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ON THE SATURATION OF THE ELECTRIC AND MAGNETIC POLARIZATION OF GASES IN QUANTUM MECHANICS

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ABSTRACT

The calculations of dielectric and magnetic susceptibility in quantum mechanics previously made by Van Vleck are extended to include higher powers of the field strength. This is necessary in fields so strong that the moment is not linear in the field strength.

Electric polarization. As noted by Debye the electric polarization of a gas results from two effects: (a) a change in the spacial orientation of the rigid or permanent moment of the molecule, (b) the inducing of an elastic polarization or deformation of the molecule.

1. *Rigid molecules.* The effect of (a) is calculated in §2 to all powers of the field strength and yields exactly the classical Langevin function

$$L(\mu,\ F,\ T)=\mu[\operatorname{cotgh}(\mu F/kT)-kT/\mu F]$$

provided only the (rotational) energy changes in "allowed" transitions are small compared to kT. Here μ is the permanent moment of the molecule.

2. *Deformable molecules.* The part of the moment resulting from the effect (b) (induced polarization, described with matrix elements whose frequencies are large compared to kT/h), and the part arising from the superposition of (a) and (b) is calculated in §3 to terms of the third order in the field F. The complete formula for the moment is to this order:

$$m_F=\left(\frac{\mu^2}{3kT}+p_0\right)F+\left(q_0+\frac{q_1}{kT}+\frac{q_2}{k^2T^2}-\frac{\mu^4}{45k^3T^3}\right)F^3$$

where p_0, q_0, q_1, q_2 are constants whose explicit expressions in terms of the individual matrix elements are rather complicated. The expression is of the same type form as that of Debye's, except for addition of the term q_0 and reduces identically to his type form if, following Debye, we specialize the model by supposing the restoring forces to be simple harmonic.

Magnetic polarization of atoms. Brillouin showed that if we neglect the "spin," the magnetic polarization per atom in a monatomic gas is

$$m_H=\beta\left[\frac{le^{l\beta H/kT}+(l+1)e^{-(l+1)\beta H/kT}}{e^{l\beta H/kT}-e^{-(l+1)\beta H/kT}}-\frac{1}{e^{\beta H/kT}-1}\right]=B(l\,,\beta\,,H\,,T)$$

where $l+1$ is the azimuthal quantum number of the old quantum theory and β the Bohr magneton. We show that the reason this "Brillouin" function differs from that of Langevin is because the various Cartesian components of the angular momentum matrix do not commute in multiplication, a complication not found in the electric case. The appearance of a Brillouin function (which is expressible as the difference of two Langevin functions) instead of a single L-function obviates Debye's objection that the classical Langevin theory yields infinite entropy at $T=0$ in contradiction to the Nernst heat theorem.

Magnetic polarization of atoms with spin. When now the spin is included two limiting cases can conveniently be considered; viz. those in which the spin multiplets are very small or very large compared to kT. In the first case the magnetic polarization is the sum $B(l, \beta, H, T)+B(s, 2\beta, H, T)$ of two Brillouin functions representing the orbital and spin effects respectively. In the second case we need consider only the component of the magnetic moment parallel to the total angular momentum associated with the inner quantum number j. The polarization per atom then becomes $B(j, g\beta, H, T)$ where g is the Landé-factor.

Magnetic polarization of diatomic gases. With narrow multiplets ($\Delta\nu << kT/h$) the polarization is $L(\sigma_l\beta, H, T)+B(s, 2\beta, H, T)$ while with wide multiplets the formula is instead $L((\sigma_l+2\sigma_s)\beta, H, T)$ where σ_l and σ_s have their usual spectroscopic meaning. The reason that the Langevin function appears whereas the Brillouin function alone was encountered in the atomic case, is that now only the component of orbital angular momentum parallel to the axis of figure is of the important low frequency type and with only one effective Cartesian component no questions of non-commutability can arise.

§ 1 INTRODUCTION

THE dielectric constant ϵ is connected with the average molecular electric moment $\bar{\bar{m}}_z$ in the direction of the field F, according to the relation

$$\epsilon-1=4\pi N\bar{\bar{m}}_z/F, \tag{1}$$

where N is the number of molecules per 1 cm^3 of the gas. In the usual calculations of dielectric constants, it is assumed that the electric moment $\bar{\bar{m}}_z$ can be taken proportional to the field strength. This is an adequate approximation in fields of ordinary magnitude, but in strong fields one should differentiate $\bar{\bar{m}}_z$ with respect to F instead of dividing by F in order to obtain the most convenient definition of the dielectric constant. Furthermore higher order terms in the development of $\bar{\bar{m}}_z$ in F must be considered, thus giving a dependence of dielectric constant on field strength and a tendency to saturation, whereby the electric moment approaches a finite value instead of increasing linearly with F, when F becomes very large. Actual dielectrics usually exhibit only a very small tendency toward saturation at any field strength obtainable experimentally so that only the terms in $\bar{\bar{m}}_z$ which are proportional to F and F^3 come within the range of observation. The correction term in F^3 is calculated for the general molecule in § 3, but first in § 2 we calculate $\bar{\bar{m}}_z$ correct to all powers of F for a rigid molecule with only a permanent moment, as with this restricted type of molecule the extension to all powers of F occasions no difficulty.

Similar calculations of the saturation effect will also be made for the case of magnetic rather than electric polarization, as there is considerable similarity between the electric and magnetic cases, although some important differences arise from the non-commutativeness of the angular momentum matrices involved in the magnetic case. The magnetic saturation is experimentally much easier to detect than the electric.

Throughout this paper we follow substantially the method of Van Vleck,[1] which has the advantage of freeing one from special models of atoms or molecules. He showed that the Langevin-Debye formula $N\alpha+N\mu^2/3kT$ for the susceptibility in fields too weak for saturation could be obtained by

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[1] J. H. Van Vleck, Phys. Rev. **29**, 727 (1927); **30**, 31 (1927); **31**, 587 (1928).

assuming only that the energy levels of the molecule can be separated into two categories: the "low levels" which are characterized by the fact that the spacings between them are small compared to kT, and "high levels" whose excess of energy above the normal states is large compared to kT. For greater detail in discussing these two categories of states, we refer to p. 730 of Van Vleck's[1] paper I.

Notation. In the present paper small letters $a, b, \cdots$, will be used for the "low" states and capital ones $A, B, \cdots$, for the excited states. Greek letters $\alpha, \beta, \gamma, \cdots$, will be used to denote collectively states of both types. Thus symbolically we may write $\sum_\alpha = \sum_a + \sum_A$ where $\sum_a$ means a summation over the low states $a, b, c, \cdots$, and $\sum_A$ that over the excited ones. A frequency of the type ν_{ba} is a low frequency, while one of the type ν_{Ba} is high and $\nu_{\beta a}$ can be either. Van Vleck used three indices (n, j, and m) for one state and sometimes we shall use this notation too. The index n then represents the entire group of quantum numbers whose effect on the energy is large compared to kT, m is the axial quantum number quantizing the angular momentum about the axis of the field, while j signifies all the quantum numbers (except m) such that an "allowed" change in them causes only a change in energy small compared to kT. Commonly j symbolizes one or more quantum numbers associated with the rotational fine structure. In low levels n is to have the value n_0 and for the excited ones $n > n_0$. A state a in our notation would be the same as n_0jm in the Van Vleck notation $b, c, \cdots$, similar to $(n_0j'm')$, $(n_0j''m'') \cdots$, while A or B would mean njm or $n'j'm'$ (or $n'jm$) etc.

§2. THE QUANTUM-MECHANICAL DERIVATION OF THE COMPLETE FORMULA FOR THE ELECTRIC POLARIZATION OF GASES OF RIGID MOLECULES WITH A PERMANENT ELECTRIC MOMENT

In the present section, we are concerned with molecules having only a permanent electric moment, and we neglect the "high frequency" part of the moment involved in transitions to excited states, so that the matrix elements of M^z will all be of the type (ab) and none of the type (aB). We choose the electric field F along the z-axis and $W_a(F)$ denotes the energy of a molecule in the state a and in the presence of the field F. Such a molecule has then along the z-axis an electric moment, whose time average[2] is $\bar{m}_z = -\partial W_a^{(F)}/\partial F$. We assume in the calculation of the susceptibility that the molecules are concentrated practically entirely in the low states. For their distribution over these states we use the Boltzmann distribution law, so that we obtain for the average of $\bar{m}_z$ over all molecules:

$$\bar{\bar{m}}_z = \frac{\sum_a -\partial W_a^{(F)}/\partial F \cdot e^{-W_a^{(F)}/kT}}{\sum_a e^{-W_a^{(F)}/kT}} = kT\frac{\partial Z}{\partial F} \tag{2}$$

with

$$Z = \log \sum_a e^{-W_a^{(F)}/kT} \tag{2a}$$

Let us expand the exponentials as a power series in $(W_a^{(F)} - C)/kT$ about

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[2] Cf, J. H. Van Vleck, Phys. Rev. **31**, 585 (1928), footnote 21.

some common origin C for the energy. The choice of C is not important, but should presumably be chosen so as to make the convergence as good as possible, and C might therefore conveniently be taken as the average value of W^0 for the low levels; i.e., $C=\sum_a W_a : N_a$ in which N_a denotes the total number of low states. We find then

$$Z=-C/kT+\log N_a+\log\left[1-\pi_1+\pi_2-\pi_3+\cdots\right], \tag{3}$$

where

$$\pi_p=\sum_a (W_a{}^{(F)}-C)^p/p!k^pT^pN_a. \tag{4}$$

In these π_p we could substitute the development

$$W_a{}^{(F)}-C=W_a{}^0-C+FW_a{}^{(1)}+F^2W_a{}^{(2)}+\cdots.$$

Explicit formulas for $W_a{}^1$, $W_a{}^2$, $\cdots$, could be obtained by the perturbation theory of Born, Heisenberg and Jordan, but the convergence of this development might not be good for such high powers (all powers are here required!). Such explicit formulas however are fortunately unnecessary in the present special case of only low frequency matrix elements $M^z{}_{ab}$. The sum in π_p namely can here be evaluated by means of the general theorem that

$$[W_a{}^{(F)}]^p=\sum_{\beta\gamma} S_{a\beta}[(H^{(F)})^p]_{\beta\gamma}\overset{-1}{S}_{\gamma a}.$$

In the presence of an electric field the Hamiltonian function is

$$H^{(F)}=H^0-FM^z.$$

therefore $$\sum_a (W_a{}^{(F)}-C)^p=\sum_{\beta\gamma}[(H^0-C-FM^z)^p]_{\beta\gamma}\sum_a \overset{-1}{S}_{\gamma a}S_{a\beta}$$

In the absence of excited states the indices β and γ can only indicate low levels b, c, $\cdots$. Thanks to this restriction we now have:

$$\sum_a \overset{-1}{S}_{ca}S_{ab}=\sum_\alpha \overset{-1}{S}_{c\alpha}S_{\alpha b}=\delta_b{}^c$$

therefore $$\sum_a (W_a{}^{(F)}-C)^p=\sum_b [(H^0-C-FM^z)^p]_{bb}=\sum_a [(H^0-C-FM^z)^p]_{aa} \tag{5}$$

Let us now for a moment neglect the rotational energy which is just what Langevin did in his classical theory. We shall then derive the Langevin formula for $\overline{\overline{m}}_z$. Actually this neglect is not legitimate. Therefore we shall afterwards take the rotational energy into account and show the reason why the final result remains the same. Neglecting first the rotational energy, and throughout the whole section also the spin, we may put $W_a{}^0=W_b{}^0$ $=$ ——— $=C$, so that the matrix H^0-C now becomes identically zero. We then have from (4) and (5)

$$\pi_p=(-1)^pF^p\sum_a (M_z{}^p)_{aa}/p!k^pT^pN_a. \tag{6}$$

Here N_a is the number of levels in which n always equals n_0, so that we have

$$N_a = \sum_j N_j p_j = \sum_j (2j+1) N_j$$

where p_j denotes the weight of a low state; i.e., the number of possible values of m when j and $n = n_0$ are given; and where further N_j is the number of possible indices j with $n = n_0$. Therefore $N_j = 1$ if we neglect the electron spins. A summation over the low levels a can be split up into $\sum_a = \sum_j \sum_m$ In accordance with the meaning of statistical weights, we evaluate the quantum mechanical average $\sum_a (M_z{}^p)_{aa}/N_a$ by averaging first over the m's and then the answer over j, indicated by a bar with j attached. Hence

$$\sum_a (M_z{}^p)_{aa} : N_a = \overline{\left[\sum_m (M_z{}^p)_{(n_0jm,n_0jm)} : p_j \right]}^{\,j} \tag{7}$$

Now a quantum mechanical average of $(M_z{}^p)_{(noim,noim)}$ over the axial or so-called magnetic quantum number m, which involves a discrete summation, yields the same results as a continuous classical average by means of an integration over a continuous distribution of axes. Thus:

$$\frac{\sum_m (M_z{}^p)_{(n_0jm,n_0jm)}}{p_j} = \frac{\mu_j{}^p \int \cos^p \theta d\omega}{\int d\omega} \tag{8}$$

Here μ corresponds to the value of the electrical moment of the molecule in the classical theory, while θ is the angle between μ and the z-axis, so that on the right side $m_z{}^p$ has been averaged classically over all possible orientations of the molecule in space. This theorem which has been already proved by Van Vleck for $p = 2$ holds for every value of p, as is shown in the appendix, but only on the assumption that the moment is not substantially changed by the rotation, in agreement with the fact that we deal here with rigid molecules. Consequently μ_j can be taken independent of j and so we obtain from (7) and (8)

$$\sum_a (M_z{}^p)_{aa} : N_a = \overline{\mu^p \cos^p \theta,}^{\,cl}$$

where the bar with cl denotes a classical average. Substituting these values in (6) we find:

$$1 - \pi_1 + \pi_2 - \cdots = \overline{(e^{F\mu \cos \theta / kT})}^{\,cl}$$

from which and (2), (3) the Langevin formula

$$\overline{m}_z = \mu \left[\operatorname{cotgh} \frac{\mu F}{kT} - \frac{kT}{\mu F} \right] = L(\mu, F, T). \tag{9}$$

is derived in a well known way.

Correction for rotation. Let us now include the rotational energy in our calculation. Then we have to go back to (5) where H^0-C does not vanish any longer. The procedure is best explained by evaluating the sum (5) for a definite value of p. For $p=5$ we have:

$$\sum_a [(H^0-C-FM^z)^5]_{aa} = \sum_{a,b,c,d,e} G_{(ab)}G_{(bc)}G_{(cd)}G_{(de)}G_{(ea)} \tag{10}$$

where
$$G_{(ik)} = (W_i^0-C)\delta_k^i - FM^z{}_{(ik)},$$

since H^0 is a diagonal matrix with elements W_a^0, W_b^0, $\cdots$. Let us first consider a definite term of the sum; e.g.:

$$[(H^0-C-FM^z)^5]_{kk} = \sum_{l,m,n,0} G_{(kl)}G_{(lm)}G_{(mn)}G_{(n0)}G_{(0k)}. \tag{11}$$

When we write the right hand side as a polynomial in F, the highest power of F that occurs is F^5, namely in:

$$\sum_{l,m,n,0} (-1)^5F^5 \overset{z}{M}_{kl}\overset{z}{M}_{lm}\overset{z}{M}_{mn}\overset{z}{M}_{n0}\overset{z}{M}_{0k} = (-1)^5F^5(M_z{}^5)_{kk}$$

which we get by taking from the five G-factors each time the term $-FM^z$. To build up the term with F^4 in the polynomial we have to take from four G-factors the term $-FM^z$ and from the remaining one the term $(W_i^0-C)\delta_j^i$, where i, j mean kl, lm, or ok, depending upon the place of the "remaining" G factor. Since this last term is zero unless $i=j$, the summation will not be extended over four indices l, m, n, o, but only over three, the missing one again depending on the place of the remaining G factor. So there are five possibilities, two of which are:

$$\begin{aligned} &(-1)^4F^4 \sum_{mn0}(W_k{}^0-C)\overset{z}{M}_{km}\overset{z}{M}_{mn}\overset{z}{M}_{n0}\overset{z}{M}_{0k} = (-1)^4F^4(W_k{}^0-C)(M_z{}^4)_{kk} \\ &(-1)^4F^4 \sum_{ln0}\overset{z}{M}_{kl}(W_l{}^0-C)\overset{z}{M}_{ln}\overset{z}{M}_{n0}\overset{z}{M}_{0k} \sim (-1)^4F^4(W_k{}^0-C)(M_z{}^4)_{kk}. \end{aligned} \tag{12}$$

The last equation does not hold rigorously but only if we neglect the difference between $W_l{}^0$ and $W_k{}^0$. If now all matrix elements with two low indices were different from zero, we should have to put all low energy levels equal to $W_k{}^0$, since we have to sum over l, i.e., over all low levels, and that would be the same as neglecting the rotational energy entirely, so that our approximation would be as poor as the previous one. Using note 26 of Van Vleck's paper[1] I, we remark however that the number of intermediate[3] levels (here denoted by l, m, n, o) will be very small, if we start from some initial level k, to which we have to return again as a final state after a few transitions.

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[3] The name intermediate level is chosen for those levels which belong to the intermediate indices in the range of indices occurring in products as $M_{ab}{}^z\ M_{bc}{}^z\ M_{cd}{}^z\ M_{da}{}^z$ etc. They lie therefore between the initial and final state, not with respect to energy but with respect to place in the matrix product.

There are namely selection principles for the rotational quantum number in virtue of which all matrix elements vanish which relate to two levels which do not lie close together (or at least nearly vanish in case the selection principles for some reason do not hold vigorously). All we need to assume is therefore that the energy levels in the *neighborhood* of $W_k{}^0$ may be taken equal to $W_k{}^0$. So the five possibilities will give us a term of order F^4 in (11)

$$5\cdot(-1)^4F^4(W_k{}^0-C)(M_z{}^4)_{kk}$$

and the same assumption enables us to calculate the terms with F^3, etc., the numerical coefficients being of course the binomial coefficients belonging to the fifth power:

$$10(-1)^3F^3(W_k{}^0-C)^2(M_z{}^3)_{kk}, \qquad 10(-1)^2F^2(W_k{}^0-C)^3(M_z{}^2)_{kk} \text{ etc.}$$

We only considered the term $[\quad]_{kk}$ in the sum (10). To evaluate the *sum* itself we have therefore to suppose that the very few energy levels in the neighborhood of $W_a{}^0$ may be taken equal to $W_a{}^0$, those around $W_b{}^0$ to $W_b{}^0$, in general those around an arbitrary level $W_k{}^0$ equal to $W_k{}^0$. This assumption is by no means so drastic as our previous one which includes putting *all* low levels equal to one another. Only when we chose instead of $p=5$ for example $p=50$, we might encounter an intermediate level bound to the initial one by a range of non-vanishing matrix elements and yet far away from it. There our assumption would be very likely about as bad as our previous one, but terms with a great value of p contribute very little, since they belong to the outermost part of the development which we assumed to converge. Changing our special case $p=5$ into that of an arbitrary power, we find thus in a fair[4] approximation, from which one could obtain our previous approximation by omitting the term $W_a{}^0-C$. Instead of (6) we now obtain

$$\pi_p=\overline{\left\{\sum_{m}\left[(W^0{}_{n_0j}-C-FM_z)^p\right]_{(n_0jm,n_0jm)}:p_j\right\}}:p!k^pT^p. \tag{13}$$

Here we have written $W_{n_0j}{}^0$; instead of $W_{\hat{n}_0jm}{}^0$ for $W_a{}^0$ since it signifies the energy in the absence of an external field and therefore does not depend on m. This fact is very important for the next transformation, as it permits us after the development of the *pth* power to bring $W_{n_0j}{}^0-C$ in each term before the summation sign $\sum_m$. The expression $\{\cdot\cdot\cdot\cdot\cdot\}$ in (13) is therefore a collection of quantum mechanical averages instead of the one (6) which appeared previously. But on each one our theorem (8) can be applied, taking there $p=0,\ 1,\ 2,\cdots p$ so that we obtain a *collection* of classical averages, giving us:

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[4] The degree of approximation is still higher than it is merely because of the fact that only levels lying close together had to be taken equal. If we namely assume their energy values to vary linearly, i.e. to show constant differences λ, this λ would only appear as λ^2 and higher powers in the final result the term with λ cancelling out on account of symmetry.

$$\{\cdots\}=\overline{(W^0_{n\,0j}-C-F\mu_j\cos\theta)^p}^{cl}$$

where the bar of course refers to θ. This had further to be averaged over j to find π_p in formula (13). For such a double average we use a bar with indices cl, j. We find then:

$$1-\pi_1+\pi_2-\pi_3+\cdots=\overline{(e^{-(W0_{uoj}-C-F\mu_j\cos\theta)/kT})}^{cl,j}$$

Since we assumed that μ was not appreciably affected by the centrifugal force and therefore independent of j, we have

$$\log(1-\pi_1+\pi_2-\pi_3+\cdots)=\log\overline{(e^{-(W0_{noj}-C)/kT})}^{j}+\log\overline{(e^{F\mu\cos\theta/kT})}^{cl}$$

The function Z defined in (2a) (the logarithm of the so-called "Zustandsumme") thus separates into two parts, a purely rotational part independent of F and a "magnetic" part which is the same as the Langevin value of Z we previously obtained when we neglected the molecular rotations. The first part is the same as the value of Z in the absence of a magnetic field and by (2) contributes nothing to the polarization. The inclusion of the rotation thus does not impair the validity of the Langevin formula for the polarization provided the temperature is high enough so that the quantum frequencies of rotation are small compared to kT/h.

§3 THE ELECTRIC POLARIZATION OF A GAS OF DEFORMABLE MOLECULES IN A STRONG FIELD

Deformations due to rotation, i.e. to a centrifugal force, will be neglected. Only those owing to the static electric field will be considered, so that we shall give here the quantum mechanical analog of the well known classical corrections which Debye added to the Langevin function in the case of electric polarization. Since the molecules are no longer rigid, we have here also to do with high frequency matrix elements which describe the deformation in the matrix language. This fact complicates our calculations very much. We again have here to use the equations (2), (3), (4) for $\bar{\bar{m}}_z$, Z and π_p but the evaluation of π_p in the fashion of §2 was only possible in the absence of excited levels (in the derivation of Eq. 5) i.e., in the absence of high frequency matrix elements. We must therefore find another way here. We shall be content with a development of the polarization in powers of F exact through terms in F^3. At the same time, we assume that the temperature is large enough to make an expansion of the polarization in powers of $h\nu/kT$ legitimate. Calculating with Debye only the terms with F and F^3 we see immediately from the form of the Boltzmann law that we can omit in the polarization all terms with $(kT)^{-4}$ and higher negative powers. We need therefore for the logarithms in Z an expansion exact in terms with $(kT)^{-4}$ on account of Eq. (2). Since π_p contains $(kT)^{-p}$ we write:

$$\log(1-\pi_1+\pi_2-\pi_3+\cdots)$$
$$=-\pi_1+\left(-\frac{\pi_1^{\,2}}{2}+\pi_2\right)+\left(-\frac{\pi_1^{\,3}}{3}+\pi_1\pi_2-\pi_3\right)+\left(-\frac{\pi_1^{\,4}}{6}+\pi_1^{\,2}\pi_2-\pi_1\pi_3-\frac{\pi_2^{\,2}}{2}+\pi_4\right)$$

From the above we have to develop the π's in a power series of F but need not go beyond F^4, again on account of Eq. (2). Therefore we substitute:

$$W_a^{(F)}=W_a^{0}+FW_a^{(1)}+F^2W_a^{(2)}+F^3W_a^{(3)}+F^4W_a^{(4)} \tag{14}$$

in the right side of (4) and find thus

$$\pi_p p!k^pT^pN_a=\sum_a(W_a^{0}-C)^p+\sum_{k=1,2,3,4}F^k\sum_a K_a^{(k,p)}, \tag{15}$$

introducing $K_a^{k,p}$ as the coefficient of F^k in the expansion of $(W_a^{(F)}\dot{-}C)^p$. It can be shown that $\sum_a K_a^{k,p}$ vanishes for an odd value of k, so that π_p will become an even function of F. The proof is based upon the fact that:

$$\overset{z}{M}_{(njm,n'j'm')}=-\overset{z}{M}_{(n,j,-m',n',j',-m')}$$

the ground of which is that a change of the magnetic (or axial) quantum number both in the initial and final state can be interpreted as a reversing of the direction of z. From this and from the fact that m ranges symmetrically over negative and positive values, it follows that:

$$\sum_{m'm''m'''}\overset{z}{M}_{(njm,n'j'm')}\overset{z}{M}_{(n'j'm',n''j''m'')}\cdots\overset{z}{M}_{(\dots,njm)} \tag{16}$$

is multiplied by $(-1)^k$, k being the number of matrix elements in each product, when we replace m (i.e. the axial quantum number in the initial *and* final state) by $-m$ From its definition we know that K_a^{kp} contains only terms which can be written as

$$CW_a^{(j)}W_a^{(j')}W_a^{(j'')}\cdots W_a^{(l)} \text{ with } j+j'+j''+\cdots l=k. \tag{17}$$

From the theory of Born, Heisenberg and Jordan (compare also the explicit formulas for W_a^1, W_a^2, W_a^3, and W_a^4 in (22*a*)) we know that W_a^j consists only of terms with j matrix elements arranged as in (16) and summed in the same way over the indices m', m'' $\cdots$ and over other indices which do not play a role in our proof. Therefore the term (17) and consequently also $K_a^{k,p}$ is multiplied with $(-1)^{j+j'\cdots l}=(-1)^k$ if we choose instead of a $(=n_0, j, m)$ another state $n_0, j, -m$. Now in the summation $\sum_a K_a^{k,p}$ each state $n_0 j$, m may be combined with another $n_0, j, -m$ so that all terms cancel out if $p=$odd, and thus we have proved

$$\sum_a K_a^{(kp)}=0 \quad \text{for} \quad k \text{ odd}. \tag{18}$$

Let us for the present neglect the rotational energy since we may expect from our results in §2 that this part of the energy would only affect the value of the "Zustandsumme" Z but not that of the polarization itself. Afterwards we shall correct our result again for the omission of the rotational terms. We now have

$$K_a^{(kp)}=0 \quad \text{for} \quad k<p, \tag{19}$$

since in its terms there occurs always at least one factor (W_a^o-C) which vanishes by taking $W_a^0=W_b^0=\cdots=C$. From (15), (18) and (19) we obtain:

$$\left.\begin{aligned} \pi_1 N_a kT &= F^2 \sum_a K_a^{(21)} + F^4 \sum_a K_a^{(41)} \;;\; \pi_3 N_a 3!k^3T^3 = F^4 \sum_a K_a^{(43)} \\ \pi_2 N_a 2!k^2T^2 &= F^2 \sum_a K_a^{(22)} + F^4 \sum_a K_a^{(42)} \;;\; \pi_4 N_a 4!k^4T^4 = F^4 \sum_a K_a^{(44)} \end{aligned}\right\} \tag{20}$$

The quantities $\sum_a K_a^{kp}$ now become also very simple, thanks to the assumption $W_a^0-C=0$. These are the coefficients of F^k in the expansion of $\sum_a(FW_a^1+F^2W_a^{(2)}+\cdots)^p$ and we have

$$\left.\begin{aligned} &K_a^{(41)}=W_a^{(4)}\;; && K_a^{(43)}=3W_a^{(1)}W_a^{(1)}W_a^{(2)} \\ &K_a^{(42)}=2W_a^{(3)}W_a^{(1)}+W_a^{(2)}W_a^{(2)}\;; && K_a^{(44)}=W_a^{(1)}W_a^{(1)}W_a^{(1)}W_a^{(1)} \end{aligned}\right\} \tag{20a}$$

So we need now to calculate W_a^1, W_a^2, W_a^3 and W_a^4. As is known, Born, Heisenberg and Jordan have developed a general method for the calculation of W_a^k from the matrices H^0, H^1, H^2 $\cdots$ occurring in the perturbed Hamiltonian and they gave explicitly the formulas for W_a^1, W_a^2, and W_a^3. Since in our case $H^{(2)}=H^{(3)}=\cdots=0$ it may be useful to follow another method which, although substantially equivalent, is perhaps a bit more lucid. We denote the eigen-functions and eigen-values of the Schroedinger equation in the absence of the field by u_n^o, W_n^0 and in its presence by u_n, W_n. On account of the assumed completeness of the u_n^0 we can make the expansion:

$$u_n=\sum_m(\delta_n^m+F\overset{(1)}{c_{mn}}+F^2\overset{(2)}{c_{mn}}+\cdots)u_m^0 \tag{21}$$

so that u_n reduces to u_n^0 when $F=0$. Substituting this, together with the expansion (14) for W_n into the Schroedinger equation:

$$(H^0+FH^{(1)})u_n=W_nu_n \tag{22}$$

and equating the coefficients of equal powers of F in the left and right hand side, we obtain several relations in which the operators H^0 and H^1 work upon u_1^0 u_2^0 u_3^0 $\cdots$ etc. The effect of the operator H^o is simply given by the Schroedinger equation $H^0u_n^0=W_n^0u_n^0$ and if we introduce matrix elements by means of

$$H^{(1)}u_n^0=\sum_m H_{mn}^{(1)}u_m^0$$

then our relations (22) become merely linear forms in the u_n^0 themselves. Because of the linear independence of these u_n^0 the coefficient of each u_n^0 must vanish, yielding us the following equations:

$$\overset{0}{W}_{m}\overset{(1)}{c}_{mn}+\overset{(1)}{H}_{mn}-\overset{(1)}{c}_{mn}\overset{0}{W}_{n}=\delta_{n}^{m}\overset{(1)}{W}_{n}$$

$$W_{m}{}^{0}\overset{(3)}{c}_{mn}+\sum_{k}\overset{(1)}{H}_{mk}\overset{(2)}{c}_{kn}-\overset{(3)}{c}_{mn}W_{n}{}^{0}-\overset{(2)}{c}_{mn}W_{n}{}^{(1)}-\overset{(1)}{c}_{mn}W_{n}{}^{(2)}=\delta_{n}{}^{m}W_{n}{}^{(3)}$$

$$W_{m}{}^{0}\overset{(4)}{c}_{mn}+\sum_{k}\overset{(1)}{H}_{mk}\overset{(3)}{c}_{kn}-\overset{(4)}{c}_{mn}W_{n}{}^{0}-\overset{(3)}{c}_{mn}W_{n}{}^{(1)}-\overset{(2)}{c}_{mn}W_{n}{}^{(2)}{}'-\overset{(1)}{c}_{mn}W_{n}{}^{(3)}=\delta_{n}{}^{m}W_{n}{}^{(4)}$$

originating respectively from the terms with F, F^2, F^3 and F^4 in the development of equation (22).

Putting $m=n$ in the first equation we find $W_n{}^1=H_{nn}{}^1$ since the unknown $c_{nn}{}^1$ then cancels out. For $m\neq n$, it gives $c_{mn}{}^1=H_{mn}{}^1/(W_n{}^0-W_m{}^0)=H_{mn}{}^1/h\nu_{nm}$. Putting $m=n$ in the second equation we are able to find $W_n{}^2$ since $c_{nm}{}^1$ has been found already and $c_{nn}{}^1$ and $c_{nn}{}^2$ cancel out. So we get successively the values for $W_a{}^1$, $W_a{}^2$, $W_a{}^3$, and $W_a{}^4$. The calculation goes on very easily since we always get rid of many terms, when we collect each time those with $c_{nn}{}^i$. These coefficients only play a role in the normalization of the new eigen-functions, but the energy is of course independent of them. We thus find, on writing $H_{nm}^{(1)}=-\overset{z}{M}_{nm}$

$$W_a{}^{(1)}=-\overset{z}{M}_{aa},\quad W_a{}^{(2)}=\sum_{\beta}{}'\frac{\overset{z}{M}_{a\beta}\overset{z}{M}_{\beta a}}{h\nu_{a\beta}}$$

$$W_a{}^{(3)}=-\sum_{\beta\gamma}{}'\frac{\overset{z}{M}_{a\beta}\overset{z}{M}_{\beta\gamma}\overset{z}{M}_{\gamma a}}{h^2\nu_{a\beta}\nu_{a\gamma}}+\sum_{\beta}{}'\frac{\overset{z}{M}_{aa}\overset{z}{M}_{a\beta}\overset{z}{M}_{\beta a}}{h^2\nu_{a\beta}{}^2} \tag{22a}$$

$$W_a{}^{(4)}=\sum_{\beta\gamma\delta}{}'\frac{\overset{z}{M}_{a\beta}\overset{z}{M}_{\beta\gamma}\overset{z}{M}_{\gamma\delta}\overset{z}{M}_{\delta a}}{h^3\nu_{a\beta}\nu_{a\gamma}\nu_{a\delta}}+\sum_{\beta}{}'\frac{\overset{z}{M}_{aa}\overset{z}{M}_{aa}\overset{z}{M}_{a\beta}\overset{z}{M}_{\beta a}}{h^3\nu_{a}{}^{3}{}_{\beta}}$$

$$-\frac{1}{2}\sum_{\beta\gamma}{}'\frac{2\overset{z}{M}_{a\beta}\overset{z}{M}_{\beta\gamma}\overset{z}{M}_{\gamma a}\overset{z}{M}_{aa}+\overset{z}{M}_{a\beta}\overset{z}{M}_{\beta a}\overset{z}{M}_{a\gamma}\overset{z}{M}_{\gamma a}}{h^3}\,\frac{\nu_{a\beta}+\nu_{a\gamma}}{\nu^2{}_{a\beta}\nu^2{}_{a\gamma}}$$

where a dash above a summation sign denotes that β, γ, δ always must be unequal to a. When we now exclude the rotational terms, the indices β, γ, δ $\cdots$ can only indicate excited states and have to be replaced by B, C, D $\cdots$ and the dash is no longer necessary. These equations permit us to calculate the $K_a{}^{k,p}$ of (20a) and so also the functions π_p in (20). Substituting the last ones in the development of the logarithms in Z and applying the relation (2) between $\overline{\overline{m}}_z$ and Z, we find:

$$\overline{\overline{m}}_z=pF+qF^3$$

$$q=-\frac{p^2}{2kT}+\frac{4}{N_a}\left[-P_0+\frac{P_1}{2kT}-\frac{P_2}{6k^2T^2}+\frac{P_3}{24k^3T^3}\right]. \tag{23}$$

Introducing the abbreviation:

$$(a\beta\gamma\delta a)^z = \overset{z}{M}_{a\beta}\overset{z}{M}_{\beta\gamma}\overset{z}{M}_{\gamma\delta}\overset{z}{M}_{\delta a} \tag{23a}$$

we have for P_0, P_1,P_2 and P_3 the following values:

$$\left.\begin{aligned}
P_0 &= \sum_{aBCD}\frac{(aBCDa)^z}{h^3\nu_{aB}\nu_{aC}\nu_{aD}} + \sum_{aD}\frac{(aaaDa)^z}{h^3\nu^3{}_{aD}} \\
&\quad -\frac{1}{2}\sum_{aCD}\frac{2(aCDaa)^z+(aCaDa)^z}{h^3}\,\frac{\nu_{aC}+\nu_{aD}}{\nu_a{}^2{}_C\nu^2{}_{aD}} \\
P_1 &= 2\sum_{aCD}\frac{(aaCDa)^z}{h^2\nu_{aC}\nu_{aD}} - 2\sum_{aD}\frac{(aaaDa)^z}{h^2\nu^2{}_{aD}} + \sum_{aCD}\frac{(aCaDa)^z}{h^2\nu_{aC}\nu_{aD}} \\
P_2 &= 3\sum_{aD}\frac{(aaaDa)^z}{h\nu_{aD}}, \qquad P_3 = \sum_a (aaaaa)^z
\end{aligned}\right\} \tag{24}$$

We could also express p explicitly in $K_a{}^{k,2}$ or in summations over matrix elements, but this can be omitted since p has already been calculated by Van Vleck. His result reads in our notation:

$$p = \frac{\mu^2}{3kT} - \frac{2}{3h}\sum_{n'}\frac{M_{(n_0n')}M_{(n'n_0)}}{\nu_{(n_0n')}} \tag{25}$$

where the summation over j and m has already been carried out. The first term containing the permanent molecular moment μ represents the rotational terms (those with low frequency matrix elements), while the second term, contains the high frequency elements of the matrix M defined by

$$|M_{(n_0n')}|^2 = |M_{x(n_0n')}|^2 + |M_{y(n_0n')}|^2 + |M_{z(n_0n')}|^2$$

The diagonal elements of the square of the low frequency part of the matrix M are assumed to be equal $(=\mu^2)$ (cf. Eq. (33) below).

Since the rotational terms of p are already included in Van Vleck's value, we have only to examine what corrections are occasioned in $P_0 \cdots P_3$ if we will no longer neglect the rotational terms. We have then to build up the quantities $K_a{}^{kp}$ with the aid of $W_a{}^1 \cdots W_a{}^4$ in which β, γ, δ $\cdots$ now can denote both the "low" indices b, c, d, $\cdots$ for the rotational terms and B, C, D, $\cdots$ for the deformation terms and furthermore can denote partly "low", partly "high" indices for the interaction between rotation and deformation. Also we may no longer neglect terms with $W_a{}^o - C$ in $K_a{}^{kp}$ (cf. 20a) and we have at the same time to take into account the quantities $K_a{}^{kp}$ with $k<p$, which in (19) only vanished by neglecting the rotational energy. The calculation is therefore very complicated, but for the case that low frequencies such as ν_{ab}, ν_{bc} etc. may be considered as very small[5] compared with high frequencies as ν_{aB} the final result can be put in a comparatively simple form. We find:

[5] Of course also small with respect to kT/h since only then the development has a meaning.

$$\left.\begin{aligned}P_0 &= \sum_{aBCD} \frac{(aBCDa)^z}{h^3\nu_{aB}\nu_{aC}\nu_{aD}} + \sum_{abcD} \frac{(abcDa)^z}{h^3\nu^3{}_{aD}} \\ &\quad -\frac{1}{2} \sum_{abCD} \frac{2(aCDca)^z + (aCbDa)^z}{h^3} \frac{\nu_{aC}+\nu_{aD}}{\nu^2{}_{aC}\nu_{aD}} \\ P_1 &= 2\sum_{abCD} \frac{(abCDa)^z}{h^2\nu_{aC}\nu_{aD}} - 2\sum_{abcD} \frac{(abcDa)^z}{h^2\nu_a{}^2{}_D} + \sum_{abCD} \frac{(aCbDa)^z}{h^2\nu_{aC}\nu_{aD}} \\ P_2 &= 3\sum_{abcD} \frac{(abcDa)^z}{h\nu_{aD}}\ ; \quad P_3 = \sum_{abcd} (abcda)^z \end{aligned}\right\} \tag{26}$$

Comparing this result with that of (24) we could find a rule as to how to construct (26) from (24). As we said already, the derivation is very complicated and laborious and will therefore not be given here, since the result is already obvious enough, when compared with that of (24) Still we might derive some equations needed in the proof and giving an idea about the way in which to reach the final result.

We shall first prove the relation:

$$L = \frac{1}{\nu_{ab}\nu_{ac}\nu_{aD}} + \frac{1}{\nu_{ba}\nu_{bc}\nu_{bD}} + \frac{1}{\nu_{ca}\nu_{cb}\nu_{cD}} = \frac{1}{\nu_{aD}\nu_{cD}\nu_{bD}} = \frac{1}{\nu^3{}_{aD}} \tag{27}$$

neglecting $\nu_l/\nu_H{}^4$ in comparison with 1, where ν_l denotes a low frequency and ν_H some high one. On account of $h\nu_{aD} = W_a{}^0 - W_D{}^0$ there will occur many negative frequencies. We write more cyclically:

$$L = \frac{-(\nu_{bc}\nu_{cD}\nu_{Db}) + (\nu_{cD}\nu_{Da}\nu_{ac}) - (\nu_{Da}\nu_{ab}\nu_{bD})}{-\nu_{ab}\nu_{bc}\nu_{ca}\nu_{aD}\nu_{bD}\nu_{cD}} = \frac{u}{v}\,. \tag{28}$$

The nominator U vanishes if we assume $W_b{}^0 = W_a{}^0$ or $W_c{}^0 = W_a{}^0$ or $W_c{}^0 = W_b{}^0$ and U can therefore be factored into

$$u = f\nu_{ab}\nu_{bc}\nu_{ca}$$

introducing a function f which we now will determine without any calculation. Although contrary to the physical meaning of $W_D{}^0$ we may still mathematically determine the value of U for one of the assumptions

$$W_D{}^0 = W_a{}^0 \quad \text{or} \quad W_D{}^0 = W_b{}^0 \quad \text{or} \quad W_D{}^0 = W_c{}^0\,. \tag{29}$$

For each of these assumptions we find immediately $U = -\nu_{ab}\nu_{bc}\nu_{ca}$ and from that we suspect that for an arbitrary value of $W_D{}^0$

$$U = -(\nu_{bc}\nu_{cD}\nu_{Db}) + (\nu_{cD}\nu_{Da}\nu_{ac}) - (\nu_{Da}\nu_{ab}\nu_{bD}) = -\nu_{ab}\nu_{bc}\nu_{ca}\,.$$

To prove that this equation holds identically, we consider it first as a quadratic equation for the determination of $W_D{}^0$. From the above we already know three solutions: namely, the values (29). But a quadratic equation with three different roots must be an identity. Using this value for U we get for L the second value in (27) and in an allowed approximation the third value.

This relation (27) is a typical one and we shall show how it is used to oust the low frequencies from the denominators containing both low and high ones. This of course is always very important since our final result consisted solely of terms with only high frequencies in the denominator. From §2 we know, that we do not need to pay attention to terms which contain entirely low frequencies and corresponding matrix elements, since they may affect Z only by a constant and have no influence on the polarization. Let us therefore consider some "mixed" terms, such as[6]:

$$\sum_{\alpha\beta\gamma\delta}{}' \frac{M^z_{a\beta}M^z_{\beta\gamma}M^z_{\gamma\delta}M^z_{\delta a}}{h^3\nu_{a\beta}\nu_{a\gamma}\nu_{a\delta}} = \sum_{a\beta\gamma\delta} \left\{\begin{array}{ccccc} a & \beta & \gamma & \delta & a \\ & \neq & \neq & \neq & \\ & a & a & a & \end{array}\right\}^z \tag{30}$$

occurring among others in $W_a{}^4$ and so in P_0 and of whose indices β, γ, δ we will take only one "high." It contains then among other terms:

$$\left\{\begin{array}{ccccc} a & b & c & D & a \\ & \neq & \neq & & \\ & a & a & & \end{array}\right\}^z + \left\{\begin{array}{ccccc} a & b & C & d & a \\ & \neq & & \neq & \\ & a & & a & \end{array}\right\}^z + \left\{\begin{array}{ccccc} a & B & c & d & a \\ & & \neq & \neq & \\ & & a & a & \end{array}\right\}^z$$

Since we have to sum over the indices a, b, c, d, A, B, C, D, we can arbitrarily change the name of the indices in the three terms independently. This means only that we arrange the terms in the entire group in another way, gathering each time three others together.

We take now:

b, c, D, a instead of a, b, C, d in the second term
c, D, a, b " " a, B, c, d " " third "

This alteration of names is so chosen that the symbols then appearing denote the same product of matrix *elements*, so that e.g.

$$(abcDa)^z = (bcDab)^z = (cDabc)^z.$$

This only means that $M_{ab}{}^zM_{bc}{}^zM_{cD}{}^zM_{Da}{}^z = M_{bc}{}^zM_{cD}{}^zM_{Da}{}^zM_{ab}{}^z$, etc. and has nothing to do with commutativeness of matrices. Our sum so becomes:

$$\sum \left\{\begin{array}{ccccc} a & b & c & D & a \\ & \neq & \neq & & \\ & a & a & & \end{array}\right\}^z + \sum \left\{\begin{array}{ccccc} b & c & D & a & b \\ & \neq & & \neq & \\ & b & & b & \end{array}\right\}^z + \sum \left\{\begin{array}{ccccc} c & D & a & b & c \\ & & \neq & \neq & \\ & & c & c & \end{array}\right\}^z$$

Although the "arguments" $\{\cdots\}^z$ contain the same product of matrix elements, we cannot yet combine these three sums together into a single one, on account of the various secondary conditions of inequality between some of the lower indices. Therefore we make a division in the following way:

$$\left\{\begin{array}{ccccc} a & b & c & D & a \\ & \neq & \neq & & \\ & a & a & & \end{array}\right\}^z = \left\{\begin{array}{c} a\ \ b\ \ c\ \ D\ \ a \\ \text{all unequal} \end{array}\right\}^z + \left\{\begin{array}{ccccc} a & p & p & D & a \\ & \neq & & & \\ & a & & & \end{array}\right\}^z$$

and similarly for the other arguments. Thus we obtain for our entire sum:

$$\sum_{abcD} \frac{(abcDa)^z}{h^3}\left(\frac{1}{\nu_{ab}\nu_{ac}\nu_{aD}} + \frac{1}{\nu_{bc}\nu_{bD}\nu_{ba}} + \frac{1}{\nu_{cD}\nu_{ca}\nu_{cb}}\right)$$

$$+\sum_{apD} \left\{\begin{array}{ccccc} a & p & p & D & a \\ & \neq & & & \\ & a & & & \end{array}\right\}^z + \sum_{bpD} \left\{\begin{array}{ccccc} b & p & D & p & b \\ & \neq & & & \\ & b & & & \end{array}\right\}^z + \sum_{cpD} \left\{\begin{array}{ccccc} c & D & p & p & c \\ & & \neq & & \\ & & c & & \end{array}\right\}^z$$

We see now how the first part of it can be transformed with our relation (27) into a sum of terms with only high frequencies, which one might recognize in the expression for P_0 in (26). For the transformation of the second part we need to combine it with other terms of $W_a{}^{(4)}$. Even the terms with $W_a{}^0 - C$ as a factor can be treated in some analogous way. A typical relation we need then is

$$\frac{\nu_{a0}}{\nu_{ab}\nu_{ac}\nu_{aD}} + \frac{\nu_{b_0}}{\nu_{ba}\nu_{bc}\nu_{bD}} + \frac{\nu_{c0}}{\nu_{ca}\nu_{cb}\nu_{cD}} = -\frac{1}{\nu^2{}_{aD}}$$

when $\nu_l/\nu_H{}^3$ is neglected in comparison to 1. Then we wrote only mathematically without thinking of a real absorption or emission frequency $W_{a0} - C = h\nu_{ac}$. The above relations and transformations are, we hope, enough to give an idea of the proof.

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[6] The new symbol is related to the old one of (23a) in the following way

$$\{a\beta\gamma\delta a\}^z = (a\beta\gamma\delta a)^z / h^3\nu_{a\beta}\nu_{a\gamma}\nu_{a\delta}$$

Let us now return to our formula (26) for $P_0 \cdots P_3$. In our q-formula (23) we need only these quantities divided by N_a, i.e. we need there several quantum mechanical average values and we showed in § 2 how to transform these into classical ones. Still there is a difference on account of the presence of high energy levels. The summation over the low intermediate levels will lead to a function of the molecular moments in the unexcited states, that over the high ones will remain in our answer as a sum. For the details we refer to the appendix; only some important points will be given below.

The $x'y'z'$ axes are fixed in the molecule and their positions with respect to the xyz axes (fixed in space) are indicated by the Eulerian angles $\theta\varphi\psi$. Since we have for the classical moments:

$$M^z = -M^{x'} \sin\theta \cos\psi + M^{y'} \sin\theta \sin\psi + M^{z'} \cos\theta,$$

and since we have to consider for the q-formula only matrix-products of four factors M^z, it will be clear that the application of our rule for the calculation needs the classical averages:

$$\begin{gathered}\overline{\sin^4\theta \cos^4\psi} = \overline{\sin^4\theta \sin^4\psi} = \overline{\cos^4\theta} = 1/5 \\ \overline{\sin^4\theta \cos^2\psi \sin^2\psi} = \overline{\sin^2\theta \cos^2\theta \cos^2\psi} = \overline{\sin^2\theta \cos^2\theta \sin^2\psi} = 1/15\end{gathered} \tag{31}$$

while many other averages vanish. The first three values will be connected with the terms containing four elements of the matrix $M^{x'}$ or four of $M^{y'}$ or of $M^{z'}$ and the last three with each of the terms of the right side of

$$(a\beta\gamma\delta a)^{i,i'} = \overset{i}{M}_{a\beta}\overset{i}{M}_{\beta\gamma}\overset{i'}{M}_{\gamma\delta}\overset{i'}{M}_{\delta a} + \overset{i}{M}_{a\beta}\overset{i'}{M}_{\beta\gamma}\overset{i}{M}_{\gamma\delta}\overset{i'}{M}_{\delta a} + \overset{i}{M}_{a\beta}\overset{i'}{M}_{\beta\gamma}\overset{i'}{M}_{\gamma\delta}\overset{i}{M}_{\delta a} \tag{32}$$

This new symbol will be useful further on. Here and throughout the whole paper we suppose *always* $i' \neq i$ and both can denote $x'y'$ or z'. Since the other average values besides those in (31) vanish, the matrices M^i and $M^{i'}$ are always represented by an even number of elements in the remaining terms.

These classical averages replace only quantum mechanical averages over the axial quantum number (m) so that our rule gives e.g.

$$15 \sum_{abcd} (abcda)^z : N_a = \left[3 \sum_i \sum_{a'b'c'd'} (a'b'c'd'a')^i + \sum_{ii'} \sum_{a'b'c'd'} (a'b'c'd'a')^{ii'} \right] : N_{a'}$$

where the dash on $a, b, \cdots$ indicates that the summation is to extend over all quantum numbers originally involved in $a, b, \cdots$ except over the axial quantum numbers. Consequently we had in the right hand side to divide by N_a' instead of N_a. If at the beginning we had described the state of a molecule by means of its $x'y'z'$ system, we should have had no axial quantum number entering into our formulas and so in some respects the indices $a'b'c' \cdots$ may be related to the states described in the $x'y'z'$ system.

Now if we neglect the deformation of a molecule by rotation, the sum

$$\sum_{b'} M^i{}_{a'b'} M^i{}_{b'c'} = \mu_i^2 \delta^{c'}{}_{a'} \tag{33}$$

must be a diagonal matrix, which we may suppose in accordance with our assumption as constant, i.e. the same for each of the $N_a{}'$ states a'. Since i can denote x', y' or z', terms such as (33) correspond classically to the squares of the electric moments of the molecule along the principal axes, when $x'y'z'$ are properly chosen in the molecule, e.g. symmetrically in a diatomic one. So we have:

$$\sum_{abcd}(abcda)^z:N_a=\sum_i \mu_i{}^4+\sum_{i,i'}\mu_i{}^2\mu_{i'}{}^2=\mu^4.$$

To obtain the last term in the second expression, we used the fact that M^i and $M^{i'}$ commute with one another:

$$(M^iM^iM^{i'}M^{i'})_{a'a'}+(M^iM^{i'}M^iM^{i'})_{a'a'}+(M^iM^{i'}M^{i'}M^i)_{a'a'}=3(M^iM^iM^{i'}M^{i'})_{a'a'}$$

This was permitted for *electric* moments, since they are proportional to coordinates and all coordinates commute; but for magnetic moments this would not have been allowed.

More complicated is the calculation of:

$$\sum_{abcD}\frac{(abcDa)^z}{h^p\nu^p{}_{aD}}:N_a=\sum_{a'b'c'D'}\left[\frac{1}{5}\sum_i\frac{(a'b'c'D'a')^i}{h^p\nu^p{}_{a'D'}}+\frac{1}{15}\sum_{i,i'}\frac{(a'b'c'D'a')^{i,i'}}{h^p\nu^p{}_{a'D'}}\right]:N_{a'} \tag{34}$$

There the first sum in the right side is transformed as follows:

$$\sum_{a'b'c'D'}\frac{(a'b'c'D'a')^i}{h^p\nu^p{}_{a'D'}}:N_{a'}=\mu_i{}^2\sum_{a'D'}\frac{\overset{i}{M}_{a'D'}\overset{i}{M}_{D'a'}}{h^p\nu^p{}_{a'D'}}=\mu_i{}^2\sum_{n'}\frac{|\overset{i}{M}_{(n0n')}|^2}{h^p\nu^p{}_{(n0n')}}$$

where we assumed in accordance with the sum rule (cf. Van Vleck for $p=1$) that the fraction in the middle part of the above equation when summed over D' is independent of the choice of a' from the low states. This fraction depends therefore only on the indices n. Further, we used the fact that $M_{n_0n'}{}^i$ and $M_{n',n_0}{}^i$ are complex conjugate so that their product is the square of their absolute value, indicated by | |. For the other term in the right side of Eq. (34) we have the result

$$\sum_{a'b'c'D'}\frac{(a'b'c'D'a')^{i,i'}}{h^p{}_{na'D'}}:N_{a'}=\mu^{i2}\sum_{n'}\frac{|\overset{i}{M}_{(n0n')}|^2}{h^p\nu^p{}_{(n0n')}}+2\mu_i\mu_i{}'\sum_{n'}\frac{|\overset{i}{M}_{n0n'}\overset{i'}{M}_{n'n0}|}{h^p\nu^p{}_{n0n'}}$$

as follows from the definition of the symbol $(\quad)^{ii'}$ in (32) and also from the further relation:

$$\sum_{b'}\overset{i}{M}_{a'b'}\overset{i'}{M}_{b'c'}=\mu_i\mu_i{}'\delta_{a'}^{c'}$$

Thus the whole right side of (34) has now been found. The result is

$$\sum_{abcD}\frac{(abcDa)^z}{h^p\nu^p_{aD}}:N_a=-\frac{1}{30}\sum_{i\,i'}\{\mu_i{}^2(3a_p{}^{ii}+a_p{}^{i'i'})+2\mu_i\mu_i{}'a_p{}^{ii'}\}$$

if we introduce the abbreviations:

$$-2\sum_{n'}\frac{|\overset{i}{M}_{n_0n'}|^2}{h^p\nu^p{}_{n_0n'}}=a_p{}^{ii};\qquad -2\sum_{n'}\frac{|\overset{i}{M}_{n_0n'}\overset{i'}{M}_{n'n_0}|}{h^p\nu^p{}_{n_0n'}}=a_p{}^{ii'}=a_p{}^{i'i}$$

Still another kind of transformation is necessary for:

$$\sum_{abCD}\frac{(aCbDa)^z}{h^2\nu_{aC}\nu_{aD}}:N_a=\frac{1}{5}\sum_i\sum_{n'n''}\frac{\overset{i}{M}_{n_0n'}\overset{i}{M}_{n'n_0}\overset{i}{M}_{n_0n''}\overset{i}{M}_{n''n_0}}{h^2\nu_{n_0n'}\nu_{n_0n''}}$$

$$+\frac{1}{15}\sum_{i'i'}\sum_{n'n''}\frac{M^{i}_{n_0n'}M^{i}_{n'n_0}M^{i'}_{n_0n''}M^{i'}_{n''n_0}+M^{i}_{n_0n'}M^{i'}_{n'n_0}M^{i}_{n_0n''}M^{i'}_{n''n_0}+M^{i}_{n_0n'}M^{i'}_{n'n_0}M^{i'}_{n_0n''}M^{i}_{n''n_0}}{h^2\nu_{n_0n'}\nu_{n_0n''}}$$

$$=\frac{1}{20}\sum_{i}(a_1{}^{ii})^2+\frac{1}{60}\sum_{i'i'}(a_1{}^{ii}\cdot a_1{}^{i'i'})+\frac{1}{30}(a_1{}^{ii'})^2.$$

The first two terms in the last member will be found immediately from the definition of $a_1{}^{ii}$ where one also may use n'' instead of n'. The last term results from the fact that

$$\frac{1}{15}\sum_{ii'}\Bigg[\sum_{n'}\frac{M^{i}_{n_0n'}M^{i}_{n'n_0}}{h\nu_{n_0n'}}\Bigg]\Bigg[\sum_{n'}\frac{M^{i}_{n_0n'}M^{i'}_{n'n_0}+M^{i'}_{n_0n'}M^{i}_{n'n_0}}{h\nu_{n_0n'}}\Bigg]$$

$$=\frac{1}{30}\sum_{ii'}\Bigg[\sum_{n'}\frac{M^{i}_{n_0n'}M^{i'}_{n'n_0}+M^{i'}_{n_0n'}M^{i}_{n'n_0}}{h\nu_{n_0n'}}\Bigg]^2=\frac{1}{30}(a_1{}^{ii'})^2$$

Where the second expression follows from the preceding one by dividing this by 2 and counting the indices i and i' in the first factor twice, combining a term i, i' with a term i', i for which the second factor is the same. Dividing the following sum into two others which can be treated in a similar way to the preceding one, we find

$$\sum_{abCD}\frac{(aCbDa)^z}{h^3}\,\frac{\nu_{aC}+\nu_{aD}}{\nu_{aC}{}^2\nu_{aD}{}^2}:N_a=\frac{1}{10}\sum_{i}(a_1{}^{ii}\cdot a_2{}^{ii})+\frac{1}{30}\sum_{i_1i'}(a_1{}^{ii}a_2{}^{i'i'})+\frac{1}{15}\sum_{ii'}a_1{}^{ii'}a_2{}^{ii'}$$

In order to throw the other averages in our g-formula into a compact form, we introduce a new symbol for the sum of two others already defined in (23a) and (32):

$$(\cdots)^{3i+i,i'}=3(\cdots)^{i}+(\cdots)^{i,i'} \tag{34a}$$

and find then after a classical averaging:

$$\sum_{aBCD}\frac{(aBCDa)^z}{h^3\nu_{aB}\nu_{aC}\nu_{aD}}:N_a=\frac{1}{15}\sum_{ii'}\sum_{n'n''n'''}\frac{(n_0n'n''n'''n_0)^{3i+i,i'}}{h^3\nu_{n_0n'}\nu_{n_0n''}\nu_{n_0n'''}}=I$$

$$\sum_{abCD}\frac{(abCDa)^z}{h^2\nu_{aC}\nu_{aD}}:N_a=\frac{1}{15}\sum_{ii'}\sum_{n'n''}\frac{(n_0n_0n'n''n_0)^{3i+i,i'}}{h^2\nu_{n_0n'}\nu_{n_0n''}}=II$$

$$\sum_{abCD}\frac{(aCDba)^z}{h^3}\,\frac{\nu_{aC}+\nu_{aD}}{\nu_{aC}{}^2\nu_{aD}{}^2}:N_a=\frac{1}{15}\sum_{i'i'}\sum_{n'n''}\frac{(n_0n_0n'n''n_0)^{3i+i,i'}}{h^3}\,\frac{\nu_{n_0n'}+\nu_{n_0n''}}{\nu_{n_0n'}{}^2\nu_{n_0n''}{}^2}=III$$

All quantum mechanical averages in our q-formula (23) have now been calculated. Using these and the value (25) of p, which can be written in the form:

$$p=\frac{\mu^2}{3kT}+\frac{1}{3}\sum_{i}a_1{}^{ii}$$

we find at last:

$$\overline{\overline{m}}_z=\left(p_0+\frac{\mu^2}{3\,k\,T}\right)F+\left(q_0+\frac{q_1}{kT}+\frac{q_2}{k^2T^2}-\frac{\mu^4}{45k^3T^3}\right)F^3$$

with

$$3p_0=\sum_{i}a_1{}^{ii}$$

$$15q_0=\sum_{i,i'}\left[a_1{}^{ii}(3a_2{}^{ii}+a_2{}^{i'i'})+2\mu_i{}^2(3a_3{}^{ii}+a_3{}^{i'i'})\right]$$

$$+\sum_{i,i'}4\mu_i\mu_i{}'a_3{}^{ii'}-60(I-III)$$

$$45q_1=(a_1^{x'x'}-a_1^{y'y'})^2+(a_1^{y'y'}-a_1^{z'z'})^2+(a_1^{z'z'}-a_1^{x'x'})^2$$
$$+\sum_{i,i'}[6\mu_i^2(3a_2^{ii}+a_2^{i'i'})+12\mu_i\mu_{i'}a_2^{ii'}]+180II$$
$$(45/2)q_2=(\mu_{x'}^2-\mu_{y'}^2)(a_1^{x'x'}-a_1^{y'y'})+(\mu_{y'}^2-\mu_{z'}^2)(a_1^{y'y'}-a_1^{z'z'})$$
$$+(\mu_{z'}^2-\mu_{x'}^2)(a_1^{z'z'}-a_1^{x'x'})+3\sum_{i,i'}\mu_i\mu_{i'}a_1^{ii'}.$$

The terms with p_o, q_o, q_1 and q_2 would vanish for rigid molecules, since then the high frequency elements involved in a_p^{ii}, $a_p^{ii'}$ would not exist.

In the special case considered by Debye in which the deformation can be described by means of harmonically bound particles, our formulae for W would not have contained third and higher powers of the field strength, i.e. all quantities whose first power possesses two or more frequencies in the denominator would not have appeared. So we would have to omit in our general answer the quantities I, II, III, a_2^{ii}, $a_2^{i'i'}$, $a_2^{ii'}$, a_3^{ii}, $a_3^{i'i'}$, $a_3^{ii'}$.

Further we have $a_1^{i,i'}=0$ if the $x'y'z'$ system is so chosen in the molecule that corresponds with the axes of the deformation ellipsoid in the classical theory.

Thus q_0 and the second line of q_1, q_2 would vanish and the result would have been exactly the formula of Debye[7] in which his coefficients a_{11}, a_{22}, a_{33} have to be replaced by our $a_1^{x'x'}$, $a_1^{y'y'}$, $a_1^{z'z'}$ the latter being therefore the quantum mechanical interpretation of the classical binding coefficients.

MAGNETIC SATURATION IN QUANTUM MECHANICS

The calculation of the magnetic saturation differs from the electric in two respects: (a) in the non-commutativeness of the magnetic moment or angular momentum matrices, and (b) the presence of a term in the Hamiltonian function E which is quadratic in the magnetic field H. It is well known that the commutation rules for the components of the angular orbital momentum are:

$$L^{y'}L^{z'}-L^{z'}L^{y'}=L^{x'}ih/2\pi \tag{35}$$

and those obtained by a cyclic interchanging of the indices.

According to Van Vleck and others the Hamiltonian[8] function in the presence of a magnetic field H is:

$$E=E^0+HE^{(1)}+H^2E^{(2)}$$

with

$$E^{(1)}=(e/2mc)\sum_i(p_{\phi i}+2p_{\psi i})\ ;\ \ E^{(2)}=(e^2/8mc^2)\sum_i R_i^2.$$

Here p_{ϕ_i} and p_{ψ_i} are the components of orbital and spin angular momentum of the ith electron in the direction of the applied magnetic field, which we assume lies along the z axis. The factor 2 multiplying p_ψ is of course due to the anomaly in the spin magnetic moment. The generalized momenta p_ϕ

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[7] Debye, Handbuch der Radiologie, Vol. VI, p. 779.

[8] We indicate the Hamiltonian here with E to avoid confusion with the magnetic field strength H.

and p_ψ are conjugate to azimuth angles ϕ and ψ specifying the motion[9] of the electron and its spin axis respectively around the z axis. This specification of the spin axis by means of Eulerian angles would, of course, presumably imply some kind of mechanical model for the electron spin, but fortunately the results are the same if we use Dirac's recent relativistic theory which frees us from using a model. The differences (a) and (b) tend to make the calculation more difficult than in the electric case, but these difficulties are usually offset by the fact that in paramagnetic terms the effect of the high frequency elements in the magnetic moments is negligible. The term proportional to H^2 is that responsible for diamagnetism and is negligible in comparison with the paramagnetic terms in paramagnetic atoms or molecules. Consequently we shall disregard this term in the balance of this section. We may mention, however, that a long calculation shows that if we neglect the spin, the influence of the diamagnetic term E^2 on the magnetic moment is, to terms in H^3:

$$-(e^2/6mc^2)(\xi+\eta+\zeta)H+(e^2/90mc^2k^2T^2)\left[(\xi-\eta)(\boldsymbol{\mu}_1{}^2-\boldsymbol{\mu}_2{}^2)\right.$$
$$\left.+(\eta-\zeta)(\boldsymbol{\mu}_2{}^2-\boldsymbol{\mu}_3{}^2)+(\zeta-\xi)(\boldsymbol{\mu}_3{}^2-\boldsymbol{\mu}_1{}^2)\right]H^3$$

where ξ, η, ζ are the time averages of $\sum_i x_i'^2$, $\sum y_i'^2$, $\sum_i z_i'^2$ respectively, the primed axes being fixed in the molecule, *e.g.* coinciding with its principal axes of inertia. Also $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$, $\boldsymbol{\mu}_3$ have been used to denote the components of magnetic moments along these three principal axes.[10]

Paramagnetic atoms without spin. Here $p_\psi=0$ and $\sum p_\phi$ is a diagonal matrix whose elements are $mh/2\pi$ where m is the usual magnetic quantum number. If we neglect the diamagnetic effect, the energy is given rigorously to all powers of H by:

$$W_a=W_a{}^0+m\beta H$$

where $\beta=he/4\pi mc$ denotes the Bohr magneton.

Brillouin[11] has shown that then the magnetic moment is

$$\overline{\overline{m}}_z=\beta\left[\frac{le^{l\beta H/kT}+(l+1)e^{-(l+1)\beta H/kT}}{e^{l\beta H/kT}-e^{-(l+1)\beta H/kT}}-\frac{1}{e^{\beta H/kT}-1}\right]=B(l,\beta,H,T) \tag{36}$$

as he shows this is the same as

$$\overline{\overline{m}}_z=\beta\sum_{m=-j}^{m=+j}me^{m\beta H/kT}:\sum_{m=-j}^{m=+j}e^{m\beta H/kT} \tag{37}$$

The right hand side of (36) we shall call a "Brillouin function" and denote it by $B(l,\beta,H,T)$.[12] As the square of the magnetic moment is $l(l+1)\beta^2$ one might at first thought expect $B(l,\beta,H,T)$ to be the same as $L((l^2+l)^{\frac{1}{2}}\beta,$

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[9] R_i is the radius vector from the ith electron to the nucleus.

[10] Bold face letters denote always magnetic moments.

[11] Brillouin, J. de Physique **8**, 74 (1927).

[12] The introduction of the constant β parameter in this formula might appear superfluous here but will be very useful afterwards.

H, T) where $L(\mu, H, T)$ is the Langevin function defined in Eq. (9) now with H instead of F. Actually this is not the case, as one easily verifies that

$$B(l,\beta,H,T)=L((l+\tfrac{1}{2})\beta,H,T)-L(\tfrac{1}{2}\beta,H,T). \tag{38}$$

The difference is due to the non-commutativeness of the various components of the angular momentum matrices. This can be seen as follows. If one follows a method analogous to that used in the electric case, rather than Brillouin's simple method, one finds that to terms in H^3:

$$\overline{\overline{m}}_z=\mathfrak{P}H+\mathfrak{Q}H^3 \tag{39}$$

where

$$\mathfrak{P}=\frac{\sum_a(\mathfrak{M}^z\mathfrak{M}^z)_{aa}}{N_akT},\quad \mathfrak{Q}=\frac{\sum_a(\mathfrak{M}^z\mathfrak{M}^z\mathfrak{M}^z\mathfrak{M}^z)_{aa}}{6N_ak^3T^3}-\frac{\mathfrak{P}^2}{2kT} \tag{40}$$

Here $\mathfrak{M}$ denotes the magnetic moment matrix. If one could perform the spacial averaging in the same way as in the electric case, Eq. (39) would become:

$$\overline{\overline{m}}_z=H\boldsymbol{\mu}^2/3kT-H^3\boldsymbol{\mu}^4/45k^3T^3$$

the first terms of a Langevin function, whereas actually it will be shown to give:

$$\overline{\overline{m}}_z=H\boldsymbol{\mu}^2/3kT-H^3[\boldsymbol{\mu}^4+\tfrac{1}{2}\boldsymbol{\mu}^2\beta^2]/45k^3T^3 \tag{41}$$

being the first terms of $B(l, \beta, H, T)$ if we set $\boldsymbol{\mu}^2=l(l+1)\beta^2$. The term with β in (41) is due to the non-commutativeness of angular moment matrices, as will now be shown. Neglecting the spin, we have

$$\mathfrak{M}^z=-eL^z/2mc \tag{42}$$

where the matrix L corresponds to the total orbital impulse moment of the electrons and L^z to its component $\sum_i p_{\phi_i}$ along the z-axis. Using again an $x'y'z'$ system fixed in the molecule we find by averaging over the Eulerian angles and following the same procedure as in the appendix:

$$15\sum_a(L^zL^zL^zL^z)_{aa}:N_a=\sum_{i,i'}(LLLL)^{3i+i,i'} \tag{43}$$

where i and $i'\neq i$ again denote $x'y'z'$ and the symbol in the right hand side is defined in (34a). Here we reach the point from which calculations of the electric and magnetic polarization no longer parallel each other. For the L^i and $L^{i'}$ the commutation rules (35) are valid. By applying these and using (32) one finds

$$\begin{aligned}(LLLL)^{x'y'}_{aa}&=(L^{x'}L^{x'}L^{y'}L^{y'})_{aa}+(L^{x'}L^{y'}L^{x'}L^{y'})_{aa}+(L^{x'}L^{y'}L^{y'}L^{x'})_{aa}\\&=3(L^{x'}L^{x'}L^{y'}L^{y'})_{aa}-(2L^{x'}L^{z'}L^{y'}+L^{x'}L^{y'}L^{z'})_{aa}ih/2\pi.\end{aligned}$$

According to the commutation rules we may interchange x' and y' if we reverse at the same time the sign of $ih/2\pi$. Adding the resulting $(LLLL)^{y'x'}$ to $(LLLL)^{x'y'}$ and replacing the indices $x'y'$ in this sum in a cyclic way we find by summing

$$\begin{aligned}\sum_{ii'}(LLLL)^{i,i'}_{aa} &= 3\sum_{ii'}(L^iL^iL^{i'}L^{i'})_{aa}-\left[L^{x'}(L^{z'}L^{y'}-L^{y'}L^{z'})+L^{y'}(L^{x'}L^{z'}-L^{z'}L^{x'})\right.\\ &\qquad \left.+L^{z'}(L^{y'}L^{x'}-L^{x'}L^{y'})\right]_{aa}ih/2\pi\\ &=3\sum_{ii'}(L^iL^iL^{i'}L^{i'})_{aa}-(h^2/4\pi^2)\sum_i L^iL^i.\end{aligned}$$

Adding $3\sum_i(L^iL^iL^iL^i)_{aa}$ we obtain

$$\sum_{ii'}(LLLL)_{aa}{}^{3i+i,i'}=(3L^4-(h^2/4\pi^2)L^2)_{aa}. \tag{44}$$

Furthermore we have still in $\mathfrak{P}$:

$$\sum_a(LL)_{aa}:N_a=\sum_i L^iL^i:3=(L^2)_{aa}:3. \tag{45}$$

Using (40), (42), (43), (44), (45) and setting $(L^2)_{aa}\,(e/2mc)^2=\boldsymbol{\mu}^2$ one obtains at last Eq. (4) so that the ground for the difference between L and B is explained. It will be noted that the complication in the space averaging from the non-commutativeness arises only when the terms in the moment of order H^3 and higher are included. It did not appear in Van Vleck's work, as he considered only the part of the moment which is linear in H and here we have only to find the average $\mathfrak{P}$ where no "mixed" terms $(L^iL^{i'})_{aa}$ appear after the classical averaging (cf. 45).

From the above it follows that as soon as we deal in the following with non-commutative or commutative matrices, we expect in the answer for the polarization always respectively a Brillouin or Langevin function as their contributions.

Still in another respect is the relation (38) instructive. It gives the answer to an objection of Debye[13] against the Langevin function for the magnetic polarization. Debye finds for the entropy S per cc of a gas in a magnetic field:

$$S=(S)_{H=0}-\int x(d\sigma/dx)dx$$

where $x=H/T$ and σ is the polarization per cc. Taking $\sigma=NL(\mu,H,T)$ where N is the number of molecules per cc he finds (written in our notation)

$$S=(S)_{H=0}-Nk[\log{(2\boldsymbol{\mu}x/k)}-1+(1+2\boldsymbol{\mu}x/k)e^{-2\boldsymbol{\mu}x/k}+\cdots]$$

making $S=\infty$ for $T=0$ contrary to the theorem of Nernst requiring a finite entropy for $T=0$. Using for σ not one Langevin function, but the difference of two of them (according to 38) one finds instead of the fatal log $(2\mu x/k)$ now $\log{[(2l+1)\beta x/k]}-\log{(\beta x/k)}$ which remains finite for $T=0$ and $x=\infty$.[14]

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[13] P. Debye Ann. der Phys. **81**, 1154 (1926).

[14] At first thought it would appear as though the validity of the Langevin formula in the electric case would lead us into Debye's difficulty of infinite entropy at $T=0$, when an electric field is applied. However in our analysis of the electric case, we supposed the intervals in the

Atoms with spin. We must now seek to incorporate the spin, which was not included by Brillouin. First of all, we consider a gas of *atoms* with spin. Here we must deal with two limiting cases, viz. multiplet structures narrow and wide compared to kT. The intermediate case is too intractable to be readily treated and will not be considered here. Let us first consider:

Narrow multiplets. From the quantum mechanical theorem of spectroscopic stability, we know that by an increase of field strength the magnetic polarization only increases on account of the increase of H, not on account of a change in the structure of the formula. In other words, a Paschen-Back effect may change the type of quantization or the formula for an *individual* Zeeman component but not the expression for the susceptibility. The reason that this is possible is that the susceptibility is always a statistical thing, involving a summation over all possible states rather than the properties of one particular state. To find the polarization formula, we can therefore choose the field strength so that the calculations become as simple as possible, i.e. in the case of a field so strong that it overpowers the coupling between L and S (the spin moment) and gives separate spacial quantization of L and S. The components $\sum p_\phi$ and $\sum p_\psi$ of orbital and spin moments parallel to the axis of figure are then diagonal matrices of elements $m_l h/2\pi$ and $m_s h/2\pi$. In the several states the quantum numbers m_l and m_s range from $-l$ to $+l$ respectively from $-s$ to $+s$, where $L = lh/2\pi$ and $S = sh/2\pi$. We have now rigorously to all powers of H:

$$\overline{\overline{m}}_z = \beta \frac{\sum_{ml} \sum_{ms} (m_l + 2m_s) e^{(m_l+2m_s)\beta H/kT}}{\sum_{m_l} \sum_{ms} e^{(m_l+2m_s)\beta H/kT}}$$

Since

$$\sum_{m_l} \quad \sum_{ms} m_l e^{(m_l+2m_s)\beta H/kT} = \left[\sum_{m_l} m_l e^{m_l \beta H/kT} \right] \left[\sum_{ms} e^{m_s \beta H/kT} \right]$$

and analogous formulae hold for the other double sums we always can cancel one sum in the denominator against one in the numerator and find using the expression (37) for the Brillouin function:

$$\overline{\overline{m}}_z = B(l, \beta, H, T) + B(s, 2\beta, H, T).$$

Here the use of β as parameter, (see footnote 12) will become clear since the last term could not be written as $B(2s, \beta, H, T)$ this corresponding to a sum over $4s+1$ terms instead of $2s+1$.

Wide multiplet structure. If on the other hand, the multiplet structure is wide compared to kT, i.e., $h\Delta\nu \gg kT$ the interaction between L and S is very strong and these cannot be quantized separately. L and S form always the same resultant J around which they rotate very rapidly. J itself rotates

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rotational fine structure small compared to kT, a condition not fulfilled in the vicinity of $T = 0$. Instead, special formulae for the susceptibility are required at low temperature. These have been given by Mensing and Pauli, VanVleck, and Kronig in the special case of rigid non-gyroscopic diatomic molecules. Such formulae make the entropy finite at $T = 0$ as will indeed any quantum formula involving a discrete succession of energy states rather than a continuous classical distribution.

slowly around H and gives us therefore low frequency matrix elements. Now the low frequency matrix elements play the most important role in our answer as in the magnetic case the effect of the high frequency elements is usually negligible. Neglecting therefore the matrix elements corresponding with rotations around J, we can treat J as we should have treated L in an atom without spin. There is still a difference, $jh/2\pi$ being the value of the mechanical impulse moment J the corresponding magnetic moment is not $j\beta$ but $gj\beta$ on account of the anomaly of the spin, which contributes also to J. Therefore is the answer here:

$$\overline{\overline{m}}_z=B(j,g\beta,H,T).$$

Diatomic molecules. We consider first those with *narrow* multiplet structure ($h\Delta\nu\ll kT$). Since the multiplet structure is due to the different possible orientations of the spin, we know that in this case $S^{x'}$,$S^{y'}$ and $S^{z'}$ are all of low frequency and since they do not commute, the spin will give the contribution $B(s,2\beta,k,T)$ to the final result. To find that of L we can confine ourselves to its low frequency elements, namely the components $L^{z'}$ of L parallel to the axis of symmetry of the diatomic molecule. The components $L^{x'}$ and $L^{y'}$ perpendicular to this axis consist entirely of matrix elements of the unimportant high frequency type. The reason for this is that a change of the quantum number σ_l in $L^{z'}=\sigma_l h/2\pi$ gives always a large difference in energy as appears from the spectroscopic data. This is equivalent to the statement that the vector L precesses rapidly about the axis of figure. So we have only to deal with $L^{z'}$ and this commuting with itself, will give a Langevin function, so that the polarization for molecules with narrow multiplets will be:

$$\overline{\overline{m}}_z=L(\sigma_l\beta,H,T)+B(s,2\beta,H,T).$$

In the remaining case, that of *wide* multiplet structure, also $S^{x'}$ and $S^{y'}$ consist exclusively of high frequency elements, while those of $S^{z'}$ are only of low frequency and are to be added to the elements of $L^{z'}$ in order to give the total effective moment. Since all components along one axis commute, we have here

$$\overline{\overline{m}}_z=L((\sigma_l+2\sigma_s)\beta,H,T).$$

APPENDIX

Equivalence of Quantum Mechanical and Classical Spacial Averages

In the derivation of the Langevin formula for the electric polarization of a gas of rigid molecules in § 2 we needed the theorem (8).

$$\sum_m (M_z{}^p)_{(n_0jm,n_0jm)}:p_j=\mu^p\int\cos^p\theta d\omega:\int d\omega$$

On account of the assumed rigidness we had to deal only with low levels, so that we could throughout take $n=n_0$ in the "intermediate"[3] levels which appear in writing out the element of a matrix product when $p > 1$. Still we prefer to give a more general theorem holding also for elastic molecules, where $n \neq n_0$ is possible in the intermediate levels. This will include the first theorem as a special case. The statement of this generalization can better be given when we have found the analytical expression for it. We make use of this extension in § 3 for the derivation of Debye's correction terms.

Our theorem now is based upon considerations analogous to those of Van Vleck[1] on the principle of spectroscopic stability, where he considered the second power of the moment. As already mentioned the x, y, z and the x', y', z' systems of axes are fixed respectively in space and in the molecule, the relative position being determined by means of the well known Eulerian angles θ, ϕ, ψ. The wave function $U_{njm}(x_1 \cdots x_f, y_1 \cdots y_f, z_1 \cdots z_f)$ for a molecule with f different particles (electrons and protons) can be written very approximately (i.e. neglecting rotational distortion of electronic motions) in the form:

$$U=\psi_{njm}(x_1' \cdots z_f', \theta, \phi, \psi)=u_n(x_1'y_1'z_1' \cdots x_f'y_f'z_f')f_{njm}(\theta, \phi, \psi) \qquad (46)$$

where u_n is independent of j on account of the assumed rigidness of the molecule with respect to the centrifugal force. The matrix elements in the xyz system are defined by.

$$M^z{}_{(njm,n'j'm')}=\int \psi_{njm}M^z\psi_{n'j'm'}dx_1 \cdots dz_f \qquad (47)$$

where

$$M^z= \sum\nolimits_k e_k z_k=\lambda_{x'z}M^{x'}+\lambda_{y'z}M^{y'}+\lambda_{z'z}M^{z'}.$$

In this equation $M^{x'}$ etc. are not matrices but the classical moments $\sum_k e_k x_k'$ etc. k ranging from 1 to f and $\lambda_{x'z}$, $\lambda_{y'z}$ $\lambda_{z'z}$ denote the ordinary direction cosines connecting the z axis with the $x'y'z'$ axes and are functions of θ, ϕ, ψ.

Now
$$dx_1 \cdots dz_f=dV d\omega \qquad (48)$$

where dV and $d\omega$ denote the phase elements for the coordinates occurring respectively in u_n, f_{njm}. We will use q, q', q'' $\cdots$ to denote arbitrarily and independently from each other the axes x',y',z'. (The indices i and i' did not fit, since we assumed always $i' \neq i$). We find then by substituting

$$M^z{}_{(njm,n'j'm'}=\sum_q \int u_n M^q u_{n'} dV \int f_{njm}\lambda_{qz}f_{n'j'm'}d\omega=\sum_q M^q{}_{nn'}\lambda_{qz(njm,n'j'm')} \qquad (49)$$

Using this substitution for each of the factors in, for example

$$\sum_m [(M^z)^3]_{(n_0jm,n_0jm)}$$

$$=\sum_m \sum_{n'j'm',n''j''m''} M^z_{(n_0jm,n'j'm')}M^z_{(n'j'm',n''j''m'')}M^z_{(n''j''m'',n_0jm)}$$

we obtain.

$$\sum_m [(M^z)^3]_{(n_0jm,n_0jm)} = \sum_{qq'q''} a_{qq'q''} \left\{ \sum_{n'n''} M^{q}_{n_0n'} M^{q'}_{n'n''} M^{q''}_{n''n_0} \right\} S_{qq'q''} \tag{50}$$

where the coefficients $a_{qq'q''}$ are numerical values and further

$$S_{qq'q''} = \sum_m \sum_{j'm'} \sum_{j''m''} \lambda_{qz}(n_0jm, n'j'm')\lambda_{q'z}(n'j'm', n''j''m'')\lambda_{q''z}(n''j''m'', n_0jm).$$

To evaluate S we need the rules of multiplication for the λ-elements. These, defined in (49) by an integral can be regarded as defined equally well by the expansion

$$\lambda_{qz} f_{n'j'm'} = \sum_{jm} \lambda_{qz(njm,n'j'm')} f_{njm}$$

where it is to be particularly noted that unlike the usual definition of matrix elements the index n, which is not here an index of summation, has different values n, n' on the right and the left hand side, i.e. the f on the left hand side belongs to a different set of orthogonal functions than that on the right.

To derive first the multiplication rules for *two* λ-elements we take

$$\lambda_{qz}\lambda_{q'z} f_{n''j''m''} = \sum_{jm} (\lambda_{qz}\lambda_{q'z})_{(njm,n''j''m'')} f_{njm} \tag{51}$$

We develop the left hand side again, but now in two steps, in each of which we use a different constant value of n', n'' of the index n

$$\lambda_{qz}(\lambda_{q'z} f_{n''j''m''}) = \lambda_{qz} \sum_{j'm'} \lambda_{q'z(n'j'm',n''j''m'')} f_{n'j'm'}$$

$$= \sum_{j'm'j''m''} \lambda_{q'z(n'j'm',n''j''m'')} \lambda_{qz(njm,n'j'm')} f_{njm}.$$

Comparing this answer with (51) we find the multiplication rule

$$(\lambda_{qz}\lambda_{q'z})_{(njm,n''j''m'')} = \sum_{j'm'} \lambda_{qz(njm,n'j'm')} \lambda_{q'z(n'j'm',n''j''m'')}$$

from which we see easily the extension to the case of a product of more than two λ's. We have therefore

$$S_{qq'q''} = \sum_m (\lambda_{qz}\lambda_{q'z}\lambda_{q''z})_{(n_0jm,n_0jm)} = \sum_m \int \lambda_{qz}\lambda_{q'z}\lambda_{q''z} \left| f_{n_0jm} \right|^2 d\omega.$$

Now $\sum_m |f_{n_0jm}|^2$ is independent of the choice of the system $x'y'z'$, i. e. independent of θ, ϕ, ψ according to the spectroscopic stability principle previously mentioned, so that it can be replaced by a constant C_{n_0j} giving

$$S_{qq'q''} = C_{n_0j} \int \lambda_{qz}\lambda_{q'z}\lambda_{q''z} d\omega. \tag{52}$$

Substituting (52) in (50) the left hand side of (50) will contain C_{noj}. To get rid of this constant we divide (50) by the statistical weight p_j. Now we have, using the normalization of the f's

$$p_j=\sum_{m=-j}^{m=+j}1^m=\sum_m\int\left|f_{n_0jm}\right|^2d\omega=C_{n_0j}\int d\omega$$

so that the above mentioned division leads to

$$\frac{1}{p_j}\sum_m\left[(M^z)^3\right]_{(n_0jm,n_0jm)}$$

$$=\sum_{qq'q''}\frac{\int a_{qq'q''}\lambda_{qz}\lambda_{q'z}\lambda_{q''z}d\omega}{\int d\omega}\left[\sum_{n'n''}M^{q}_{n_0n'}M^{q'}_{n'n''}M^{q''}_{n''n_0}\right]. \qquad (53)$$

This analytical statement of the theorem for the special case of a third order expression in $(M^z)^p$ can immediately be extended to any other power. In words, the general theorem reads as follows: *The average of the diagonal elements of* $(M^z)^p$ *taken over the axial quantum numbers* m *with a given value of* j *and* n *can be calculated by resolving the matrices in a geometrical way along the principal axes of the molecule and averaging the resulting terms classically over all orientations of the molecule.* If there are no excited states possible, the sum inside the square brackets in (53) becomes simply $\mu^q\mu^{q'}\mu^{q''}$ and the whole right side of (53) is then classically built. If we can reckon with these $\mu^q,\mu^{q'},\mu^{q''}$ classically, i.e. if the M's commute in multiplications (as they do in the electric case) the right side of (53) is then of course equivalent to the classical average $\overline{\mu^3\cos^3\theta}^{cl}$ and we obtain for an arbitrary power our relation (8). In the magnetic case μ^q and $\mu^{q'}$ would not commute for $q'\neq q$ so that our relation (8) does not hold for Magnetic Moments (cf. the example in 42, 43, 44) whereas (53) is still valid as it did not require the different components of the M's to commute.

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