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ON DIELECTRIC CONSTANTS AND MAGNETIC SUSCEPTIBILITIES IN THE NEW QUANTUM MECHANICS PART III—APPLICATION TO DIA- AND PARAMAGNETISM

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Abstract

1. General mathematical theory.—Modifications are given in the general derivation of the Langevin-Debye formula by means of quantum mechanics published in part I which are required by the moment now being magnetic rather than electric. The main additions are the appearance of a diamagnetic term, and allowance for the fact that the magnetic moment consists of two parts arising respectively from orbital electronic motions and from the electrons' internal spins. These parts cannot always be treated as rigidly coupled to form a "permanent" resultant moment. The Hamiltonian function used for the internal spin is that of a spherical top.

2. Diamagnetism.—The writer's previous claim that Pauli's formula for the diamagnetic susceptibility can be applied to molecules as well as atoms is shown to be invalid because of the anomalous fact that the square of the angular momentum, unlike the average angular momentum, does not vanish even in S states when there is more than one nucleus. Pauli's formula is instead an upper limit to the diamagnetism in non-monatomic molecules and is a good approximation when the Schrödinger wave function has nearly as much symmetry as in an atomic S state.

3. Paramagnetism of atoms.—Limiting values for the paramagnetic susceptibilities of atoms are $\chi=N[4s(s+1)+k(k+1)]\beta^2/3kT$ and $\chi=[Ng^2j(j+1)\beta^2/3kT]+N\alpha$ where β is the Bohr magneton and α is a constant. These two formulas are rigorously applicable when the multiplet intervals are respectively very small or very large compared to kT, and are valid regardless of whether the magnetic field is strong enough to change the quantization by producing a Paschen-Back effect. The formula for small multiplets yields susceptibilities slightly different from those given by Laporte and Sommerfeld's expression for this case, and is much simpler, as they overlooked the contribution of the portion of the magnetic moment which is perpendicular to the invariable axis.

4. Paramagnetism of molecules.—The susceptibility is calculated on the basis of the Hund theory of molecular quantization. Formulas are given applicable to his couplings of type (a) and type (b) provided in the former the multiplet intervals are either very large or very small compared to kT. The experimental susceptibilities for O_2 and ClO_2 are in accord with the assumption that the normal states are respectively ^3S and ^2S terms. In the particular case of S terms the numerical results are the same in the atomic and molecular formulas, but, unlike previous theories, it is not necessary to suppose the orbits are as freely oriented in molecules as in atoms. Polyatomic molecules may have lower paramagnetic susceptibilities than diatomic ones because the dissymmetry causes large fluctuations in electronic angular momentum.

5. Paramagnetism of nitic oxide.—Spectroscopists have recently found that the normal states of the NO molecule are ^2P terms separated by 120.9 cm^{-1}. This permits an unambigous calculation of the susceptibility of NO which agrees with the experimental value within 1.5 per cent. Deviations from Curie's law are calculated which result from the doublet interval being comparable with kT. These deviations should be detectable experimentally if the susceptibility of NO could be measured over a wide temperature range.

In PART I[1] a very general derivation was given of the Langevin-Debye formula for the temperature variation of the susceptibility. This proof was based on the new quantum mechanics, and assumed only that the molecule has a "permanent" moment of constant magnitude, and that the energy intervals between the various component levels of the normal state are small compared to kT. The latter requirement implies that the precession frequencies of the moment vector are small compared to kT/h Part II[2] was less mathematical, and described various applications of the theory of part I to phenomena connected with dielectric constants. Part III will similarly discuss applications to magnetism. The theories of electric and magnetic polarizations are sufficiently similar so that the analysis in part I gave simultaneously the main elements of a proof of Langevin's formula for the paramagnetic susceptibility and of Debye's formula for the dielectric constant. However, in the detailed demonstration in part I we assumed for simplicity that the moment of the molecule was electrical rather than magnetic, and so before proceeding to the magnetic applications we must in section 1 give the modifications in the derivation which are required by the fact that magnetic moments result from angular momentum, both of the orbital and spin type, rather than from electrostatic charge distributions. This section may be omitted by readers not interested in the mathematical detail. As mentioned in part I, we believe our analysis is considerably more comprehensive than most of the usual treatments with specialized models, but at the same time it must be emphasized that we do not aim to probe into the electrodynamics of the interior of the electron which is responsible for the anomalous spin moment.

Note added in proof. A remarkable paper by Dirac (Proc. Roy. Soc., Feb. 1928) has just appeared in which he shows that the requirement that the Schroedinger wave equation have the invariance demanded by relativity is adequate to give the terms ordinarily ascribed to internal spins of the electron. Thus our treatment of the electron as a spherical top to derive the Hamiltonian function inclusive of spin terms in a magnetic field suddenly loses much of its interest. However, it must at the same time be emphasized that all the essential results of the present paper are unaltered; the only difference is that our work prior to about p. 594 becomes rather antequated, as Dirac's postulates give a Hamiltonian function such as (5) directly and elegantly. From there on everything goes as before. The internal spin may indeed be a myth, but as Dirac's magnetic terms are the same to the first order as for a top model of the electron, the phrase "internal spin" may well continue to be a convenient label for Dirac's duality effect. The calculation of the susceptibility (unlike the ordinary linear Zeeman effect) necessitates, to be sure, knowledge of the energy through terms of the second order in the magnetic field H. Here there is only an academic difference between the Hamiltonian with the top model and Dirac's Hamiltonian, as in the latter

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[1] J. H. Van Vleck, Phys. Rev. **29**, 727 (1927). This and the following reference are referred to as respectively parts I and II throughout the present paper.

[2] J. H. Van Vleck, *Ibid.* **30**, 31 (1927).

the duality or apparent spin anomaly introduces no terms at all in H^2 in an Eq. analogous to our (4) whereas we show that with the spherical top such terms, which represent diamagnetic induction in the internal motion, are negligible because the radius of an electron is small compared to the radius of an orbit.

1. General Mathematical Theory

Hamiltonian function. The first step is to derive expressions for the Hamiltonian function and magnetic moment in a magnetic field. We shall start the calculation with classical mechanics and later give the quantum modifications. If we regard the molecule as composed of a number of charged particles (nuclei and electrons) then it is well known that in a magnetic field derived from a vector potential A, the Lagrangian function is[3] $L_0+\sum_i(\epsilon_i/c)\ (\mathbf{v}_i\cdot A)$, where L_0 is the Lagrangian function in the absence of the field and where ϵ_i and $\mathbf{v}_i$ are respectively the charge and vector velocity of a particle. The summation, of course, extends over all the particles in the system. For simplicity in printing we shall henceforth omit the subscript i, so that an expression such as $\sum p_\phi$, for instance, means $\sum_i p_{\varphi_i}$, etc. In virtue of their large masses, the nuclei have such small velocities that we may disregard[4] their contribution to the sum. Hence the summations will be taken only over the electrons in the system, permitting us to put $\epsilon_i=-e$ with $e=+4.774\times10^{-10}$. It is, however, to be understood that the coordinates and velocities of the nuclei will still enter in the part L_0 of the Lagrangian function. As the Uhlenbeck and Goudsmit[5]

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[3] Cf., for instance, Schott, "Electromagnetic Radiation," p. 284.

[4] According to Langevin's formula the paramagnetic susceptibility coming from a particle of charge ϵ and mass m moving in an orbit with an angular momemtum p is proportional to $p^2\epsilon^2/m^2$. This shows that the paramagnetic susceptibility coming from nuclei is small compared to that coming from electrons, for the value of ϵ/m for nuclei is less than 10^{-3} that for electrons, while the average value fo p for nuclear motions (i.e. the average rotational quantum number in band spectra) is well under 10^2 quantum units $h/2\pi$ at ordinary temperatures. As a matter of fact the contributions of the nuclei to the susceptibility are even smaller than suggested by this estimate, for at ordinary temperatuers the rotational quantum numbers specifying the motion of the nuclei about the center of gravity, though $<10^2$, are sufficiently large so that the part of the susceptibility due to nuclear angular momentum is nearly the same as though we used classical theory, where the angular momentum assumes a continuous distribution of values. Now Miss van Leeuwen (Leyden Thesis; also J. de Physique (6), 2, 361, 1921) has shown that when there is a classical distribution of angular momenta the paramagnetic and diamagnetic susceptibilities cancel, leaving zero resultant susceptibility. Consequently the contribution of the nuclei to the susceptibility is very approximately zero and can be disregarded in comparison with the electronic terms even in molecules whose electrons give only diamagnetic effects. The magnetic moments due to nuclear motions can, however, be detected in the Stern-Gerlach effect (Knauer and Stern, Zeits. f. Physik, **39**, 780, 1926). It has been variously suggested that nuclei have internal spins, as do electrons, but the contribution to the susceptibility is, of course, negligible because of the factor $1/m^2$. The molecular rotation may change the susceptibility slightly by distorting the electronic angular momentum, but this is a second order effect which we will not consider.

[5] Uhlenbeck and Goudsmit, die Naturwissenschaften **13**, 953 (1925); Nature, **117**, 264 (1926).

electron which possesses an internal or "spin" degree of freedom is quite generally accepted, we cannot treat the electron as a point charge, but rather a continuous charge distribution. Hence we cannot use a Lagrangian function of quite the form given above, but instead must take it to be

$$L=L_0+\sum\iiint(\rho/c)(\mathrm{v}\cdot A)dV, \tag{1}$$

where dV denotes an element of volume of the electron and ρ is the corresponding charge density. Far too little is known at present about the mechanics of the spin electron to determine how v and A are distributed in its interior. Nevertheless, following Darwin[6] and others, we will treat the electron as a charged spinning body of spherical symmetry, the justification for this model being that it is adequate to give the facts connected with the Zeeman effect.[7] Then as generalized coordinates specifying each electron we may use three cylindrical coordinates R, z, ϕ fixing its center, and three Eulerian angles[8] θ, ψ, ζ associated with its internal spin. If the magnetic field is of uniform magnitude H and directed along the z-axis, then $A_x=-\frac{1}{2}Hy$, $A_y=\frac{1}{2}Hx$, $A_z=0$, and it is readily seen that (1) becomes

$$L=L_0+(H/2c)\sum[-eR^2\dot{\phi}+D(\dot{\psi}+\dot{\zeta}\cos\theta)]. \tag{2}$$

Here D denotes the electrical moment of inertia $\iiint\rho(R-R_0)^2dV$ of an electron, where R_0 is the value of R at its center. The second and third right-hand terms of (2) are respectively the contributions of the orbital and internal motions of the electron to the integral in (1). These two contributions are separated by adapting to electrical rather than gravitational density the familiar mechanical theorem that the angular momentum of a system relative to a fixed point equals the angular momentum relative to the center of gravity plus the angular momentum which would result if all the mass were located there.

The momenta conjugate to the various generalized coordinates q_k are $p_k=\partial L/\partial\dot{q}_k$. Hence p_R, p_z, p_θ have the same kinematical significance[9] as

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[6] C. G. Darwin, Proc. Roy. Soc. **115A**, 1 (1927).

[7] There is, however, the much-emphasized difficulty of double-valued Schroedinger characteristic functions; see Darwin, ref. 6, also Proc. Roy. Soc. **116A**, 227 (1927); Pauli, Zeits. f. Physik, **43**, 601 (1927).

[8] Here θ and ψ denote polar and azimuth angles specifying a given axis in the electron, while ζ is the third Eulerian angle required to determine the amount of rotation around this axis. Darwin notes[6] that by a proper transformation it is possible to eliminate one of the three internal coordinates of the electron from the Hamiltonian function because the choice of axis is immaterial in a body with spherical symmetry; this however, need not concern us, in the present work.

[9] The physical basis for the need of modifying the definition of momenta in a magnetic field is perhaps more apparent when it is recalled that the angular momentum of a dynamical system about an axis is not an adiabatic invariant when a magnetic field is applied along this axis. For instance, in the simple case of a system of one particle without internal spin, p_ϕ is instead an adiabatic invariant and the extra term $-HeR^2/2c$ in the definition of p_ϕ is just equal and opposite to the change in angular momentum brought about by application of the

without the magnetic field, whereas p_ϕ, p_ψ, p_ζ are modified by the addition of terms linear in H. For instance, p_ϕ equals $\partial L_0/\partial\dot{\phi} - HeR^2/2c$, where $\partial L_0/\partial\dot{\phi}$ is the ordinary definition $mR^2\dot{\phi}$ (neglecting relativity corrections etc. to be mentioned on p. 593).

In accordance with general dynamical theory, the Hamiltonian function is $\sum_k \dot{q}_k(\partial L/\partial \dot{q}_k) - L$. Since the added terms in the Lagrangian function are linear in the generalized velocities, this is the same as $\sum_k \dot{q}_k(\partial L_0/\partial \dot{q}_k) - L_0$. Thus the Hamiltonian function E is exactly the same as in the absense of the field except that some of its arguments are modified. The physical meaning of this is, of course, that magnetic forces do no work, so that the energy is the same function of the coordinates and velocities as in their absence. Among the arguments of E we must now take

$$p_\phi + HeR^2/2c, \quad p_\psi - DH/2c, \quad p_\zeta - DH\cos\theta/2c \tag{3}$$

instead of p_ϕ, p_ψ, p_ζ, for the expressions (3) are the same functions $\partial L_0/\partial\dot{q}_k$ of the coordinates and velocities as are p_ϕ, p_ψ, p_ζ when $H=0$. Thus the Hamiltonian function is

$$E = \sum(1/2m)\left[p_R^2 + p_z^2 + (p_\phi^{0\,2}/R^2)\right] + T + V + U$$
$$+ \sum(1/2I)\left[p_\theta^2 + p_\zeta^{0\,2} + \operatorname{cosec}^2\theta\,(p_\psi^0 - p_\zeta^0\cos\theta)^2\right], \tag{4}$$

where p_ϕ^0, p_ψ^0, p_ζ^0 are abbreviations for the expressions given in (3) and hence are functions of H. This result is one which has been often given[10] except for inclusion of the spin terms. The first sum in (4) is the orbital kinetic energy. The second line is the kinetic energy of internal spin, with I denoting the electron's moment of inertia. T is the kinetic energy of the nuclei, whose magnetic effect we have disregarded. V is the mutual electrostatic potential of the charges composing the molecule. U is the mutual intra-atomic magnetic energy, including that resulting from the torques on the electrons' spin axes exerted by the other charges in the atom or molecule. These torques are, of course, responsible for the "spin doublets," "multiplet structures," etc. U, unlike V, is a function of the momenta as well as the coordinates, and hence will involve H, as in a magnetic field the arguments (3) must be used. However, U is already small, and its dependence on H enters as essentially a correction term, so that its contribution

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field. Thus in such a system it is the elements of the matrix p_ϕ and not $mR^2\dot{\phi}$ which must be equated to integral multiples of $h/2\pi$ in the new quantum mechanics. In other words we must quantize the constant angular momentum before application of the field rather than the fluctuating value in the field. When we consider spin effects or more than one particle, an individual p_ϕ is not constant even in the absence of the field and cannot be quantized; it is rather the sum $\Sigma(p_\phi + p_\psi)$ which equals the magnetic quantum number times the factor $h/2\pi$.

[10] The orbital part of the Hamiltonian function (4) has often been given in the literature including the magnetic terms resulting from the modification in the definition of the momenta (cf., for instance, Born, Atommechanik, p. 239). The part of (4) resulting from spin kinetic energy is obtained by modifying in accordance with (3) the arguments of the usual expression for the Hamiltonian function of a spinning body, which is given, for example, in Born's Atommechanik, p. 31.

to the part of the Hamiltonian function involving H is very small in comparison with the ordinary paramagnetic terms. This contribution is, in fact, shown in fine print below to be of the same order as the relativity corrections to the Zeeman effect and henceforth will be disregarded. Furthermore we may neglect the terms in H^2 in the spin kinetic energy of the electron in comparison with those in H^2 in the orbital kinetic energy, for D^2/I is very small in comparison to e^2R^2/m since the internal radius of an electron is insignificant compared to the radius of an orbit. This will later be seen to mean that the internal spins make no contribution to diamagnetic susceptibilities. With this discarding of inconsequential terms, the Hamiltonian function (4) may be written with the aid of (3)

$$E=E_0+(He/2mc)\sum(p_\phi+2p_\psi)+(H^2e^2/8mc^2)\sum R^2, \tag{5}$$

where E_0 is a Hamiltonian function of the same form and arguments as in the absence of the field, and the remaining terms may be regarded as perturbative ones. In forming (5) we suppose, following Uhlenbeck and Goudsmit, that $D/2cI=-e/mc$, or that the ratio of spin magnetic moment to spin angular momentum is twice the corresponding orbital ratio.

Magnetic moment. The magnetic moment of the molecule in the direction of the applied field is

$$M_z^{(H)}=-(e/2c)\sum R^2\dot{\phi}+(D/2c)\sum(\dot{\psi}+\dot{\zeta}\cos\theta). \tag{6}$$

The first right-hand term ensues since the equations of electron theory show that the magnetic moment due to the orbital motion of a charge $-e$ is[11] $-(e/2c)\mathbf{r}\times\mathbf{v}$. The second term is the analogous expression for the magnetic moment of a spinning charge distributed with spherical symmetry, for $\dot{\psi}+\dot{\zeta}\cos\theta$ is the z-component of spin, and D is the electrical moment of inertia. Instead of using (6) it is convenient to have a formula expressing $M_z^{(H)}$ in terms of the coordinates and momenta rather than coordinates and generalized velocities. Such a formula is immediately deducible from the Hamiltonian function by a simple differentiation, for

$$M_z^{(H)}=-\partial E/\partial H. \tag{7}$$

To prove (7) we note that E involves H only through the arguments (3) and consequently

$$-\frac{\partial E}{\partial H}=-\sum\left(\frac{\partial E}{\partial p_\phi}\,\frac{eR^2}{2c}-\frac{\partial E}{\partial p_\psi}\,\frac{D}{2c}-\frac{\partial E}{\partial p_\zeta}\,\frac{D\cos\theta}{2c}\right). \tag{8}$$

The identity of (8) and (6) follows immediately since by Hamilton's equations $\partial E/\partial p_\phi=\dot{\phi}$, etc.

Relativity Corrections. We have so far for simplicity used Newtonian mechanics. It is, however, not difficult to determine the relativity corrections for the orbital part of the magnetic moment. In the relativity mechanics, the part of the Hamiltonian function arising from

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[11] See, for instance, "Theories of Magnetism," p. 21 (Bulletin no. 18 of the National Research Council).

the orbital kinetic energy is[12] $\sum mc^2[(1+Km^{-2}c^{-2})^{1/2}-1]$ instead of $\sum K/2m$, where $K=p_R{}^2+p_z{}^2+p_\phi{}^{0^2}/R^2$. By expanding the radical as a series in H, it is easy to show that the relativity corrections change the part of the orbital energy which is of the first order in H by a factor γ, where $\gamma=(1-\mathrm{v}^2/C^2)^{1/2}$. This result has, in fact, already been obtained by Sommerfeld, Debye,[13] and Pauli.[14] The relativity corrections to the paramagnetic and diamagnetic susceptibilities, second order Zeeman effect, etc. can likewise be calculated. Here the correction factors are of the same order of magnitude as $\gamma-1$.

We give only a subordinate place to the relativity corrections because usually they do not appreciably affect the susceptibilities. It is readily found[14] that in a hydrogenic atom the time average of γ, which is the significant part of γ for the first order Zeeman terms is $1-(2\pi^2Z^2e^4/n^2h^2c^2)=1-2.7\times10^{-5}Z^2/n^2$, where n is the principal quantum number and Z is the effective nuclear charge. This expression differs appreciably from unity only for the innermost orbits. Many such orbits (*e.g.* the K orbits), however, have no orbital angular momentum, and furthermore the inner orbits are grouped in "closed configurations" without resultant angular momentum, such as are completed in forming inert gases, so that $\sum p_\phi$ taken over a completed group vanishes even when the individual angular momenta do not vanish. Since similar orbits have the same average value of γ, the sum $\sum\bar{\gamma}p_\phi$ also vanishes, and thus there are no first order terms involving important relativity corrections. Pauli[14] shows, however, that these corrections would be contrary to experiment if we supposed the inner groups had a resultant angular momentum, as in the old Landé model of a magnetic atom core which has been discarded since the advent of the spin electron. It is not immediately obvious, especially in the quantum mechanics, that the phase relations in a completed group are such that $\sum\gamma p_\phi$ vanishes instantaneously as well as on the average, so that conceivably even with zero resultant angular momentum the inner orbits might give rise to appreciable rapidly fluctuating terms proportional to $\bar{\gamma}-\gamma$ in the Hamiltonian function, and thus make a contribution to the paramagnetic part of the second order Zeeman effect. This, however, seems quite improbable. Individual electrons do not compensate each other as regards their contribution to diamagnetism, but the inner electrons have such small values of r^2 that they are responsible for a small fraction of the total diamagnetism, and so here also the relativity corrections are unimportant.

Along with the orbital relativity corrections one must consider the term arising because the intra-atomic magnetic energy U involves H through the arguments (3). Thomas and Frenkel[15] have shown that in a hydrogenic atom the secular part of U is the mean value of $e^2Z(\boldsymbol{p}_1\boldsymbol{p}_2)/2r^3m^2c^2$ where r is the radius of the orbit and $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ are respectively the orbital and spin angular momentum vectors. To calculate accurately the correction coming from U it would be necessary (unlike the usual calculation of spin doublets to terms in $1/c^2$ for $H=0$) to know the periodic part of U, for the product of this part of U and the factor R^2 involved by (3) will give a significant secular contribution. Unfortunately the periodic part of U is unknown at present, but for calculating only orders of magnitude we may assume U is given rigorously by the preceding expression. In a magnetic field the change in $\boldsymbol{p}_1$, is by (3) of the order HeR^2/c, while we neglect the change in $\boldsymbol{p}_2$ since the spin electrical moment of inertia is small compared to eR^2. Thus to first order terms in H the contribution of U to the additional energy due to the magnetic field is roughly of the order $\pi HZ^2e^5/nhmc^3$, as R^2/r^3 is of the order $4\pi^2Ze^2m/n^2h^2$. This contribution is clearly comparable with the relativity correction to the Zeeman terms, which is the mean value of $eH(\gamma-1)p_\phi/2mc$ and in fact involves the constants e, h, c in the same way. In the foregoing we have discussed primarily the effect on the energy, but the corresponding corrections to the magnetic moment can be deduced from Eq. (12) below.

In studying internal spins of the electrons it is probably quite vital that one use relativity mechanics, as Breit, Thomas,[16] and others show that the spin may be so rapid that peripheral

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[12] Cf. for instance, Born, Atommechanik, p. 232.

[13] A. Sommerfeld, Phys. Zeits. **17,** 491 (1916). P. Debye, *Ibid.* **17,** 507 (1916).

[14] W. Pauli, Jr., Zeits. f. Physik, **31,** 373 (1925).

[15] L. H. Thomas, Nature, **117,** 514 (1926). J. Frenkel, Zeits. f. Physik, **37,** 243 (1926).

[16] G. Breit, Proc. Nat. Acad. **12,** 451 (1926). L. H. Thomas, Phil. Mag. **3,** 1 (1927).

velocities are comparable with that of light. However, far too little is known about the internal structure of the electron to permit us to use the relativistic analysis, as in the preceding work we would have to know how the charge distributes itself inside the electron. Nevertheless, the value $-e/mc$ for the ratio of spin magnetic moment to spin angular momentum seems well established from evidence on the Zeeman effect and multiplet separations, and this must be regarded as applying inclusive rather than exclusive of relativity corrections since they are important for the spins. (Then m denotes the rest mass, and spin angular momentum is to be defined in the generalized relativity sense which allows for variation of mass with speed). In using this value of the ratio we have thus perhaps rather illogically incorporated the relativity corrections in our Newtonian model of the electron's spinning motion. We use this model simply to show that internal spins do not contribute appreciably to diamagnetism, and also, as do others, because it is a convenient way of formulating what is known about the electron's spinning motion in the absence of an adequate electrodynamics of its interior. (Note added in proof: Dirac's work alredy quoted clears up this situation greatly.)

Passage to quantum mechanics. In studying actual molecular systems it is, of course, necessary to use quantum mechanics, but fortunately the adaptation of the preceding analysis to this is immediate. The Hamiltonian function is still (5), and Eq. (7) is still applicable. Only, of course, the coordinates and momenta, also E and $M_z^{(H)}$, are now matrices.[17] The justification for these statements is that the Hamiltonian function (5) involves no non-commutative products, except possibly in E_0. In other words there are no terms of interest involving simultaneously a coordinate and its canonically conjugate momentum, so that by the correspondence principle there can be no ambiguity in the quantum adaptation. This is the same argument as that given by Heisenberg and Jordan[18] in their paper on the Zeeman effect, in which they use a matrix Hamiltonian function similar to (5) except for omission of the diamagnetic term. If we use the abbreviation

$$M_z = -(e/2mc)\sum(p_\phi + 2p_\psi), \tag{9}$$

then a typical matrix element of the perturbative part of the Hamiltonian function is by (5)

$$-HM_z(njm;\ n'j'm') + (H^2e^2/8mc^2)\sum R^2(njm\ ;\ n'j'm'). \tag{10}$$

We use in (10) and elsewhere in this paper the same notation as in part I, except we no longer print matrices in bold-face type, and the reader is referred to p. 733 of I for a full explanation of its significance. Briefly, the first index n represents the totality of quantum numbers whose effect on the energy is large compared to kT, while the index j represents those, other than m, whose effect is smaller than, or comparable with kT. The third

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[17] As already mentioned on p. 731, part I, we use the matrix rather than wave formulation of the new quantum mechanics. The same results are, of course, obtained with either formulation in virtue of their general mathematical identity, and the popularity of susceptibility calculations by means of the wave equation seems rather surprising inasmuch as the matrix method has usually yielded the susceptibility formulas first and most directly. Except for the spin terms, a wave equation corresponding exactly to the Hamiltonian function (5) is deducible from the generalized Schroedinger equation given by Gordon (Zeits. f. Physik, **40**, 117, 1926) and others, which includes the vector as well as electrostatic potentials.

[18] W. Heisenberg and P. Jordan, Zeits. f. Physik, **37**, 263; (1927).

index m is the magnetic quantum number specifying the spacial orientation, and is not to be confused with the mass of the electron, which appears as a factor in the denominator and is also denoted by m. It is to be clearly understood that $R^2(njm;\, n'j'm')$ denotes an element of R^2, not the square of an element of R. Also it is to be noted that the summation sign immediately preceding R^2 means a sum over all the electrons in the molecule, and is not to be confused with the other sums of the matrix elements over various quantum numbers indicated by subscripts after the summation signs.

Energy and moment of a stationary state. The effect of the magnetic field on the energy may now be calculated by the perturbation theory for the new quantum mechanics which has been developed by Born, Heisenberg, and Jordan,[19] provided the field is weak enough to permit power series development in H. We may suppose the system non-degenerate as this involves no essential loss of generality in calculating susceptibilities (see note 19 and p. 740 of part I). If we retain terms through H^2, the energy of the state njm is

$$W^{(H)}(njm) = W(njm) - HM_z(njm\,;\,njm) + H^2 \sum\nolimits'_{n'j'm'} \frac{|\, M_z(njm\,;\,n'j'm')\,|^2}{h\nu(njm\,;\,n'j'm')} + (H^2e^2/8mc^2) \sum R^2(njm\,;\,njm), \qquad (11)$$

as the first and second terms of (10) correspond to H_1, H_2 in the notation of Born, Heisenberg, and Jordan. The prime after the summation sign means that the one term $n'j'm' = njm$ is to be excluded. The frequencies ν, energy elements $W(njm)$, and other matrix elements appearing on the right-hand side of (11) are to be calculated for $H = 0$, as indicated by the absence of the superscript$^{(H)}$.

The time average of the magnetic moment of a state in the direction of the applied field can be obtained directly from (11) by means of the formula[20,21,22]

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[19] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 557 (1927); especially Eqs. (29) and (31), p. 567.

[20] Eq. (12) is not to be confused with (7), as (12) gives the average rather than instantaneous value of the magnetic moment defined by (6); also the Hamiltonian function E in (7) is the energy expressed in terms of the generalized coordinates and momenta, whereas in (12) W denotes the energy expressed as a function of the quantum numbers. The distinction between the instantaneous and average values of the magnetic moment is only a nominal one, at least with the definition (6) we use, for (6) is based on the conventional formula $(-e/2mc)\mathbf{r}\times\mathbf{v}$ of the electron theory for the orbital magnetic moment and this formula is valid only on the average, as in its derivation terms are omitted which average out if the motion is recurrent.

[21] It is interesting to note that formulas similar to (7) and (12) also hold in the case of electric rather than magnetic polarization. In the electric case $E = E_0 + \sum Fez$ so that $\partial E/\partial F = \sum ez = -M_z^{(F)}$ and from this a formula analogous to (12) can be established by the same method as that given above.

[22] Eq. (12) can also be established by application of the principle of adiabatic invariance. As magnetic forces do no work, the change in energy of a stationary state when subject to a magnetic field is due to the work done by electric forces attendant to creation of a magnetic

$$\overline{M}_z^{(H)}=-\partial W^{(H)}/\partial H \text{ or } M_z^{(H)}(njm\,;\,njm)=-\partial W^{(H)}(njm)/\partial H. \qquad (12)$$

Eq. (12), which is even taken by some writers as the definition of the moment, is easily proved to follow from our definition (6) by the theorem that the change in energy brought about by the addition of a perturbative term to the Hamiltonian function is to the first order the mean value of this term. This is a well known theorem in the old quantum theory, and Born, Heisenberg, and Jordan[19] show that it also holds in the new quantum mechanics, with, of course, the understanding that the requisite mean value is formed by keeping only diagonal elements in the matrix representing the perturbative term. If we change the magnetic field from H to $H+\Delta H$ and if we neglect terms in $(\Delta H)^2$, the term thereby added to the Hamiltonian function is $(\partial E/\partial H)\Delta H$, and by the theorem just quoted the corresponding change $\Delta W^{(H)}$ in energy is very approximately the average value of this term. Eq. (12) now follows on using (7).

The formula for the magnetic moment obtained by combining (11) and (12) is similar to Eq. (3) of part I except that it applies to magnetic rather than electric polarization, and except for addition of the diamagnetic term, which arises from the second line of (11) and finds no analog in the electrical case. It is to deduce this term that we have given most of the preceding analysis, as otherwise we could have started directly with a formula similar to (3) of part I. The diamagnetic effect is essentially a correction for the fact that in a magnetic field the moment is no longer given by (9) because of modifications in the kinematical significance of the canonical momenta. Even without the diamagnetic term, however, the time average $M_z^{(H)}(njm;\,njm)$ of the z-component of magnetic moment of a stationary state in the presence of the field would not equal the time average $M_z(njm;\,njm)$ of this component in its absence, for there is another term in H^2, on the first line of (11), which is similar to that in the electrical case. This other term is associated with the type of second-order Zeeman effect for which the formula is given by E. Hill and the writer in a preliminary abstract (No. 41) on p. 715 of this issue, and would be absent were Larmor's theorem applicable.

Calculation of susceptibility. Because of the similarity of (11–12) to Eq. (3) of part I, the analysis in sections 2 and 3, part I, may now be applied, and should be read conjunctly by those desirous of following the present section in detail. The addition of the diamagnetic term occasions no particular difficulty, for it was shown on p. 744, part I, that the effect of averaging over the various quantum-allowed orientations is to replace R^2 by $2r^2/3$, just as in the classical theory where the orientations are random. We use r^2 to denote $x^2+y^2+z^2$, the square of the radius, while $R^2=x^2+y^2$. We now separate the matrix M_z defined by (9) into "high" and "low" frequency elements, as fully explained on p. 733, part I, which are denoted respectively

field, which can be shown to give (12) if the field is applied adiabatically. We do not use this method because it would require us to enter into the rather involved quantum mechanics of non-conservative systems. However, a paper by Born shows how the concept of adiabatic invariance can be given a meaning in the new mechanics (Zeits. f. Physik, **40**, 167, 1927).

by $M_z(njm;\, n'j'm')$ $(n' \neq n)$ and $\mu_z(jm;j'm')$. Similar expressions without the subscript z will be used to denote the high and low frequency elements of the scalar magnitude of the magnetic moment vector measured, of course, before application of the field H.

There is, however, one respect in which it is necessary to modify the calculation of the susceptibility given in section 3, part I. The magnetic moment in general consists of two parts, viz., the "orbital" and "spin" moments. In the various component levels constituting the normal state these two parts may be inclined to each other at different angles, so that their vector resultant may have different values. Thus we cannot always suppose the resultant magnetic moment "permanent," so that we cannot always effect the simplification given at the top of p. 738, part I. Instead the contribution of the low frequency elements must be expressed as in the first line of (12), part I. If we make only the fundamental assumption that the "low" and "high" frequencies are respectively small and large compared to kT/h, the analysis in part I shows that the formula for the susceptibility is

$$\chi = N\alpha + N\overline{\overline{\mu^2}}/3kT, \tag{13}$$

where by (6) and (12), part I,

$$\overline{\overline{\mu^2}} = \frac{\sum_{j,m}\left[\left\{\sum_{j'm'} \left| \mu(jm\,;j'm' \right|^2\right\} e^{-W(nj)/kT}\right]}{\sum_{j,m} e^{-W(nj)/kT}}\,. \tag{14}$$

Eq. (13) differs from (1), part I, only in the insertion of the double bar in the second right-hand term. The expression (14) has the significance of being the time average of the square of the low frequency part of the magnetic moment vector, this average itself being averaged over the various component levels of the normal state weighted in accordance with the Boltzmann factor $e^{-W(nj)/kT}$. This follows since by the rules for matrix multiplication the expression in the inner sum of the numerator of (14) is a diagonal element of the matrix μ^2, i.e. the time average of μ^2 for the state njm, which is no longer assumed to have a numerical value invariant of j. The sum over j, m, of course gives the average over the various component levels of the normal state. We use a double rather than single bar in (13, 14) in order to emphasize the distinction between the statistical mean (14) of the time average, and pure time average for a single state.

The term $N\alpha$ in (13) represents the diamagnetic effect, together with the contribution of the high frequency elements, which may be simplified as on pp. 738–740, part I. Using (17), part I, and adding the diamagnetic term, the value of this term is seen to be

$$N\alpha = \frac{2N}{3h} \sum_{n'(n' \neq n)} \frac{\left| M(n\,;n') \right|^2}{\nu(n'\,;n)} - \frac{Ne^2}{6mc^2} \sum \overline{r^2}, \tag{15}$$

where $M(n;n')$ is defined as on p. 739, part I. In order to make the denominator positive, we use the emission frequencies $\nu(n';\, n)$ which have the opposite sign from the negative or absorption frequencies $\nu(n;\, n')$ used in (17), part I. We have assumed in (15) that the matrix element $r^2(njm;\, njm)$ representing the time average of the square of the radius of a given orbit for the state njm has the same magnitude in all the component levels of the normal state; i.e., has a value invariant of j or m, which we denote by $\overline{r^2}$. This condition is usually met in gases, as the magnetic quantum number m merely quantizes the spacial orientation, and in atoms the various j-levels usually represent various relative orientations of the spin and orbital angular momenta. Such differences only in orientation clearly do not affect the size or shape of an orbit. In molecules the index j may in addition be associated with a splitting into components due to different amounts of molecular rotation, but the rotational quantum number does not influence the magnitude of r if we neglect the slight centrifugal expansion studied on p. 54, part II.[2]

2. Diamagnetism—Discussion of Eq. (15)

If the magnetic moment matrix M contains low frequency elements, the second right-hand term of (13) is usually much greater than the first, and the material is paramagnetic. If, however, the moment contains only high frequency elements; i.e., vanishes if we average over the high frequency part, this second term vanishes. The susceptibility is then given by (15), and is paramagnetic or diamagnetic according as the first or second-right-hand member of (15) is the greater. Now the expression (15) is independent of the temperature as long as the number of molecules N per cc. does not vary. This is in accord with the fact that experimentally in gases the diamagnetism is usually independent of the temperature at constant density. On the other hand the diamagnetism of many solids vary with the temperature. A possible explanation of this difference is that in solids conditions are more complicated than assumed above in deriving (15), so that possibly the different levels constituting the normal state do not have the same radii. When this is the case it is necessary to replace $\overline{r^2}$ by the statistical mean of the time average of r^2, i.e., by an expression $\overline{\overline{r^2}}$ defined by an equation identical with (14) except that μ is replaced by r; the term $N\alpha$, of course then varies with temperature due to varying distributions among orbits of different sizes. Also (15) breaks down if the frequencies $\nu(n';\, n)$ are not all large compared to kT/h.

Diamagnetism of atoms. If it were not for the spin anomaly, the constancy of angular momentum in atoms would also imply the constancy of magnetic moment, and the matrix M would consist solely of diagonal elements so that the first right member of (15) would be wanting. Actually because of different ratios for the spin and orbital parts, the resultant magnetic moment and angular momentum vectors are not parallel, and M contains periodic elements whose frequencies are classically that of the mutual precession of the spin and orbital angular momenta, and quantically are proportional to the energy intervals in multiplets whose components differ as to inner quantum number. However, the normal level of a diamagnetic atom is ordinarily a ^1S state, for the existence of either a spin or orbital angular momentum different from zero implies paramagnetism (see also note 34). Consequently the periodic terms in the moment matrix still disappear, and the expression for the susceptibility becomes

$$\chi = -(e^2N/6mc^2)\sum \overline{r^2}. \tag{16}$$

This formula is one which has been derived clasically by Pauli,[23] and as noted by Glaser and Barnett,[24] differs by a factor 2 from the original Langevin-Weber formula, which was derived not with real electronic motions, but with the assumption of hypothetical particles confined to move in one plane. Pauli assumed Larmor's theorem, which is legitimate in singlet states.

The average value of r^2 needed in Eq. (16) is easily deduced for hydrogenic atoms from Waller's formula for mean values in Keplerian motion in the new quantum mechanics, and has been calculated by the writer[25] and by Pauling,[26] both of whom find $\overline{r^2} = \frac{1}{2}a_0^2n^2(5n^2-3k^2-3k+1)$, where $a_0 = h^2/4\pi^2mZe^2 = .53\times 10^{-8}Z^{-1}$, the radius of a one-quantum orbit in the old theory, while n is the principal quantum number, and k is one unit lower than the conventional azimuthal quantum number of the old theory. The old quantum theory would have $-3(k+1)^2$ in place of $-3k^2-3k+1$. An experimental value of the diamagnetic part of the susceptibility of atomic hydrogen can only be deduced rather indirectly by applying the method of mixtures to compounds. Even if hydrogen gas could be dissociated into the monatomic form, it would be paramagnetic like the alkali vapors because of spin doublets. However, approximate comparisons of the theory with experiment can be made by assuming the orbits in other atoms to be approximately hydrogenic in character if a proper value be assigned the effective nuclear charge. Such comparisons have been given by the writer for helium,[25] and especially by Pauling[26] for a large number of other atoms. The reader is referred to their papers for details. The diamagnetism calculated for atomic hydrogen and helium is three times as great as in the old quantum theory, and agrees much better with experiment.

Diamagnetism of molecules. In non-monatomic molecules the first right member of (15) does not vanish. The reason is that the total electronic angular momentum contains fluctuating terms due to the continual transfer of angular momentum back and forth between the electrons and nuclei even though the resultant angular momentum of the entire molecule is constant. The low frequency and constant elements of the magnetic moment vanish, to be sure, in a diamagnetic molecule but because of this transfer effect the high frequency elements will not disappear even if the molecule is in a^1S state. This statement will be proved in detail in the following paragraphs in fine print. Hence in non-monatomic molecules the square of the magnetic moment or of the electronic angular momentum does not vanish even when

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[23] W. Pauli, Jr., Zeits. f. Physik, **2**, 201 (1920).

[24] A. Glaser, Dissertation, Munich, 1924; S. J. Barnett, Phys. Rev. **25**, 835 (1925).

[25] J. H. Van Vleck, Proc. Nat. Acad. **12**, 662 (1926).

[26] L. Pauling, Proc. Roy. Soc. **114A**, 181 (1927).

the average amount is zero. This result at first seems contrary to the correspondence principle, for in classical theory most diamagnetic models of the molecule have zero magnetic moment instantaneously as well as on the average. The explanation of this paradox is that the expression in classical mechanics which corresponds to the first right member of (15) involves the derivatives with respect to the action variables of the amplitudes in the Fourier expansion of the magnetic moment,[27] and these derivatives, of course, do not necessarily vanish because the amplitudes themselves do. Also, the frequencies involved in transfers of angular momentum between nuclei and electrons are, in the terminology of band spectroscopists, "electronic frequencies" associated with transitions from normal to excited states. In applying the correspondence principle we must consider both the initial and final states in classical models, and classically the excited states may be paramagnetic and have non-vanishing amplitudes in the Fourier expansion of the moment because of the transfer effect. This effect is, of course, absent in atoms, and the periodic part of their magnetic moment arises only because of the spin anomaly previously discussed.

Proof that periodic part of electronic angular momentum does not vanish in non-monatomic molecules.[28] We shall neglect the spin moment, as this does not enter appreciably in the transfer effect. From the relations between matrix and wave mechanics established by Schroedinger, Eckart, or Dirac, a diagonal matrix element of the square of the orbital electronic angular momentum is

$$P^2(n;\ n) = -(h^2/4\pi^2)\int \cdots \int u_n^*[(\sum P_x)^2+(\sum P_y)^2+(\sum P_z)^2]u_n dx_1 \cdots dx_s dy_1 \cdots dz_s \qquad (17)$$

where u_n is the Schroedinger wave function for the state n, u_n^* is its conjugate, and P_x is the operator $y\partial/\partial z - z\partial/\partial y$, with similar definitions of P_y, P_z. The index n symbolizes the aggregate of all the electronic quantum numbers. To prove (17) different from zero it suffices to prove that $P_z^2(n;n)$ does not vanish. Let us suppose that the axis joining two of the nuclei is located in the xy plane and makes an angle θ with the x-axis. Let us introduce the new coordinates

$$x_i' = x_i \cos\theta + y_i \sin\theta,\ y_i' = -x_i \sin\theta + y_i \cos\theta,\quad z_i' = z_i \quad (i = 1, \cdots, s)$$

which are fixed relative to the nuclei, and let us suppose that $u_n(x_1', \cdots, z_s')$ is expressed in terms of the coordinates $x_1, \cdots, z_s$ and θ. Then we find

$$P_z^2(n;\ n) = P_z'^2(n;\ n) = -(h^2/4\pi^2)\int \cdots \int u_n^* \partial^2 u_n/\partial\theta^2 dx_1 \cdots dz_s. \qquad (18)$$

Now (18) has a value $P_z'^2(n;n)$ invariant of θ, and so it is immaterial if we average over θ. This permits a partial integration with respect to θ which throws (18) into the form

$$P_z^2(n;\ n) = (h^2/4\pi^2)\int \cdots \int |\partial u_n/\partial\theta|^2 dx_1 \cdots dz_s. \qquad (19)$$

The expression (19) can clearly vanish only if u_n is independent of θ. This is, however, incompatible with the fact that the wave equation involves θ through the mutual potential energy of the electrons and the two nuclei under consideration. In other words the wave function in the xyz system will be different depending on how the molecular axis is oriented relative to this system. Thus the square of the electronic angular momentum will vanish only if u is a

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[27] This may be verified by noting that Eq. (17), part II, is the classical analog of (3), part I.

[28] This method of proof is suggested by Born and Oppenheimer's paper on molecules, Ann. der Physik. **84,** 457 (1927).

a function only of the relative positions of the electrons and their distances from a single fixed center. This is, of course, possible only if the nuclei exerted no forces or if all the nuclei coincided, *i.e.* an atom.

It may be remarked that the above proof applies to a molecule with any number of nuclei and electrons. In the particular case of a diatomic molecule we may distinguish between the different behaviors of the components of angular momentum parallel and perpendicular to the axis of figure. The parallel component is constant, and an integral multiple of $h/2\pi$ and so may vanish, as it does in S states. The perpendicular component is easily shown to vanish on the average (due, essentially to the continual precession of the electronic angular momentum vector about the axis of the molecule), but its square does not vanish, as we have taken the z-axis in (18) perpendicular to the line joining the nucleus. In the very special case of a molecule with only one electron, the vanishing of (17) or (18) requires that the wave function be a function of r only.[29]

The foregoing shows that I was in error in stating in a former article[25] that Pauli's formula (16) could be applied to molecules as well as atoms. Instead the complete expression (15) must be used.[30] The cause of my mistake was that I naturally supposed the electronic angular momentum vanished instantaneously rather than only on the average. I am indebted to Dr. Kronig for questioning my extension of Pauli's formula to molecules. His letter, which advanced considerations closely related to those given in note 30, led me to discover the need of always including both terms of (15) in non-monatomic molecules. This modification does not affect my calculation[25] of the diamagnetism of H_2, as this was made by treating the hydrogen molecule as a hydrogenic atom with properly adjusted "effective charge," and with this rough approximation the first right member of (15) is zero, as it vanishes for atoms in the S state.

Experimentally most gases are found to be diamagnetic, and this shows that the first right member of (15) is ordinarily less than the second in ^1S molecules. Perhaps the symmetry of the wave function is often sufficiently close to that of a ^1S atom so that (16) is a fair approximation. It is to be noted that in any case Pauli's formula (16) is an upper limit to the diamagnetic susceptibility.

3. PARAMAGNETISM OF ATOMS

We shall treat only the case where the spin angular momenta can be considered firmly coupled together to form a resultant spin angular momen-

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[29] This can also be seen by transforming to polar coordinates in the manner of L. Brillouin, J. de Physique, **8**, 74 (1927), especially footnote, p. 77.

[30] A simple general illustration of the need of considering both members of (15) is furnished by a hypothetical system of two concentric rigid bodies of spherical symmetry, *i.e.*, two spherical magnetons, of electrical and mechanical moments of inertia D_1, I_1 and D_2, I_2 respecitvely. The diamagnetic susceptibility to be expected if we treat the magnetons as separate bodies and keep only terms analogous to the second member of (15) is readily shown to be $-(N/4c^2)(D_1^2/I_1+D_2^2/I_2)$, whereas if we let the two magnetons be rigidly joined together to form a single body, the true susceptibility is $-(N/4c^2)(D_1+D_2)^2/(I_1+I_2)$, as D_1+D_2 and I_1+I_2 are the total moments of inertia. Thus a different result is apparently obtained depending on whether we treat the magnetons as a single rigid body or as two bodies so strongly coupled as to form a virtually rigid whole. The cause for this discrepancy is that when the magnetons are considered as separate bodies the first right member of (15) will not vanish if there is interaction between them.

tum vector $\boldsymbol{P}_s$ of permanent magnitude, and where the orbital angular momenta likewise form a resultant $\boldsymbol{P}_k$ of permanent size. The quantum mechanics shows that the matrix elements of the squares of these vectors are then

$$P_s^2(n\,;\,n)=s(s+1)h^2/4\pi^2,\qquad P_k^2(n\,;\,n)=k(k+1)h^2/4\pi^2,\tag{20}$$

where $s=\frac{1}{2}$ in doublets, 1 in triplets, etc., while k is the Russell-Saunders quantum number which quantizes the total orbital angular momentum. Thus $k=0$, 1, 2, 3 in S, P, D, F terms. This k (often denoted by l) is not to be identified with the azimuthal quantum number of an individual electron unless there is only one not in a completed group. The type of coupling which we are considering is characteristic of the simpler forms, of spectra, the so-called "normal multiplets" or "multiplet structures of the first order." The extension of the theory to other types of coupling where the interaction between individual spin and orbital momenta is stronger than the coupling of spin or orbital momenta among themselves, furnishes no particular difficulty.

The spin and orbital magnetic moment vectors are, of course, connected with the corresponding angular momentum vectors by the relations

$$\boldsymbol{M}_s=-e\boldsymbol{P}_s/mc,\qquad \boldsymbol{M}_k=-e\boldsymbol{P}_k/2mc.\tag{21}$$

The various values of the total angular momentum $\boldsymbol{P}$, which is the resultant of $\boldsymbol{P}_s$ and $\boldsymbol{P}_k$, give the various components of a "multiplet" level. Because of the different proportionality factors in the two Eqs. (21), the resultant magnetic moment is not in general parallel to $\boldsymbol{P}$. We may consider two limiting cases, in which the separation of components, or in other words the energy of interaction between $\boldsymbol{P}_s$ and $\boldsymbol{P}_k$, is respectively very large or very small compared to kT.

1. *Multiplet intervals small compared to kT.* As already mentioned on p. 598, the only periodic elements involved in the magnetic moment vector of an atom are those associated with the mutual precession of the spin and orbital angular momentum vectors. Thus when the multiplet intervals are small compared to kT, these elements will be entirely of the "low frequency" category, and the first right member of (15) disappears. If then we neglect the small diamagnetic effect always superposed on the paramagnetic we may set $\alpha=0$ in the expression (13) for the susceptibility. Since $\boldsymbol{\mu}$ is the resultant of the vectors $\boldsymbol{\mu}_s$ and $\boldsymbol{\mu}_k$ we have

$$\boldsymbol{\mu}^2=\boldsymbol{\mu}_s^2+\boldsymbol{\mu}_k^2+\boldsymbol{\mu}_s\cdot\boldsymbol{\mu}_k+\boldsymbol{\mu}_k\cdot\boldsymbol{\mu}_s.\tag{22}$$

By $\boldsymbol{\mu}$, $\boldsymbol{\mu}_s$, $\boldsymbol{\mu}_k$ we mean the "low frequency parts" of the vectors $\boldsymbol{M}$, $\boldsymbol{M}_s$, $\boldsymbol{M}_k$. Now in the absence of high frequency elements the distinction between the $\boldsymbol{\mu}$'s and $\boldsymbol{M}$'s disappears, and we may take $\boldsymbol{\mu}_s\cdot\boldsymbol{\mu}_k=\boldsymbol{\mu}_k\cdot\boldsymbol{\mu}_s$ in (22) since $\boldsymbol{P}_s$ and $\boldsymbol{P}_k$ commute in multiplication (cf. ref.[18]).

Since the temperature factor $e^{-W/kT}$ may be disregarded under the supposition of energy intervals small compared to kT, the statistical average of the product $\boldsymbol{\mu}_s\cdot\boldsymbol{\mu}_k$ may be taken as zero. This is an obvious result in very strong fields, where $\boldsymbol{P}_s$ and $\boldsymbol{P}_k$ are quantized separately relative to the axis of the field and hence have no correlation between their directions if we average over all orientations. Furthermore the statistical average of this product is invariant of the field strength (neglecting small saturation terms proportional to H^2) and hence vanishes in all fields if it does in very strong ones, for an easy extension[31] of the spectroscopic stability relations given in section 4, part I, shows that it is invariant of the mode of quantization if the system is made degenerate with respect to j, m by neglecting the interaction between $\boldsymbol{P}_k$ and $\boldsymbol{P}_s$ and between H and both $\boldsymbol{P}_k$, $\boldsymbol{P}_s$. We can also verify directly that the statistical average of $\boldsymbol{P}_k \cdot \boldsymbol{P}_s$ vanishes in weak fields by noting that here $P^2(nj;\, nj) = j(j+1)h^2/4\pi^2$, so that using (20) and a relation between the components of P analogous to (22) we have

$$\overline{\overline{\boldsymbol{P}_s \cdot \boldsymbol{P}_k}} = (h^2/4\pi^2 B) \sum_{j=|k-s|}^{j=k+s} (2j+1)\left[j(j+1) - s(s+1) - k(k+1)\right] = 0.$$

The constant factor B in the denominator is the total number $B = (2k+1) \cdot (2s+1)$ of components constituting the normal state and the factor $2j+1$ is the a-priori probability or number of m components belonging to a given value of the inner quantum number j.

The values of the first two terms of (22) are furnished immediately by (20, 21). Since (20) does not involve the indices j, m, the insertion of a double bar over these terms in substituting (22) in (13) is unnecessary. Since the preceding paragraph shows the third and fourth terms of (22) give no effect on the average, we see that the expression (13) for the susceptibility becomes

$$\chi = N\left[4s(s+1) + k(k+1)\right]\beta^2/3kT \tag{23}$$

where β is an abbreviation for the Bohr magneton

$$\beta = he/4\pi mc. \tag{24}$$

It is to be emphasized that the derivation of (23) has not rested upon a quantization peculiar to a particular field strength, as this is not involved in (20). Consequently if we neglect saturation effects, which are disregarded throughout the article, and which are ordinarily small in paramagnetic media, the susceptibility is invariant of the field strength, even though the Paschen-Back effect may materially alter individual Zeeman components. As we have so often mentioned, such results are typical of the new mechanics. If the field is so strong that the separation of Zeeman components is larger than the multiplet intervals, it would be necessary to develop the energy in descending rather than in ascending powers of H as assumed in part I, but (23) then clearly applies if we neglect small terms proportional to $1/H, \cdots$, as there is then separate spacial quantization of the spin and orbital momenta; our main result is that (23) applies also in weak fields.

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[31] A proof similar to that given in section 4, part I, establishes the invariance of sums of products of the form fg^* as well as ff^*.

2. *Multiplet intervals large compared to kT.* When the separation of multiplet components is large compared to kT, only the one component which has the lowest energy is the normal state. The matrix elements of $\boldsymbol{M}$ are now all of the "high frequency" type unless $J=J'$. Here J is the inner quantum number, which we denote by a capital letter when it is different than the general index j used throughout parts I, II, III. In the previous case 1, J and j were identical, but now J belongs to the high frequency category n. The low frequency part of $\boldsymbol{M}$ is now only the part which is parallel to the resultant angular momentum $\boldsymbol{P}$ and so does not involve the precession about the "invariable axis" of $\boldsymbol{P}$. Heisenberg and Jordan's analysis[18] shows that the square of this part of $\boldsymbol{M}$ is $g^2J(J+1)\beta^2$ where g is the Landé g-factor $(3/2)+(s^2+s-k^2-k)/2(J^2+J)$. Thus (13) becomes

$$\chi=Ng^2J(J+1)\beta^2/3kT+N\alpha. \tag{25}$$

The first member of (25) can also be deduced from quite elementary considerations, as is usually done, by noting that in the present instance the mean square of the magnetic quantum number m is $J(J+1)/3$ in either the old[32] or new[33] quantum theory. The second member, given by (15), is usually disregarded, as it is often small. A later paper by E. Hill and the writer on the second order Zeeman effect shows that in the present case it becomes

$$N\alpha=\frac{N\beta^2}{6(2j+1)h}\left[\frac{f(j)}{\nu(j-1\,;j)}+\frac{f(j+1)}{\nu(j+1\,;j)}\right]-\frac{Ne^2}{6mc^2}\sum\overline{r^2} \tag{26}$$

with the abbreviation $f(j)=j^{-1}[(s+k+1)^2-j^2][j^2-(s-k)^2]$. Usually the normal state is a minimum or maximum of J, depending on whether the multiplet is normal or inverted, and then the first or second term of (25) vanishes. The frequencies in the denominator of (26), although assumed large compared to kT/h, are usually small enough to make the sum of the first two terms large compared to the third, except in S states, where only the diamagnetic effect remains.[34]

Comparison with other work. We shall omit comparisons of Eqs. (23, 25) with experiment, as we have nothing new to contribute. In the absence of

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[32] Sommerfeld, "Atombau," 4th Ed., pp. 630–648 and references.

[33] J. H. Van Vleck, Nature, **118,** 226 (1926).

[34] A peculiar situation arises when the only level in which there is normally an appreciable concentration of electrons is a multiplet-component which has a zero inner quantum without being an S-term. The first member of (25) will then vanish, so that the susceptibility will be equal to the expression (26), and further the second term of (26) will be different from zero. Thus the material will exhibit a weak paramagnetism which is independent of the temperature, in striking contrast to the usual Curie law. Hund interprets the lowest level in Eu^{+++} as a ^7F term having $j=0$, while Laporte and Sommerfeld consider the lowest level in Cr^{++} to be a ^5D term likewise with $j=0$. These are thus cases in which there might conceivably be this weak paramagnetism invariant of temperature. However, the strong paramagnetism of Eu^{+++} and Cr^{++} seems to show pretty definitely that in these ions there is an appreciable concentration of electrons in states having inner quantum numbers different from zero, so that if the assignment $j=0$ to the lowest level is really correct there must be other components separated from the lowest by an interval small compared to kT/h.

data on paramagnetic monatomic vapors, most of the experimental check is furnished by monatomic ions in solution. The calculations of other writers[32,35] have ordinarily been made on the supposition that only one multiplet component need be considered, so that (25) is applicable. Now neglecting the second right hand term, Eq. (25) is exactly the formula which Sommerfeld and others have derived with the old quantum theory, so that it is unnecessary to revise their comparisons with experiment. This agreement between the old and new theories is rather fortuitous, and results because both give the same z-components of the angular momentum P even though they give different values of P and of the angle between P and z. This agreement, however, applies only with "strong" special quantization in the old theory, and as discussed by the writer on p. 37, part II, and also in an earlier note,[33] the new mechanics has the great advantage that it is immaterial whether there is weak or strong special quantization. The most satisfactory experimental confirmation of (25) consistent with existing spectroscopic data seems to be found in Hund's[35] calculation of the susceptibilities of the rare earths.

The susceptibilities of ions of the iron group, also even the rare earths in some cases, are not adequately explained by Eq. (25) without contradicting spectroscopic theory on normal terms. In a noteworthy article Laporte and Sommerfeld[36] attribute this to the fact that the multiplet intervals may not be large compared to kT. They show that susceptibilities in the iron group are intermediate between those predicted for very wide and very narrow multiplets, provided "inverted" multiplets are assumed in some instances. One correction, however, must be noted to the work of Laporte and Sommerfeld. Their formula for the limiting case of intervals small compared to kT is not (23) but a considerably more complicated expression (their Eq. 6). The reason is that they overlook the fact that the second as well as first order Zeeman effect, in other words both terms on the first line of (11), contribute to the second right member of the susceptibility expression (13) in narrow multiplets. This extra contribution results from the component of magnetic moment perpendicular to the resultant angular momentum, as the Landé g-factor embodies only the parallel component. The effect of this correction is usually not large and so leads to no important change in their results. (It makes the magneton numbers $\mu_w(0)$ in their table 2 become 0, 14.9, 22.2, 25.8, 27.2, 29.4 instead of 0, 14.5, 21.6, 24.7, 26.0, 29.6)

When spectroscopists have accurately determined the width of multiplets contiguous to the normal state it will, of course, be possible to make exact calculations of the susceptibility by means of equations such as (5), part I, instead of relying on the limiting formulas (23) and (25) which are rigorously applicable only to infinitely narrow or wide multiplets.

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[35] F. Hund, Zeits. f. Physik, **33**, 855 (1925).

[36] Laporte and Sommerfeld, *Ibid.*, **40**, 333 (1926).

4. Paramagnetism of Molecules

Diatomic molecules will first be treated. Hund[37] has emphasized that in such molecules we must distinguish between two kinds of coupling of the spin axis relative to the rest of the molecule, which he disignates as types (a) and (b). In (a) the energy of interaction between the spin and orbital angular momentum is large compared to that between the spin and the angular momentum due to rotation of the molecule as a whole, and consequently the spin axis is firmly quantized relative to the "axis of figure" which connects the two nuclei. In (b) the reaction between the spin and the molecular rotation is the more important; the spin axis then no longer makes a fixed angle with the axis of figure, and instead the spin angular momentum vector and the remaining (or orbital+rotational) angular momentum of the molecule are quantized relative to each other to form a resultant represented by the quantum number j. In either (a) or (b) the component of the orbital angular momentum $\boldsymbol{P}_k$ which is parallel to the axis of figure equals $\sigma_k h/2\pi$, where σ_k is an integer. The perpendicular component of $\boldsymbol{P}_k$ will generally belong entirely to the high frequency category, for the effect of the value of σ_k (unlike σ_s below) on the energy is very considerable, or, interpreted kinematically, the vector $\boldsymbol{P}_k$ precesses rapidly about the axis of figure. This ineffectiveness of the perpendicular component is perhaps the main distinction from the atomic case, and is exemplified by the fact that terms in band spectra are classified as of the $S, P, D, F, \cdots$, type according as $\sigma_k = 0, 1, 2, 3, \cdots$, rather than on the basis of the value of k. Thus in (22) we must identify μ_k^2, the square of the low frequency part of the orbital moment, with the square $\sigma_k^2\beta^2$ of the component of this moment parallel to the axis of figure. At first thought it may appear as though $\sigma_k(\sigma_k+1)$ should enter in place of σ_k^2, as it so often does in quantum mechanics, but the square under consideration is one of a component rather than of the entire magnitude of a vector, and so can have the same value $\sigma_k^2\beta^2$ as in the old quantum theory. (In the hydrogen atom, for instance, the square of the z-component of angular momentum is $r^2h^2/4\pi^2$, not $r(r+1)h^2/4\pi^2$, where r is the magnetic quantum number.) That our value of the square is correct, can of course, also be verified by writing down the matrix elements[38] representing the x, y, z projections of this component, and then actually calculating the square.

Case (a). In (a) the component of spin angular momentum parallel to the axis of figure is $\sigma_s h/2\pi$, where σ_s is a half or whole integer according as the multiplicity is even or odd. A multiplet is generated by giving σ_s different

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[37] F. Hund, Zeits. f. Physik, **36,** 657 (1926); **42,** 93 (1927).

[38] These matrix elements are those of the symmetrical top and have been given by Dennison (Phys. Rev. **28,** 318, 1926); Kronig and Rabi (Ibid. **29,** 262, 1927) and Rademacher and Reiche (Zeits. f. Physik, **41,** 453, 1927). They are, of course, the equivalent of the Hönl-London intensity formulas. In applying these matrices to our problem, it is, of course, necessary to determine the constant factors in accordance with a magnitude $\sigma_k h/2\pi$ parallel to the axis of figure, as in Condon's (Phys. Rev. **30,** 781, 1927) work on the Zeeman effect. This means, for instance, taking $a_j = b_j = 0$, $c_j = \sigma_k\beta$ in Dennison's paper.

values ranging from $-s$ to $+s$. As with atoms, the susceptibility will be different according as the intervals in such a multiplet are small or large relative to kT. In the former event the matrix elements of the spin moment vector will be entirely of the low frequency type, for the only motion of the spin vector relative to the figure axis is a precession about the axis of figure, whose frequency is identified with the multiplet intervals. Therefore there is no distinction between M_s^2 and μ_s^2, permitting us to calculate μ_s^2 from (20) and (21). Furthermore the statistical average of the product $\boldsymbol{\mu}_s\cdot\boldsymbol{\mu}_k$ is zero, for with narrow multiplets we may neglect the temperature factor, so that components in which the sign of σ_s is the same as or opposite to that of σ_k have the same weight. Thus by (13) and (22) the susceptibility now becomes neglecting the small term (15)

$$\chi=N[4s(s+1)+\sigma_k^2]\beta^2/3kT. \tag{27}$$

In the alternative event that the multiplet intervals in case (a) are large compared to kT, the quantum number σ_s assumes in the normal state only the one value which gives the lowest energy. The matrix elements representing the component of the spin moment vector perpendicular to the axis of figure belong to the "high frequency" type, for they represent transitions $\Delta\sigma_s=\pm 1$ to other multiplet components which must now be classed as excited states. Thus only the parallel component of the spin moment is effective, and so μ_s^2 is given by an expression $4\sigma_s^2\beta^2$ analogous to that for μ_k^2. Furthermore $\boldsymbol{\mu}_s\cdot\boldsymbol{\mu}_k=\boldsymbol{\mu}_k\cdot\boldsymbol{\mu}_s$ is now simply $2\sigma_k\sigma_s\beta^2$, and so we have

$$\chi=N(2\sigma_s+\sigma_k)^2\beta^2/3kT, \tag{28}$$

as is also obvious from the fact that now the low frequency part of M is the component $(2\sigma_s+\sigma_k)\beta$ parallel to the figure axis.

Case (b). In Hund's (b) coupling, the matrix elements of the spin moment are clearly all of the low frequency kind, for case (b) arises only when the spin multiplets are narrow compared to the spacing between the different rotational energy levels, and it has already been shown in part II, pp. 34 and 46–49, that the latter intervals can be considered small relative to kT. Further the statistical average of the product $\boldsymbol{\mu}_s\cdot\boldsymbol{\mu}_k$ is zero, as follows by the spectroscopic stability relation indicated in note 31 or as can also be seen by averaging the expression for this product in case (b) to be given by E. Hill and the writer in a later paper. Consequently the susceptibility is given by (27), the same formulas as for case (a) when in (a) the multiplets are small compared to kT. Formula (27) will likewise hold for types of coupling intermediate between (a) and (b), where the rotational and multiplet energy intervals are comparable, as (27) demands only that the spin moment contain no high frequency elements. This is just another example of the invariance of the susceptibility of the mode of quantization, so long as the magnitudes of frequencies relative to kT are unaltered. As a matter of fact, case (b) is most often encountered only when $\sigma_k=0$, as usually a value of σ_k different from zero will give sufficient interaction between orbital and spin moment to yield the firmer coupling (a).[39]

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[39] Cases, however, are known in which there is approximately (b) type coupling even with $\sigma_k=1$. Cf. Mulliken, Phys. Rev. **30**, 785 (1927).

Paramagnetism of O_2. The two common paramagnetic gases are O_2 and NO. There is at present no definite spectroscopic evidence on the proper term assignment to the normal state of the oxygen molecule, so that all that can be done is to see what assignments will explain the observed magnetism. This is nicely accounted for by supposing the normal state of O_2 to be closely spaced ^3S levels, for substitution of the values $s=1$, $\sigma_k=0$ in (27) yields a volume susceptibility $.142\times10^{-6}$ at 20°C and 76 cm pressure. Bauer and Piccard's[40] experimental value is $.1434\times10^{-6}$, while Wills and Hector find[41] $.1447\times10^{-6}$. We have here applied the formula (27) appropriate to narrow multiplets which is, of course, legitimate on account of the weak interaction between the spin and the rest of the molecule in ^3S states. The odd multiplicity demanded by ^3S states is reasonable since O_2 contains an even number of molecules. Usually, to be sure, the singlets have lower energies than the triplets, and so the expectation for the normal state would be a diamagnetic ^1S term, but an unusual assignment is not surprising inasmuch as the paramagnetism of the oxygen molecule is itself extraordinary. It is, in fact, the only known paramagnetic molecule with an even number of electrons, whereas paramagnetism is the usual rule for molecules with an odd number of electrons.[42]

The suggestion of ^3S terms for the normal state of the oxygen molecule is by no means new, for Sommerfeld,[32] Stoner,[43] and others have called attention to the fact that its susceptibility is the same as that of an atom in a ^3S state. The same susceptibility is obtained whether we set $s=1$, $k=0$ in (23) or $s=1$, $\sigma_k=0$ in (27), for the atomic and molecular formulas (23) and (27) are the same for S states, and these only. However, there does not appear to have previously been any adequate theoretical justification as to why the atomic formula could apply to a non-monatomic molecule unless we supposed the electronic angular momentum so loosely oriented to the rest of the molecule that it is quantized relative to the direction of any applied magnetic field of ordinary magnitude, so that its component in this direction is an integral or half-integral multiple of $h/2\pi$, as in the atomic case. Such a supposition would be entirely incomprehensible if the electronic angular momentum were orbital in character, but after the advent of the spin electron it is known that electronic angular momentum in S states is due to internal spins of the electron, and is there so loosely coupled to the rest of the molecule that it is by no means impossible that a magnetic field might be strong enough to uncouple the spin axis from the rest of the molecule. The wide Zeeman separations found by Watson and Perkins[44] and others in the band spectra of certain metallic hydrides are strongly suggestive of this condition. If the width of the oxygen multiplets were known we could, of

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[40] Bauer and Piccard, J. de Physique, **1,** 97 (1920).

[41] Wills and Hector, Phys. Rev. **23,** 209 (1924).

[42] N. W. Taylor, J. Amer. Chem. Soc. **48,** 854 (1926); Taylor and G. N. Lewis, Proc. Nat. Acad. **11,** 456 (1925).

[43] E. C. Stoner, Phil. Mag. **3,** 336 (1927); also "Magnetism and Atomic Structure."

[44] W. W. Watson and B. Perkins, Jr., Phys. Rev. **30,** 592 (1927) and references.

course, immediately determine how large a field would be required to produce a Paschen-Back effect on the quantization. Hund mentions that the multiplet intervals found by Fassbender[45] in the *S* states of N_2^+ are of the order .01 cm^{-1}. If the O_2 fine structure were of this magnitude a field of about 1,000 Gauss would be necessary, as the normal Lorentz Zeeman separation is $.472 \times 10^{-4}$ cm^{-1}. Such a field is lower than that used in most susceptibility measurements. The feature of the theory in the present paper, however, is that it shows that the susceptibility is the same whether there is coupling of Hund's type (b) or whether the field is strong enough to break down such coupling, and so the preceding speculations as to what field strength is required to produce a Paschen-Back effect are unnecessary.

Polyatomic molecules. When the molecule contains more than two atoms, there is in general no axis of figure about which any component of electronic angular momentum remains constant. Consequently we cannot at present assign any definite amount of orbital angular momentum to the low frequency category, and it is quite conceivable that there is so little symmetry in the forces on the electron that the orbital contribution is entirely of the ineffective, high frequency type. If this is the case, or if the molecule is in something corresponding to an *S* state, the energy of interaction of the spin axis with the rest of the molecule will presumably be small compared to kT, and then we will still have at least approximately $\mu_s^2 = 4s(s+1)\beta^2$. The susceptibility will then be $\chi = 4Ns(s+1)\beta^2/3kT + N\alpha$. This accords nicely with the susceptibility $.0557 \times 10^{-6}$ found experimentally by Taylor[42] for ClO_2 at 20°C and 76 cm, for the value calculated from this formula if we set $s = \frac{1}{2}$ and neglect $N\alpha$ is $.0534 \times 10^{-6}$. The discrepancy is no greater than Taylor's estimate of the experimental error as about 5 per cent. The assumption $s = \frac{1}{2}$ means a doublet system, and is, of course, reasonable since ClO_2 contains an odd number of electrons. In contrast to ClO_2 the low susceptibility $.009 \times 10^{-6}$ observed by Soné[46] for the triatomic molecule NO_2 is not explained by assuming a formula like that for an *S*-term in a diatomic molecule. The low paramagnetism found for NO_2 as compared to most other paramagnetic gases including NO, suggests that sometimes, though not in ClO_2, the asymmetric structure of triatomic molecules causes rapid fluctuations even in the spin angular momentum, which make this considerably less effective than in diatomic molecules.

5. PARAMAGNETISM OF NITRIC OXIDE

Nitric oxide gas provides the most striking confirmation[47] of our entire theory, both because the NO band spectrum furnishes unambiguous term assignments, and because the doublet width is of such magnitude as to test quantitatively the finer points of the theory. Various attempts have been made to explain the susceptibility of NO on a quantum basis. The best

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[45] M. Fassbender, Zeits. f. Physik, **30,** 73 (1924).

[46] T. Soné, Tohoku Univ. Sci. Reports, **11** (3), 139 (1922).

[47] A brief account of this part of the paper has been given by the writer in Nature, May 9, 1927; also presented at the Feb. 1927 meeting of the American Physical Society.

known of these is perhaps Pauli's early work,[48] now renounced by Pauli himself.[49] Sommerfeld[32] and Stoner[43] suggest the possibility that the normal states of NO are ^2S terms as this gives a susceptibility within about 15 per cent of the experimental value, a mediocre agreement. All these attempts lack adequate theoretical foundation both as regards the type of quantization and the assignment of term values, but this is only natural since both the Hund theory of molecular quantization and the quantum analysis of the NO spectrum are subsequent developments. The systematization of the NO band spectrum by Birge, Mulliken, Miss Guillery, and Jenkins, Barton, and Mulliken[50] has recently shown that the normal state of the NO molecule is a doublet P level. The doublet is "regular"; i.e., the P_1 component ($\sigma_s = -\frac{1}{2}$) has a lower energy than the $P_2(\sigma_s = +\frac{1}{2})$, but the spectroscopic data on this particular feature were not available when the writer made his susceptibility calculations which led him to conclude independently that the order was regular. Upper and lower limits to the susceptibility, corresponding to doublet widths very narrow and very wide relative to kT, can now immediately be obtained by substituting respectively $s=\frac{1}{2}$, $\sigma_k = 1$ in (27) and $\sigma_s = -\frac{1}{2}$, $\sigma_k = 1$ in (28). The upper limit would apply were the temperature so high as to give equal concentrations of molecules in the P_1 and P_2 states; it gives a Curie constant corresponding to two Bohr magnetons, and yields a volume susceptibility $.071 \times 10^{-6}$ at 20°C, 76 cm. The lower limit, on the other hand is zero, for in the lower or P_1 state, where all the molecules are concentrated at $T=0$, the components of spin and orbital moment parallel to the axis of figure are equal and opposite. The actual susceptibility observed by Bauer and Piccard[40] is $.0609 \times 10^{-6}$ and by Soné[46] is $.0610 \times 10^{-6}$, and so is much closer to the upper than the lower limit, but nevertheless intermediate between the two. The reason for this is not hard to discover, for the spectroscopists find that the doublet interval between the two P components is 120.9 cm^{-1}[51]. Now expressed in wave numbers, kT equals $.70T$, and so this interval is about $.6kT$ at ordinary temperatures. Consequently it is necessary to carry through a special calculation in which the energy intervals are allowed to be comparable with kT, thus introducing what we might call "medium frequency terms," which we have not admitted previously. The details of this computation are given below, but we will state

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[48] W. Pauli, Jr., Phys. Zeits. **21,** 615 (1920).

[49] W. Pauli, Jr., Handbuch der Physik, Band **23,** p. 274.

[50] The interpretation of the normal states of *NO* as doublet *P* levels appears to have been reached more or less independently by Mulliken and by Birge (Nature, Feb. 27, 1926) in connection with Baldet's analysis of the comet-tail bands (Comptes Rendus, **180,** 820, 1925) which indicated the existence of doublets. The evidence for this view has, however, been greatly strengthened by the extensive recent measurements of Miss Guillery (Zeits. f. Physik, **42,** 121, 1927) and of Jenkins, Barton and Mulliken (Phys. Rev. **30,** 150, 1927) on the γ and β bands respectively of *NO*.

[51] We take the doublet interval as 120.9 cm^{-1} rather than the value 124.4 quoted by Jenkins, Mulliken, and Barton, as for our purposes it is better to use energy differences which are inclusive rather than exclusive of the term $-B\sigma^2$ representing the part of the rotational energy independent of j. It makes little difference which value is used, as (34) shows that the corresponding change in the effective number of Bohr magnetons is only $\frac{1}{2}$ percent.

in advance that it gives a susceptibility $.0600 \times 10^{-6}$ at 20°C, 76 cm, agreeing with the experimental value to within 1.5 per cent, or less than the experimental error. This removes the apparent contradiction between band spectrum theory and magnetism encountered by Stoner,[43] who to explain the susceptibility even proposed an electron orbit as freely oriented in the NO molecule as in an atom. The calculation shows that there is a very vital contribution to the susceptibility from the component of spin moment perpendicular to the axis of figure, for a doublet interval comparable with kT means that this component is partially effective, as it precesses about this axis with a frequency of the order kT/h. If one overlooked the perpendicular component (as the writer naively did when he first began the work) the computed susceptibility would be too small, even if the doublet were supposed "inverted" so that the state with the higher moment parallel to the axis of figure had the lower energy.

Details of calculation. We must now go back to section 3, part I, and modify the work to admit energy intervals comparable with kT. The absorption frequencies of NO are so high that we may neglect the contribution of the "high frequency" elements of the moment matrix which correspond to transitions in the electronic quantum numbers, and which represent the part of the orbital moment perpendicular to the figure axis. If at the same time we discard the small diamagnetic term, this is equivalent to omitting the part (15) of the susceptibility. We may thus drop the index n used in part I, and the elements in which we are interested may be characterized by a set of indices σjm, where j is the rotational quantum number of the molecule, m is the magnetic quantum number specifying the component of j parallel to the field, and σ is the quantum number $\sigma = \sigma_k + \sigma_s = 1 \pm \frac{1}{2}$ proportional to to the total angular momentum parallel to the axis of figure. Elements in which $\sigma \neq \sigma'$ will be of the "medium frequency" type, while those in which $\sigma = \sigma'$ but in which j may change will be of the low frequency catagory. The analysis on pp. 733–737 of part I including simplification of the low frequency elements, is now applicable if we substitute the index σ for n, (in other words introduce "medium" for "high frequency" terms), and provided we introduce the two following modifications: 1) the abbreviated notation $\mu(jm; j'm')$ can no longer be used for $M(\sigma jm; \sigma j'm')$ as there are two values of σ, and 2) the summation must include σ in addition to j,m, since there is an appreciable concentration of molecules in both the P_1 and P_2 states.[52] Thus Eq. (12) of

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[52] The assumption at the top of p. 737, part I, that $\nu(\sigma jm; \sigma' j' m')$ can be replaced by a value $\nu(\sigma; \sigma')$ independent of j, m, however, calls for some comment, as it is not strictly valid. For one thing the values of j are different in the initial and final states but as j cannot change by more than one unit this does not cause difficulty as then the approximation is good if merely the rotational energy intervals rather than the rotational energies themselves be small compared to the doublet width (cf. note 26, part I). A more important fact is the circumstance that if spectral terms be represented by the customary formula $A + Bj(j+1)$, the constant B, which is inversely proportional to the apparent moment of inertia, has slightly different values in the P_1 and P_2 states. The theoretical reason is the rotational distortion of spin doublets (E. C. Kemble, Phys. Rev. **30**, 387, 1927). The data of Jenkins, Barton, and Mulliken shows that the difference of the B values is .049 cm^{-1}. By the classical equipartitution

part I now becomes

$$\chi=(B/3kT)\textstyle\sum_{\sigma,j,m,j',m'}\left|M(\sigma jm\,;\,\sigma j'm')\right|^2 e^{-W(\sigma j)/kT} \tag{29}$$
$$-\frac{2B}{3h}\sum_{\sigma,j,m,\sigma',j',m'(\sigma'\neq\sigma)}\frac{\left|M(\sigma jm\,;\,\sigma'j'm')\right|^2}{\nu(\sigma\,;\sigma')}e^{-W(\sigma j)/kT},$$

with the abbreviation (cf. Eq. 6, part I)

$$B=N\Big/\sum_{\sigma,j,m}e^{-W(\sigma j)/kT}. \tag{30}$$

The summation over σ, of course, embraces only the two values 1/2 and 3/2.

Now elements of the form involved in the first line of (29) arise from the component of moment which is parallel to the axis of figure, while those in the second line are to be ascribed to represent the component which is perpendicular to this axis. This can be seen by inspection of the familiar matrix formulas for the symmetrical top, and is also obvious from the fact that changes in the value of σ are identified kinematically with precessions about the axis of figure, and so will appear in the perpendicular but not the parallel component. Hence we have

$$\sum_{j'm'}\left|M(\sigma jm\,;\,\sigma j'm')\right|^2=M_{par}{}^2=(\sigma_k+2\sigma_s)^2\beta^2=(1\pm 1)^2\beta^2 \tag{31}$$

since by the foregoing and by the rules for matrix multiplication the sum in (31) is the square of the component of combined orbital and spin moment parallel to the axis of figure. Similarly

$$\sum_{\sigma'j'm'(\sigma'\neq\sigma)}\left|M(\sigma jm\,;\,\sigma'j'm')\right|=M_{perp}{}^2=4(s+s^2-\sigma_s{}^2)\beta^2=2\beta^2, \tag{32}$$

where $M_{\mathrm{perp}}{}^2$ is the square of the component of purely spin moment perpendicular to the axis of figure, for we have already mentioned that the perpendicular orbital component is of the discarded, high frequency type. The value of $M_{\mathrm{perp}}{}^2$ is that given in (32) since the square $4s(s+1)\beta^2$ of the total spin magnetic moment is equal to the sum of the squares of the perpendicular and parallel components, and since the square of the parallel spin component is $4\sigma_s{}^2\beta^2$. These results would not be true if any part of the spin moment were of the discarded, high frequency type, but actually the

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theorem the average value of the rotational energy $Bj(j+1)$ is approximately kT. As B is about 1.7, the effect of the different B values is to make the average value of $\nu(3/2\,jm;\,\frac{1}{2}\,jm)$ exceed $\Delta\nu$ by about 5 percent. Eq. (33) shows that change of x in (34) by 5 percent alters the susceptibility only about 1 percent. This is, of course, only a crude estimate of the order of magnitude of the error. An accurate calculation would have to use the amplitudes inclusive of rotational distortion to be given by E. Hill and the writer in a later paper, rather than the ideal symmetrical top matrices. Such a computation would be laborious and give only a minor correction.

We may mention that at least the P_1 levels show the characteristic "σ-type doubling" or hyperfine structure of the band spectroscopists, but it seems clear that the effect of this on the susceptibility is negligible, as the width of this hyperfine structure is negligible, and as we showed in part I the susceptibility is invariant of the way degeneracy is removed.

motion of the spin axis is very closely that of a secular precession about the axis of figure without appreciable rapid nutations.

Now $\nu(\sigma;\sigma')$ equals $\Delta\nu$ if $\sigma=\frac{3}{2}$, $\sigma'=\frac{1}{2}$, while $\nu(\frac{1}{2};\frac{3}{2})$ equals $-\Delta\nu$ where $\Delta\nu$ is an abbreviation for the frequency difference 120.9 cm^{-1} of the two doublet components. Also we may set $W(\frac{3}{2}, j)=W(\frac{1}{2}, j)+h\Delta\nu$ as $\nu(\frac{3}{2}jm;\frac{1}{2}jm)$ is approximately $\Delta\nu$. Since furthermore the expressions (31) and (32) have values invariant of j, m, the sum $\sum_{j,m}e^{-W(1/2,j)/kT}$ is thus by (30) a common factor which can be cancelled from numerator and denominator of (29). Using these simplifications and substituting (30–32) in (29) we get the final formula

$$\chi=N\theta^2/3kT, \tag{33}$$

with

$$\theta^2=4\beta^2(1-e^{-x}+xe^{-x})/(x+xe^{-x}), \qquad x=h\Delta\nu/kT=173.2/T. \tag{34}$$

Deviations from Curie's law. Eq. (34) shows that θ will not be a constant independent of T as it would according to Curie's law. Because of the formal similarity of (33) with (13) we may term θ/β the apparent number of Bohr magnetons. The variation of this expression with T predicted by (34) is shown in the following table:

Apparent Bohr magneton number θ/β as a function of absolute temperature

T	0	50	100	175	250	293	350	500	1000	∞
θ/β	0	1.098	1.489	1.713	1.806	1.836	1.864	1.908	1.954	2.000

It is seen that at room temperatures the apparent number of Bohr magnetons varies but slightly with T, so that the departures from Curies Law are not great and so may be difficult to measure. The only reliable experimental data are Bauer and Piccard's[40] and Soné's[46] value 1.85 at $T=293$, which we have already quoted as agreeing well with the theory. Curie's law has been verified to be nearly applicable to oxygen even down to liquefaction,[53] which is not surprising since the multiplet structure in S states is exceedingly fine. If the susceptibility of NO had been measured over anything like the large temperature range that it has for 0_2 the departures from Curie's law should certainly come to light. It would be most interesting if experimental data could be obtained on this.

The writer wishes to thank Professor Kronig for correspondence on diamagnetism, and Professors Mulliken and Birge for data on the NO band spectrum.

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February 1, 1928.

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[53] Onnes, "Atoms et Electrons" (Paris, 1923), p. 144.