} = 2\pi \frac{M_0^2}{e} f_e \frac{\Delta \nu}{\mu^2} = 2 \times 10^7 \frac{f_e \Delta \nu}{\mu^2} \text{ (gauss)}$$

One may expect hfs splittings  $\Delta \nu \sim 0.01 \text{ cm}^{-1}$ . Therefore for electron polarizations  $f_e$  considerably larger than 0.1 the hfs coupling is much more effective than the direct coupling of nuclear moments to the field. For larger  $\Delta \nu$  which may quite plausibly occur, one needs perhaps a 20% electron polarization for the hfs coupling to be most important. Even for electronic saturation ( $f_e > \frac{1}{2}$  say) one needs only weak fields if the temperature is of order  $0.01^\circ$ .

On the other hand the hfs term will be generally intermediate between the terms corresponding to direct field coupling with the nuclei and electrons respectively. Indeed the connection between  $A$  and  $\Delta\epsilon$  is valid only in a perturbation theory sense which requires that

$$m_J g_e H \gg \Delta_{I m_I m_J}$$

or,

$$H \gg 2\pi f_N \frac{m_e^2}{e} \Delta V = 10^4 f_N \Delta V$$

For  $\Delta V \sim 0.01$  and  $f_N \sim 0.2$  this implies an external field  $\gg 20$  gauss which will, of course, always be fulfilled.

The calculation of the nuclear polarization will be done for two cases.

In general we have

$$f_N = \frac{1}{I} \frac{\sum_{m_I} \sum_{m_J} m_I e^{\alpha m_I + \beta m_J - \gamma m_I m_J}}{\sum_{m_I} \sum_{m_J} e^{\alpha m_I + \beta m_J - \gamma m_I m_J}} \quad (15)$$

where

$$\alpha = \frac{g_N H}{kT}, \quad \beta = \frac{g_e H}{kT}, \quad \gamma = \frac{A}{kT}$$

and the sums are from  $-I$  to  $I$  over  $m_I$  and from  $-J$  to  $J$  over  $m_J$ . This can be written

$$f_N = \frac{1}{I} \frac{\partial}{\partial \alpha} \log Z_0 \quad (16)$$

where

$$Z_0 = \sum_{m_I} \sum_{m_J} e^{\alpha m_I + \beta m_J - \gamma m_I m_J} \quad (17)$$

For the partition function  $Z_0$  we have

$$Z_0 = \sum_{n=0}^{\infty} \frac{(-\gamma)^n}{n!} \sigma_n(\alpha) \sigma_n(\beta) \quad (18)$$

where

$$\sigma_n(\alpha) = \sum_{-I}^I m_I^n e^{\alpha m_I} \quad (18a)$$

$$\sigma_n(\beta) = \sum_{-J}^J m_J^n e^{\beta m_J}$$

We also have

$$\sigma_n(\alpha) = \frac{d^n \sigma_0(\alpha)}{d\alpha^n}; \quad \sigma_n(\beta) = \frac{d^n \sigma_n(\beta)}{d\beta^n} \quad (18b)$$

and

$$\sigma_0(\alpha) = \frac{\sinh \alpha (I + \frac{1}{2})}{\sinh \frac{\alpha}{2}}$$

$$\sigma_0(\beta) = \frac{\sinh \beta (J + \frac{1}{2})}{\sinh \frac{\beta}{2}} \quad (18c)$$

1. We consider first the case in which  $\gamma \ll 1$  and  $\alpha \ll 1$  but  $\gamma \gg \alpha$ .

In fact we shall neglect the direct coupling by setting  $\alpha = 0$ . Then we note that  $\sigma_n(0) = 0$  for  $n$  odd.

$$Z_0 = \sigma_0(\alpha) \sigma_0(\beta) - \gamma \sigma_1(\alpha) \sigma_1(\beta)$$

$$f_N \approx -\frac{1}{I} \frac{\gamma \sigma_2(\alpha) \sigma_1(\beta)}{\sigma_0(\alpha) \sigma_0(\beta)} = -\frac{f_0}{I} \frac{\gamma \sigma_2(0)}{\sigma_0(0)}$$

With

$$\sigma_0(0) = 2I + 1$$

$$\sigma_2(0) = \frac{1}{3} I(I + 1)(2I + 1)$$

and  $\alpha_1(\beta)/\sigma_0(\beta) = \bar{m}_J = -Jf_e$  we obtain

$$\begin{aligned} f_N &= \frac{I+1}{3} J f_e \gamma \\ &= \frac{1}{3} f_e \frac{I+1}{I} \frac{J}{2J+1} \frac{\Delta\epsilon}{kT} \quad \text{for } J \gg I \\ &= \frac{1}{3} f_e \frac{I+1}{2I+1} \frac{\Delta\epsilon}{kT} \quad \text{for } J \leq I \end{aligned} \quad (19)$$

At  $T = 0.01^\circ$ ,  $kT = 0.007 \text{ cm}^{-1}$ . Since  $f_N \sim \frac{1}{6} f_e \Delta\epsilon/kT$  we have for  $\Delta\epsilon = 0.01 \text{ cm}^{-1}$ ,  $f_N \sim \frac{1}{6} f_e$ . Essential saturation of the electronic moments therefore gives about 20% polarization of nuclei. The goal would thus be achieved with low temperatures but with comparatively weak fields.

Although one knows little about the hfs splittings to be expected it is reasonable that they may be of order  $10^{-2} \text{ cm}^{-1}$  or even larger. In this case, at  $T = 0.01^\circ$   $\gamma$  is not small compared to unity unless  $J$  and/or  $I$  are fairly large. For example, with  $\Delta\nu = 0.01$ ,  $T = 0.01^\circ$  and  $J = \frac{1}{2}$ ,  $I = 9/2$  we have  $\gamma = 2/7$ . Since terms of order  $\gamma^3$  have been neglected, the above approximation is good enough in this case. However, if  $I = \frac{1}{2}$ , say then  $\gamma = 1.4$ , and it is necessary to make a more accurate calculation.

2. We consider now that  $\gamma$  is arbitrary but that essentially complete saturation of the electronic moments has been attained; i.e.  $f_e \sim 1$  and  $|\beta| \gg 1$ .

1. We have with  $|\beta| = b$

$$\alpha_n(\beta) = (-)^n \left[ J^n e^{bJ} + (J-1)^n e^{b(J-1)} + \dots \right]$$

so that

$$z_0 \approx \sum_n \frac{\gamma^n}{n!} \frac{d^n \sigma_0(\alpha)}{d\alpha^n} \left[ J^n e^{bJ} + (J-1)^n e^{b(J-1)} \right]$$

$$= e^{bJ} \sigma_0(\alpha + \gamma J) + e^{b(J-1)} \sigma_0 [\alpha + \gamma(J-1)]$$

$$\frac{\partial z_0}{\partial \alpha} = e^{bJ} \sigma_1(\alpha + \gamma J) + e^{b(J-1)} \sigma_1 [\alpha + \gamma(J-1)]$$

We can express  $e^{bJ}$  in terms of the electron polarization  $f_e$ .

$$f_e \approx \frac{1}{J} \frac{J e^{bJ} + (J-1) e^{b(J-1)}}{e^{bJ} + e^{b(J-1)}} = \frac{1 + \frac{J-1}{J} e^{-b}}{1 + e^{-b}}$$

or 
$$e^{-b} = \frac{1 - f_e}{\frac{1}{J} - (1 - f_e)}$$

Then we have

$$f_N = \frac{1}{I} \frac{\left[1 - J(1 - f_e)\right] \sigma_1(\alpha + \gamma J) + J(1 - f_e) \sigma_1 [\alpha + \gamma(J-1)]}{\left[1 - J(1 - f_e)\right] \sigma_0(\alpha + \gamma J) + J(1 - f_e) \sigma_1 [\alpha + \gamma(J-1)]} \quad (20)$$

and

$$\sigma_1(x) = (I + \frac{1}{2}) \frac{\cosh(I + \frac{1}{2})x}{\sinh \frac{x}{2}} - \frac{1}{2} \frac{\sinh(I + \frac{1}{2})x \cosh \frac{x}{2}}{\sinh^2 \frac{x}{2}}$$

while  $\sigma_0(x)$  is defined by the first of (18c). This result is exact for  $J = \frac{1}{2}$ .

For complete saturation

$$f_N = \frac{1}{I} \frac{\sigma_1(\alpha + \gamma J)}{\sigma_0(\alpha + \gamma J)} = \varphi(\alpha + \gamma J) \quad (21)$$

where  $\varphi$  is defined by (10). Thus, when the electronic moments are completely lined up, the nuclear magnets are polarized as if by direct coupling with a total field given by the sum of the applied field and the effective field  $H_{\text{eff}}$ . For  $\Delta V = 0.01$ ,  $\mu' = 2.79$  (protons!)  $H_{\text{eff}} \sim 7 \times 10^4$  gauss and even without the effect of the applied field we get a nuclear polarization for  $I = J = \frac{1}{2}$  ( $\gamma J = 0.71$ )

equal to

$$f_N = 2 \coth \gamma J - \coth \frac{\gamma J}{2} = 0.37$$

For the special case  $J = 1$  the result (20) does not apply insofar as the correction terms due to incomplete saturation vanish. For  $J = 1$  (20) is replaced by

$$f_N = \frac{1}{I} \frac{(1 + f_e) \sigma_1(\alpha + \gamma) + (1 - f_e) \sigma_1(\alpha - \gamma)}{(1 + f_e) \sigma_0(\alpha + \gamma) + (1 - f_e) \sigma_0(\alpha - \gamma)} \quad (22)$$

and this result is exact. For  $\alpha = 0$ , this becomes

$$f_N = \frac{f_e}{I} \frac{\sigma_1(\gamma)}{\sigma_0(\gamma)} = f_e \phi(\gamma) \quad (23)$$

cf. (10). Again this result is exactly what was to be expected. Also for arbitrary  $\alpha$  (direct coupling) the result (21) applies in the case of complete saturation.

The remaining question which needs discussion is the question of the hfs splittings to be expected. As has been mentioned, one cannot obtain this information from such experimental evidence as exists. One could, to be sure, measure the hfs splitting by resonance absorption of microwaves. However, in the absence of such information one may try to calculate the hfs splitting. Here there are two difficulties: (1) One does not know the electron configurations except that in almost all cases one is certainly not dealing with configurations containing  $s$  electrons; (2) The configurations are rather complex involving many electrons, none of which are in penetrating orbits.

These difficulties are perhaps not important if all one wishes is an order of magnitude estimate. We may use the results applicable to single electrons since it appears that the presence of many electrons does not change the order

of magnitude of  $\Delta V$ . For non-s electrons, the hfs splitting depends on the screening effect of other electrons, the degree of ionization and other factors which are rather difficult to estimate in our case. However, most of these uncertainties are eliminated if one expresses the hfs coupling constant in terms of fine structure splittings which can be taken from observations. Then one has

$$A = \frac{\mu^2}{1840} \frac{l(l+1)}{j(j+1)(l+\frac{1}{2})} \frac{1}{Z_1} \Delta V_f \text{ cm}^{-1} \quad (24)$$

where  $l$  and  $j$  refer to a single electron,  $Z_1$  is the effective nuclear charge and is somewhat less than  $Z$  because of screening, while  $\Delta V_f$  is the doublet separation in ordinary fine structure. Generally, values of  $\Delta V_f$  vary from 100 - 1000  $\text{cm}^{-1}$ . Taking  $\Delta V_f \sim 500$ ,  $Z_1 \sim 50$ ,  $\mu^2 \sim 1$ ,  $l \sim j \sim 3$  which should represent typical values, we have

$$A \sim 1.5 \times 10^{-3} \text{ cm}^{-1}$$

and

$$\Delta E \sim 2IJ A \sim 0.03 \text{ cm}^{-1}$$

for  $I \sim J \sim 3$ .

This estimate, it is true, is quite rough. However, it should be sufficient to indicate that hfs splittings of order  $0.01 \text{ cm}^{-1}$  are reasonable to expect.