

Theory of the Microwave Zeeman Effect in Atomic Oxygen

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Slight deviations of the coefficient of the linear Zeeman term from the elementary Landé value arise from the following effects: (a) small departures from Russell-Saunders (R-S) coupling, (b) the motion of the nucleus, (c) relativity corrections, (d) interplay between the magnetic field and various kinds of magnetic interactions within the atom, and (e) the Schwinger electro-dynamical corrections. In the present paper an effort is made to estimate the magnitude of the effects (a), (b), (c), (d) with the goal of examining whether the residual discrepancy between Rawson and Beringer's measurements on oxygen and the ideal Landé value is in accord with Schwinger's formula for (e).

The effect (d) may be further divided into modulation by the magnetic field, or Larmor precession, of (d_1) ordinary spin-orbit, (d_2) spin-other-orbit, and (d_3) orbit-orbit interaction. The theory for c and d_1 has already been developed by Margenau and Breit, and d_2 to a certain extent by Lamb, while that for b was first

given by Phillips. The corrections (d) can in each case be obtained by substituting $\mathbf{p}+e\mathbf{A}/c$ for \mathbf{p} in the corresponding magnetic interaction terms in the Pauli two-component Hamiltonian function, but can also be derived more fundamentally from the four-component Dirac equation. From the standpoint of the Dirac equation, the segregation of (c) from other magnetic effects is rather artificial, but (c) has the simple physical interpretation that it is tantamount to substituting the transverse mass for the rest mass in the ordinary Zeeman energy.

The numerical estimate of effects (b)-(d) requires knowing the wave functions in some detail. Certain rather crude approximations are made in the present paper, including omission of exchange terms in some places. However, the agreement between the calculated and observed Zeeman coefficients after all the corrections (a-e) are included is gratifying.

INTRODUCTION

BY using quantum electrodynamics, Schwinger¹ has shown that the gyromagnetic ratio g_s of the electronic spin is $g_s=2(1+\alpha/2\pi)$, where α is the fine structure constant, rather than exactly 2, as prescribed by the one-particle Dirac theory. A higher-order approximation calculated by Karplus and Kroll² gives for g_s the value

$$g_s=2\left(1+\frac{\alpha}{2\pi}-2.973\frac{\alpha^2}{\pi^2}\right)\approx 2\times 1.001145. \quad (1)$$

These theoretical results have stimulated several very accurate measurements³ of atomic gyromagnetic ratios or Landé factors, with microwave or molecular beam techniques to measure the Zeeman splittings of an atomic multiplet in an applied magnetic field.

From the observed values of these Landé factors one should be able in principle to deduce g_s by a straightforward calculation if the type of vector coupling prevailing in the atom is known. In practice this problem is complicated by the necessity of applying to the value of g_s obtained in this way a certain number of corrections, which take into account relativistic and diamagnetic effects, the departures from a simple vector coupling scheme, etc. The only cases considered so far have been those of a single electron outside of closed shells. The recent measurement by Rawson and Beringer⁴ of the microwave Zeeman effect in atomic oxygen, which has four $2p$ electrons outside of closed shells, requires a more comprehensive treatment. The present article constitutes an attempt at such a treatment.

¹ J. Schwinger, *Phys. Rev.* **73**, 416 (1947).

² R. Karplus and N. M. Kroll, *Phys. Rev.* **77**, 536 (1950).

³ P. Kusch and A. M. Foley, *Phys. Rev.* **74**, 250 (1948); Koenig, Prodell, and Kusch, *Phys. Rev.* **88**, 191 (1952).

⁴ E. B. Rawson and R. Beringer, *Phys. Rev.* **88**, 677 (1952).

THE MICROWAVE ZEEMAN EFFECT IN ATOMIC OXYGEN

The ground state of atomic oxygen is $2p^4$. Russell-Saunders coupling is known to predominate in oxygen. From the configuration $2p^4$ the spectral terms 3P , 1D , 1S can be constructed. The two singlets 1D , 1S are, respectively, 15 867.7 and 33 792.4 wave numbers above the ground multiplet 3P_2 . The levels 3P_1 and 3P_0 are separated from 3P_2 by 158.5 and 226.5 wave numbers, respectively.

An applied magnetic field splits 3P_1 and 3P_2 into 3 and 5 magnetic sublevels, respectively. Rawson and Beringer have been able to measure the energies of the transitions a , b , c , d , e , f depicted in Fig. 1, or rather the magnetic fields at which resonances occur for a fixed oscillator frequency ν . These fields H_a, H_b, \dots, H_f were measured in relative magnitude by the frequencies f_a, f_b , etc. of the proton resonance in these fields. An absolute calibration could be made from the known value of the proton moment in Bohr magnetons, $g_p/2$.

The fields used are not infinitely small and incipient Paschen-Back effect due to the off-diagonal matrix

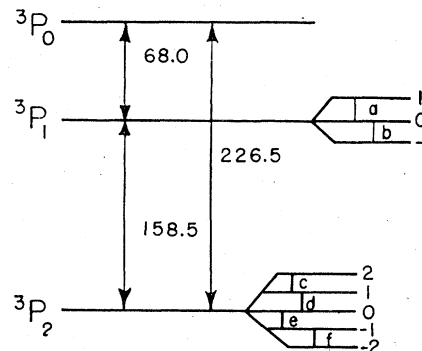


FIG. 1. Energy levels of atomic oxygen in a magnetic field.

elements of the Zeeman Hamiltonian between the different multiplets 3P_2 , 3P_1 , 3P_0 cannot be disregarded. Solving the secular equations, we find that the fields H_a , H_b , etc., are given by the following approximate equations:

$$h\nu = g_1\beta H_a + C_1 H_a^2 = g_1\beta H_b - C_1 H_b^2, \quad (2)$$

$$h\nu = g_2\beta H_c + C_2 H_c^2 = g_2\beta H_f - C_2 H_f^2, \quad (3)$$

$$h\nu = g_2\beta H_d + C_3 H_d^2 = g_2\beta H_e - C_3 H_e^2. \quad (4)$$

In these formulas β is the Bohr magneton; g_1 and g_2 the Landé factors of the multiplets 3P_1 and 3P_2 ; C_1 , C_2 , and C_3 are constants which depend on the distances between the different 3P multiplets.

These formulas are very good approximations, for it is easily shown that terms of the third order in H are missing if Russell-Saunders coupling is assumed in the calculation of off-diagonal matrix elements, and fourth-order terms are completely negligible (smaller than one part in a million of the linear terms).

These equations have to be supplemented by the proton resonance conditions:

$$g_p\beta H_a = hf_a; \quad g_p\beta H_b = hf_b, \quad \text{etc.} \quad (5)$$

From (2) and (5) we get

$$g_1 = g_p \frac{\nu}{f_a} \left(\frac{1 + f_a^2/f_b^2}{1 + f_a/f_b} \right). \quad (6)$$

In the same way from (3), (4), and (5), two independent values are obtained for g_2 .

It is important to notice that in (6) the Paschen-Back quadratic corrections have been eliminated experimentally rather than calculated. We can, however, calculate them by second-order perturbation theory from the known multiplet splittings. It is best to express them in terms of differences $H_a - H_b$, $H_c - H_f$, $H_d - H_e$, as is done in Table I. We see that the assumption of Russell-Saunders coupling for the calculation of the off-diagonal matrix elements works very well. (A calculation by Rawson and Beringer⁴ giving 17.2 gauss for $H_b - H_a$ and indicating a very strong departure from R-S coupling was the result of an arithmetical error.)

Two other points can be made with respect to terms quadratic in H : (a) it follows from the agreement between the two columns of Table I that all other corrective terms in H^2 , such as the quadratic diamagnetic corrections, must be small; (b) even if they were not small, all those corrections would be eliminated by the experimental procedure as far as determination of g_1 and g_2 are concerned.

Only corrections linear in H need to concern us.

The experimental results of Rawson and Beringer⁴ are

$$g_1 = 1.500971, \quad g_2 = 1.500905, \quad (7)$$

with an uncertainty of a few parts in a million.

TABLE I. Differences between the values of magnetic fields at resonance, due to second-order effects.

| | Measured | Calculated |
|-------------|-------------|------------|
| $H_b - H_a$ | 10.20 gauss | 10.22 |
| $H_d - H_e$ | 0.581 gauss | 0.580 |
| $H_f - H_c$ | 1.744 gauss | 1.742 |

On the other hand the theory for R-S coupling gives

$$g_1 = g_2 = \frac{1}{2}(g_l + g_s),$$

where g_l is the orbital gyromagnetic ratio. If we take g_l equal to unity and g_s as given by (1), we find

$$g_1 = g_2 = 1.501145. \quad (8)$$

The discrepancy between (7) and (8) is 174×10^{-6} for g_1 and 240×10^{-6} for g_2 , which is much larger than the experimental error. These are the discrepancies which have to be explained away through the different corrections previously mentioned.

The problem of calculating these corrections can be formulated in general terms as follows: According to first-order perturbation theory, we describe the linear change in the energy of an atom, induced by an applied field H , as the expectation value of a certain operator Z (for Zeeman) taken over the unperturbed wave function ψ . Errors can result either from an incorrect choice of ψ or an incorrect Z . In the approximate theory which gave (8), we took Z to be given by $\beta \mathbf{H} \cdot (\mathbf{L} + g_s \mathbf{S})$ and ψ to be an eigenstate of L and S . Neither of these assumptions is quite correct and we shall examine them in turn.

CORRECTIONS CAUSED BY DEPARTURE FROM R-S COUPLING (WRONG ψ)

Because of magnetic interactions involving the spin, *viz.* spin-orbit, spin-other-orbit, and spin-spin interactions, L and S are not perfectly good quantum numbers. (Magnetic orbit-orbit interactions, however, do not affect R-S coupling.) Several observations are in order at this juncture.

(a) In the case of the 3P_0 and 3P_2 terms, perturbations by, respectively, the states 1S and 1D also belonging to the configuration $2p^4$ can cause deviations from Russell-Saunders coupling even if configuration interaction is neglected. In the case of the 3P_1 term, however, this is not the case, and here it is customarily said⁵ that the departures from Russell-Saunders coupling are due to combination of magnetic (mainly spin-orbit) interactions and configuration coupling through electrostatic repulsion between electrons—for instance, a $(2p)^4 {}^3P$ term may through configuration interaction get an admixture of $(2p)^3 3p {}^3P'$, and if ${}^3P'$ is not a pure R-S state, neither will be 3P . It is, however, preferable to get the configuration interaction completely out of the picture by disregarding the central field approximation

⁵ See, for instance, M. Phillips, Phys. Rev. 88, 202 (1952).

from which the configuration coupling idea stems. Before spin-dependent terms are introduced L and S are good quantum numbers even though the "configuration quantum numbers" relating to individual electrons are not rigorous. For the ground state of oxygen, for instance, it is a very good approximation to say that it is 3P , a much poorer one to say that it is $(2p^4) {}^3P$. The ideal g value is impaired only insofar as spin-dependent magnetic terms blend states of different L , S and so cause slight deviations from Russell-Saunders coupling.

(b) When such a blending is included, the wave function of the atom instead of being $\psi(L, S, J)$ becomes of the form

$$\psi = [\psi_0(L, S, J) + \alpha\psi'(L', S', J)](1 + \alpha^2)^{-\frac{1}{2}}. \quad (9)$$

The admixture coefficient α will be of the order of magnitude $\mathfrak{M}/\Delta E$, where \mathfrak{M} represents the magnetic interactions (mainly spin-orbit) and ΔE is the distance between the different R-S terms mixed together. Since the Zeeman Hamiltonian $Z = \beta H(g_l L_z + g_s S_z)$ commutes with L and S , the expectation value $\langle Z \rangle = \langle \psi | Z | \psi \rangle$, where ψ is defined by (9), will differ from $\langle \psi_0 | Z | \psi_0 \rangle$ only through terms quadratic in α . The correction will thus be small.

(c) The departure from the interval rule should not be considered as a measure of the departure from R-S coupling. In oxygen the ratio $({}^3P_2 - {}^3P_1)/({}^3P_1 - {}^3P_0)$ has the value $158.5/68 = 2.33$ instead of 2 exactly as required by Landé's rule. But as shown by Aller, Ufford, and Van Vleck⁶ this is due mainly to the fact that the magnetic interactions which produce the Zeeman splittings are not only the spin-orbit coupling but also the spin-other-orbit and spin-spin couplings. The first-order contributions of the latter two to the intervals have no reason to, and in fact do not obey Landé's rule. The difference between 2.33 and 2.00 is in no way a measure of the admixture α from wave functions with different L and S .

The term most likely to cause any perturbation in oxygen is 1D_2 perturbing 3P_2 . If we call ξ the spin-orbit coupling coefficient of a $2p$ electron, the main part of the admixture α of 1D_2 in 3P_2 is

$$\alpha = (2)^{-\frac{1}{2}} \xi / (E_D - E_P).$$

For the state $\psi = ({}^3P_2 + \alpha {}^1D_2)(1 + \alpha^2)^{-\frac{1}{2}}$, $J_z = 2$, we find:

$$\begin{aligned} 2g_2 &= \langle \psi | g_l L_z + g_s S_z | \psi \rangle = (1 + \alpha^2)^{-1} (g_l + g_s + 2\alpha^2 g_l) \\ &\simeq g_l + g_s - \alpha^2 (g_s - g_l), \\ g_2 &\simeq \frac{1}{2} (g_l + g_s) - \frac{1}{2} \alpha^2. \end{aligned}$$

This gives a correction $\Delta g_2 = -\frac{1}{2} \alpha^2$ to the value (8). If we take $\zeta = 146.6$ (Garstang),⁷ $E_D - E_P = 15\,800 \text{ cm}^{-1}$, we find

$$\Delta g_2 \simeq -21 \times 10^{-6}. \quad (10)$$

All other excited states in atomic oxygen which might

be coupled to 3P_1 or 3P_2 through magnetic interactions, belong to different configurations (this expression has to be taken with certain reservations; the configuration is a much worse quantum number in oxygen than L or S) and are about 10^5 wave numbers away from 3P . The nearest is $2s^2 2p^3 ({}^4S) 3p {}^5P$, which is 86 600 wave numbers above 3P . Although we do not know the magnitude of the matrix element of the magnetic interaction between 3P_1 and $3p {}^5P_1$, there seems to be no good reason why it should be significantly larger than the one between 3P_1 and 1D_1 (the opposite is much more likely); and, the energy difference $3p {}^5P_1 - {}^3P_1$ being about 6 times larger than ${}^1D_1 - {}^3P_1$, we shall expect the corresponding correction for g_1 to be smaller than 10^{-6} and disregard it.

CORRECTION TO THE ORBITAL GYROMAGNETIC RATIO CAUSED BY MOTION OF NUCLEUS

Because the nucleus has a finite rather than infinite mass, the orbital gyromagnetic ratio is not exactly unity. The general theory of the effect of the motion of the nucleus on the orbital g factor has been developed by Phillips.⁸ We must make the application to the particular case of oxygen, which is somewhat more complicated than the explicit examples treated in her paper. The theory developed on the first page of her article shows that the orbital gyromagnetic factor for a neutral atom is, in general,

$$g_L = \left(1 - \frac{m}{M}\right) - \frac{m}{ML_z} \langle \Phi | B_z | \Phi \rangle, \quad (11)$$

where M is the mass of the nucleus, and Φ is the wave function of the atom, inclusive of spin but exclusive of the trivial factor which depends only on the coordinates of the center of gravity and which represents a uniform translational motion of the whole atom. B_z is the z component of the vector

$$\mathbf{B} = \sum_{i < j} \mathbf{b}_{ij}, \quad (12)$$

with

$$\mathbf{b}_{ij} = \hbar^{-1} [\mathbf{r}_i \times \mathbf{p}_j + \mathbf{r}_j \times \mathbf{p}_i].$$

The quantity B_z is readily shown to be proportional in R-S coupling to the component L_z of orbital angular momentum in the direction of the applied field, and so the g factor given in (11) is independent of how the atom is oriented, as must be the case if the expression is meaningful.

In Russell-Saunders coupling the total spin S is a good quantum number and we can assume Φ to be also an eigenstate of S and S_z . We can expand Φ into a sum of Slater determinants $\Phi = \sum \alpha_p D_p$, where $D_p = (a_1, a_2, \dots, a_z)$ and the a_i are one-electron states (spin included);

$$\langle \Phi | \mathbf{B} | \Phi \rangle = \sum_{p, p'} \alpha_p^* \alpha_{p'} \langle D_p | \mathbf{B} | D_{p'} \rangle. \quad (13)$$

In order to facilitate the estimate of $\langle \Phi | \mathbf{B} | \Phi \rangle$, we make the restrictive assumption that all the occupied

⁸ M. Phillips, Phys. Rev. **76**, 1803 (1949).

⁶ Aller, Ufford, and Van Vleck, Astrophys. J. **109**, 42 (1949).

⁷ R. H. Garstang, Monthly Notices Roy. Astron. Soc. **111**, 115 (1951).

one-electron states outside of closed shells have the same parity. This is generally the case for atoms in their ground state.

It is then easy to show, by the application of the rules of calculation of Slater determinants, that because of parity and symmetry considerations, (12) reduces to

$$\langle \Phi | \mathbf{B} | \Phi \rangle_z = \sum |\alpha_p|^2 \langle D_p | \mathbf{B} | D_p \rangle_z, \quad (14)$$

and

$$\langle D_p | \mathbf{B} | D_p \rangle_z = - \sum_{i,j} \langle a_i(1) a_j(2) | \mathbf{b}_{12} | a_j(1) a_i(2) \rangle_z,$$

where a_i is an occupied one-electron state outside of closed shells and a_j is inside a closed shell and corresponds to the same spin as a_i . The existence of (14) is a consequence of the Pauli principle which establishes a correlation between electrons of the same spin.

If the expansion of the wave function in Slater determinants is known, the expression (13) can forthwith be evaluated.

We consider now the case of atomic oxygen with the electronic configuration $(2p)^4$, but all the formulas apply to the case of any atom having only s and p electrons in closed shells, and outside of closed shells p electrons only, that is, to any atom from lithium to fluorine and from aluminum to chlorine.

In that case it is easy to show that $\langle B \rangle_z / L_z$ is independent of the way in which the p electrons outside of the closed shells are coupled together (as long as it is Russell-Saunders coupling), and this quantity is given by

$$\langle B \rangle_z / L_z = - \sum_n \langle ns(1), p_+(2) | (b_{12})_z | p_+(2), ns(1) \rangle. \quad (15)$$

In (15), p_+ is the orbital state of a p electron with orbital momentum $l_z = +1$, ns is the orbital state of an s electron with principal quantum number n , and the summation is over occupied orbital s states, each orbital state being counted once only. If one uses the definition (12) of b_{ij} and the fact that for a nonrelativistic electron $\dot{p}_x = m\dot{v}_x = m\dot{x}$, the following alternative expressions can be given for (15):

$$\langle B \rangle_z / L_z = - (4/\hbar) \sum_n \langle ns | x | p_+ \rangle \langle p_+ | p_y | ns \rangle, \quad (16)$$

$$\langle B \rangle_z / L_z = - (2/\hbar) \sum_n \{ \langle p_+ | x | ns \rangle \langle ns | p_y | p_+ \rangle - \langle p_+ | y | ns \rangle \langle ns | p_x | p_+ \rangle \}, \quad (17)$$

$$\langle B \rangle_z / L_z = - i(4m/\hbar^2) \sum_n \langle ns | x | p_+ \rangle \times \langle p_+ | y | ns \rangle (E_p - E_{ns}). \quad (18)$$

In (18), E_p and E_{ns} are the total energies of the p and ns one-electron states, respectively.

If we call $f_n(r)$ and $g(r)$ the radial parts of the wave functions ns and p_+ , respectively, (16) becomes

$$\langle B \rangle_z / L_z = \frac{2}{3} \sum_n \int_0^\infty f_n(r) g(r) r^3 dr \times \int_0^\infty g(r) \frac{df_n}{dr} r^2 dr. \quad (19)$$

In the same way (18) yields

$$\langle B \rangle_z / L_z = - \frac{2}{3} \sum_n \left(\int_0^\infty f_n g r^3 dr \right)^2 (E_p - E_{ns}), \quad (20)$$

where distances and energies are measured in atomic units.

Since $E_p - E_{ns} > 0$, (20) shows that $\langle B \rangle_z / L_z$ is negative and therefore according to (11) the orbital gyromagnetic factor is larger than $1 - (m/M)$.

In order to estimate g_L numerically for oxygen, we have evaluated (19) by using Slater's⁹ analytical wave functions, and (20) by using Hartree's¹⁰ self-consistent wave functions for oxygen. In both cases it is found that the contribution of the $1s$ orbital is negligible compared with $2s$.

Slater functions and (19) lead to

$$\langle B \rangle_z / L_z = - \frac{5}{6},$$

$$g_L = 1 - \frac{m}{M} \left(1 - \frac{5}{6} \right) = 1 - \frac{m}{6M}.$$

The Hartree wave functions and (20) give $\int f_2 g r^3 dr = 1.15$ (by numerical integration or use of Lowdin's¹⁰ analytical representation) and $E_p - E_{2s} = 1.22$, thus leading to

$$\langle B \rangle_z / L_z = - \frac{2}{3} (1.16)^2 (1.22) = - 1.11.$$

Believing the Hartree functions to be a less crude approximation for this problem than the Slater wave functions, we henceforth use the formula:

$$g_L \approx 1 + 0.11(m/M) \text{ for oxygen.} \quad (21)$$

RELATIVISTIC AND DIAMAGNETIC CORRECTIONS

The general problem of the relativistic and diamagnetic corrections in a complex atom like oxygen is somewhat complicated, and it is instructive to review first the previous work on the subject.

Relativistic correction.—Breit¹¹ and Margenau,¹² both of Yale University, have calculated the magnetic moment of a Dirac electron in a central field $V(r)$ and derived the correction to be applied to the result of the nonrelativistic calculation which uses as a nonrelativistic Zeeman Hamiltonian:

$$Z_0 = \beta \mathbf{H} \cdot (\mathbf{I} + 2\mathbf{s}). \quad (22)$$

For brevity we shall refer to it as the Breit-Margenau or Yale correction. In these calculations the magnetic field is taken into account by replacing \mathbf{p} by $\mathbf{p} + e\mathbf{A}/c$ in the relativistic Dirac Hamiltonian,

$$\mathcal{H} = c(\mathbf{p} \cdot \boldsymbol{\alpha}) + \beta mc^2 + V.$$

⁹ J. C. Slater, Phys. Rev. **36**, 57 (1930).

¹⁰ Hartree, Hartree, and Swirles, Trans. Roy. Soc. (London) **A238**, 229 (1939); see also the empirical analytical representation of the Hartree results by P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

¹¹ G. Breit, Nature **122**, 649 (1928).

¹² H. Margenau, Phys. Rev. **57**, 383 (1940).

Here and elsewhere $\mathbf{A} = \frac{1}{2}(\mathbf{H} \times \mathbf{r})$ is the vector potential from which the magnetic field is derived.

The relativistic interaction between the electron and the external magnetic field is $Z = e(\boldsymbol{\alpha} \cdot \mathbf{A})$ and the expectation value $\langle Z \rangle$ of this expression gives the change in the energy of the electron produced by the applied field \mathbf{H} , and is thence a measure of the magnetic moment of the electron. In the case of slow electrons with kinetic energy much smaller than the rest mass, Margenau¹² gives the following expressions for the magnetic moment of the electron expressed in Bohr magnetons:

$$\begin{aligned} l = j - \frac{1}{2}, \quad \mu &= (j + \frac{1}{2}) \left[1 - \frac{2j+1}{j+1} \frac{\bar{T}}{2mc^2} \right], \\ l = j + \frac{1}{2}, \quad \mu &= \frac{j}{j+1} (j + \frac{1}{2}) \left[1 - \frac{2j+1}{j} \frac{\bar{T}}{2mc^2} \right], \end{aligned} \quad (23)$$

where \bar{T} is the average kinetic energy of the electron. Written in this form these formulas are not very suitable for an atom like oxygen where R-S coupling prevails. Also the physical nature of the Yale correction does not appear very clearly.

We recalculate this correction by using the well-known method of reduction of Dirac's equations to large components. In this method, a nonrelativistic operator Z' is derived such that its expectation value taken over the nonrelativistic wave function agrees with the relativistic expectation value $\langle Z \rangle$ within $\frac{1}{2}(v/c)^2$.

A straightforward calculation gives

$$Z' = \beta \mathbf{H} \cdot (\mathbf{1} + 2\mathbf{s}) \left(1 - \frac{T}{mc^2} \right) + \frac{\beta}{mc^2} \mathbf{s} \cdot (\nabla V \times \mathbf{A}). \quad (24)$$

Using integration by parts and Schrödinger's equation, one can show that the second term of (24) is equivalent to

$$-\beta \mathbf{H} \cdot \left\{ \frac{(\mathbf{r} \cdot \mathbf{s})}{r^2} \mathbf{r} - \mathbf{s} \right\} \frac{T}{mc^2},$$

and (24) can be rewritten as

$$Z' = \beta \mathbf{H} \cdot (\mathbf{1} + 2\mathbf{s}) \left(1 - \frac{T}{mc^2} \right) - \beta \mathbf{H} \cdot \left\{ \frac{(\mathbf{r} \cdot \mathbf{s}) \mathbf{r}}{r^2} - \mathbf{s} \right\} \frac{T}{mc^2}. \quad (25)$$

It is easy to show that the expectation value of (25) reduces to (23).

Equation (24) admits a simple physical interpretation. If in the nonrelativistic Zeeman Hamiltonian Z_0 given by (22) we replace the mass m of the electron by its relativistic value $m(1 - v^2/c^2)^{-\frac{1}{2}}$ and expand $(1 - v^2/c^2)^{\frac{1}{2}}$ as $1 - \frac{1}{2}v^2/c^2$, we obtain the first part of (24).

The second part is obtained as follows. In the absence of a magnetic field, there is a term in the nonrelativistic Hamiltonian of the electron representing the spin-orbit coupling which can be written as

$$\left(\frac{\hbar}{2mc^2} \right) (\nabla V \times \mathbf{p}) \cdot \mathbf{s}. \quad (26)$$

The introduction of the magnetic field modifies the spin-orbit coupling, since it changes the velocity \mathbf{p}/m of the electron by adding to it the extra velocity resulting from the Larmor precession of the electron in the magnetic field. This is equivalent to replacing \mathbf{p} by $\mathbf{p} + e\mathbf{A}/c$ in (26). If we do so, we obtain the second term of (24).

We see that (24) could have been written straightaway without mentioning Dirac's equation simply using the relativistic variation of the mass with velocity and Larmor's theorem. However, we naturally feel safer with the authority and rigor of Dirac's equation behind us. We can say that the first part of the Yale correction, $-\beta \mathbf{H} \cdot (\mathbf{1} + 2\mathbf{s})T/mc^2$, is the relativistic-correction proper. It depends only on the velocity of the electron and will always be there whatever the electromagnetic interactions between the electron and its surroundings, nuclei or other electrons. The second part, $(\beta/mc^2) \mathbf{s} \cdot (\nabla V \times \mathbf{A})$, is the result of velocity-dependent interactions between the electron and its surroundings (in the present case the central field gradient) which are modified by the change in the velocity of the electron due to Larmor precession. Both parts of the Yale correction are sometimes referred to in the literature as the relativity correction, as they disappear in the limit $c = \infty$; the same property also, however, applies to our remaining magnetic corrections which are superposed when there is more than one electron and which we discuss in the following sections. We therefore prefer to use the term relativity correction only in connection with the first part of (25).

Lamb's diamagnetic correction.—Lamb¹³ has considered the case of an electron outside of a core formed of closed shells. In an external field a current is induced in the core, caused by the Larmor precession of the electrons in this field. It is given by $\mathbf{j} = (e^2/mc)\rho\mathbf{A}$, where ρ is the electronic density in the core. This current in turn produces a vector potential,

$$\mathbf{A}'(r) = -\frac{e^2}{mc^2} \int \frac{\mathbf{A}(\mathbf{r}')\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\tau'. \quad (27)$$

Lamb then considers the interaction of the spin magnetic moment of the valence electron with the magnetic field $\text{rot}\mathbf{A}'$:

$$\langle \beta \boldsymbol{\sigma} \cdot \text{rot}\mathbf{A}' \rangle. \quad (28)$$

This gives an extra term in the Hamiltonian, proportional to the external field \mathbf{H} , which results in a correction to the magnetic moment of the electron.

Since Lamb considers s electrons only, he retains solely the spherically symmetrical part of the interaction (28). For the same reason he does not consider any diamagnetic effects resulting from orbit-orbit interaction. We shall use the term Lamb correction for (28) rather than the less general expression valid for s electrons only that Lamb derives from (28).

¹³ W. Lamb, Phys. Rev. **60**, 817 (1941).

The general case.—We are now ready to tackle the general problem of the corrections to the magnetic moment of a complicated atom like oxygen.

We know that in an atom there are velocity dependent interactions between electrons, the so-called Breit interactions, as well as interactions between the electrons and the nucleus. Their contribution \mathcal{K} to the non-relativistic Hamiltonian is written below:

$$(A) \quad \mathcal{K} = -\frac{Ze^2\hbar}{4m^2c^2} \sum_i \left[\nabla_i \left(\frac{1}{r_i} \right) \times \mathbf{p}_i \right] \cdot \boldsymbol{\sigma}_i \quad (29)$$

$$(B) \quad + \frac{e^2\hbar^2}{4m^2c^2} \sum_{i \neq k} \left[\nabla_i \left(\frac{1}{r_{ik}} \right) \times \mathbf{p}_i \right] \cdot \boldsymbol{\sigma}_i$$

$$(C) \quad + \frac{e^2\hbar^2}{4m^2c^2} \sum_{i \neq k} \left[\nabla_i \left(\frac{1}{r_{ik}} \right) \times \mathbf{p}_i \right] \cdot 2\boldsymbol{\sigma}_k$$

$$(D) \quad - \frac{e^2}{2m^2c^2} \sum_{i < k} \left[\frac{1}{r_{ik}} (\mathbf{p}_i \cdot \mathbf{p}_k) + \frac{1}{r_{ik}^3} (\mathbf{r}_{ik} \cdot (\mathbf{r}_{ik} \cdot \mathbf{p}_i) \cdot \mathbf{p}_k) \right].$$

(D) is written in this complicated fashion because of the noncommutability of \mathbf{p}_i and \mathbf{r}_{ik} . These interactions which were first written by Heisenberg on a purely phenomenological basis were derived by Breit¹⁴ by reduction to the large components of the following Hamiltonian:

$$\mathcal{H}_{\text{int}} = -Ze^2 \sum_i \frac{1}{r_i} + \sum_{i < k} \frac{e^2}{r_{ik}} - \frac{e^2}{2} \sum_{i < k} \left[\frac{(\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_k)}{r_{ik}} + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ik})(\boldsymbol{\alpha}_k \cdot \mathbf{r}_{ik})}{r_{ik}^3} \right]. \quad (30)$$

The last term of (30) represents the retarded velocity-dependent interactions between electrons up to the order $(v/c)^2$ and is sometimes referred to as the Möller interaction.

The reduction of the first term of (30) leads to the terms (A) in (29); the second, $\sum e^2/r_{ik}$, gives through reduction the term (B) of (29); the third or last term of (30) gives (C) and (D) of (29).

The reduction of (30) gives, of course, other terms than (29), but these are independent of velocity and do not concern us.

We will account for the presence of the magnetic field by replacing in (29) all the \mathbf{p} 's by $\boldsymbol{\pi} = \mathbf{p} + e\mathbf{A}/c$.

It is not obvious that this is the correct procedure. We know, for instance, that if in the nonrelativistic Hamiltonian $(\mathbf{p}^2/2m) + V$ we replace \mathbf{p} by $\mathbf{p} + e\mathbf{A}/c$ we completely miss the coupling $\beta\boldsymbol{\sigma} \cdot \mathbf{H}$ of the spin with the external field. It is in the Dirac equations themselves that we must replace \mathbf{p} by $\mathbf{p} + e\mathbf{A}/c$ and then carry the reduction along the lines which lead from (30) to (29).

This somewhat tedious calculation is not reproduced here. It shows that it is indeed correct to replace \mathbf{p} by $\mathbf{p} + e\mathbf{A}/c$ in (29), since all extra terms resulting from the non-commutability of the $\boldsymbol{\pi}$'s (as opposed to the \mathbf{p} 's) cancel out.

If after replacing \mathbf{p} by $\mathbf{p} + e\mathbf{A}/c$ in (29) we write out all the terms linear in \mathbf{A} and add to these the relativistic correction proper, $-\beta\mathbf{H} \cdot (\mathbf{1} + 2\mathbf{s})\bar{T}/mc^2$ for each electron, we find that all the relativistic and diamagnetic corrections are represented by the expectation value of the following (nonrelativistic) operator:

$$\begin{aligned} \delta Z = & -\beta\mathbf{H} \cdot \sum_i (\mathbf{1}_i + 2\mathbf{s}_i)T_i/mc^2 \\ & - (\beta Ze^2/2mc^2) \sum_i [\nabla_i(1/r_i) \times \mathbf{A}_i] \cdot \boldsymbol{\sigma}_i \\ & + (e^2/2mc^2)\beta \sum_{i \neq k} [\nabla_i(1/r_{ik}) \times \mathbf{A}_i] \cdot \boldsymbol{\sigma}_i \\ & + (e^2/2mc^2)\beta \sum_{i \neq k} [\nabla_i(1/r_{ik}) \times \mathbf{A}_i] \cdot 2\boldsymbol{\sigma}_k \\ & - (e^3/2m^2c^3) \sum_{i \neq k} [r_{ik}^{-1}(\mathbf{A}_i \cdot \mathbf{p}_k) \\ & \quad + r_{ik}^{-3}(\mathbf{r}_{ik} \cdot \mathbf{A}_i)(\mathbf{r}_{ik} \cdot \mathbf{p}_k)]. \quad (31) \end{aligned}$$

Our problem is now solved in principle. If one has a good set of atomic wave functions (self-consistent Hartree-Fock functions are available for oxygen,¹⁰) all one needs is to write the wave function of the whole atom as a sum of Slater determinants and take the expectation value of (31) for it. This is perfectly possible in principle and should allow a reasonably accurate estimate of the relativistic and diamagnetic corrections.

Although straightforward in principle, this calculation is lengthy because of the somewhat complicated nature of the operator (31) and of the numerical integrations involved in the use of Hartree functions. We shall introduce simplifying approximations into this calculation.

Except for the first two terms, (31) is a sum of two-particle operators, and its expectation value taken over an antisymmetric wave function involves contributions from exchange matrix elements of the type

$$\iint \psi_i^*(1)\psi_k^*(2)W(1,2)\psi_i(1)\psi_k(2)d\tau_1d\tau_2,$$

where ψ_i and ψ_k are one-electron wave functions. For simplicity we shall drop them.

We shall then be able to show that then the expectation value of (31) reduces to the sum of the Yale correction, the Lamb correction, and an extra term coming from the orbit-orbit interaction which Lamb did not consider since he dealt with s electrons only.

Let us consider the second and third terms of (31) and in these terms focus our attention more particularly on the spin of, say, electron one.

The terms containing this spin can be written

$$\frac{\beta}{2mc^2} \left[\nabla_1 \left(-\frac{Ze^2}{r_1} + \sum_{k \neq 1} \frac{e^2}{r_{1k}} \right) \times \mathbf{A}_1 \right] \cdot \boldsymbol{\sigma}_1. \quad (32)$$

With our convention to disregard the exchange matrix

¹⁴ G. Breit, Phys. Rev. 34, 553 (1929).

elements, the expectation value of (32) can be written as

$$(\beta/2mc^2) \int \psi_1^*(1) [\nabla_1 V \times \mathbf{A}_1] \cdot \boldsymbol{\sigma}_1 \psi_1(1) d\tau_1, \quad (33)$$

where

$$V(1) = -\frac{Ze^2}{r_1} + \sum_{k \neq 1} \int \psi_k^*(2) \frac{e^2}{r_{12}} \psi_k(2) d\tau_2. \quad (34)$$

We call ψ_k the wave function of the electron, spin included. Unless specified otherwise the integration over $d\tau$ includes summation over spin variables. If we observe that (34) is precisely the definition of the self-consistent potential energy of electron one, we find that (33) is the second part of the Yale correction, i.e., the expectation value of the last term of (24).

From comparison of (24), (31), and (33), it is seen that the first three terms of (31) represent the sum of the Yale corrections for all the electrons of the atom. It is, of course, obvious that only electrons outside of closed shells give a nonvanishing contribution to this correction.

(b) If we apply the same considerations to the fourth term of (31), its expectation value gives a sum of terms such as

$$-\frac{\beta e^2}{mc^2} \int \psi_1^*(1) \boldsymbol{\sigma}_1 \cdot \text{rot} \left[\int \frac{\mathbf{A}(2)\rho(2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_2 \right] \psi_1(1) d\tau_1, \quad (35)$$

with $\rho(2) = \sum_{k \neq 1} \psi_k^*(2) \psi_k(2)$. From (27) and (28) we see that (35) is precisely the Lamb correction for electron one, which we have to sum over all the electrons of the atom. Here again only electrons outside of closed shells contribute, but the fields acting on these electrons usually come from closed shells.

(c) Finally, the expectation value of the last term of (31) gives for electron one:

$$-\frac{e^3}{2mc^3} \int \psi_1^*(1) \left\{ 2 \int \frac{\rho(2)\mathbf{A}(2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_2 - \nabla_1 \left[\int \frac{\{(\mathbf{r}_1 - \mathbf{r}_2) \cdot \mathbf{A}(2)\} \rho(2) d\tau_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \right\} \cdot \mathbf{p}_1 \psi_1(1) d\tau_1, \quad (36)$$

and we have to add contributions from all electrons. Again only electrons outside from closed shells contribute.

CALCULATION OF RELATIVISTIC AND DIAMAGNETIC CORRECTIONS IN OXYGEN

We have now broken down our corrections into three different groups, the Breit-Margenau or Yale correction, the Lamb correction, and the orbit-orbit correction. Let us consider them in turn:

(a) *Breit-Margenau correction.*—The Breit-Margenau correction is the expectation value of the parts of (25) proportional to T/mc^2 for each electron. It is easy to show that for a p electron in a state defined by $l_z = m_l$,

$s_z = m_s$, with the z axis along the field, this can be rewritten as the expectation value of

$$-\beta H(T/mc^2) [m_l + \frac{1}{5} m_s (8 - 2m_l^2)]. \quad (37)$$

We can calculate the expectation value of (37), summed for the four $2p$ electrons for the states 1D_2 , $J_z = 2$ and 3P_2 , $J_z = 2$. The corresponding energy corrections for 1D_2 , 3P_2 for $J_z \neq 2$ then follow immediately since, with given J , general rotational transformation properties require them to be proportional to the magnetic quantum number J_z . The energy corrections for 3P_1 can be found by utilizing the invariance of the diagonal sum for $J_z = 1$ in the same way as in Goudsmit's calculation of multiplet constants, thus avoiding the need of including nondiagonal elements omitted in passing from (25) to (37). The resulting alterations to the g factors are found to be

$$\Delta g_1 = -\frac{\bar{T}}{mc^2}, \quad \Delta g_2 = -\frac{12 \bar{T}}{10 mc^2}.$$

To estimate \bar{T} we can

(1) Calculate

$$-(\hbar^2/2m) \int \psi_{2p}^* \nabla^2 \psi_{2p} d\tau$$

for Slater's rough analytical wave functions. The result is $\bar{T}/mc^2 = 1.36 \times 10^{-4}$.

(2) Make the same calculation using Löwdin's quite accurate analytical representation of Hartree's wave functions. This gives 1.36×10^{-4} .

(3) Calculate the kinetic energy by subtracting the potential from the total energy, with the integrals evaluated numerically with Hartree wave functions. One thus obtains 1.24×10^{-6} .

In the light of (1), (2), and (3) we take

$$\bar{T}/mc^2 = 1.3 \times 10^{-4}.$$

The result is then

$$\Delta g_1 = -130 \times 10^{-6}, \quad \Delta g_2 = -156 \times 10^{-6}. \quad (38)$$

This value of \bar{T} is considerably higher than those considered in discussions of atomic beams experiments on alkalis. This fact is not surprising. In oxygen each $2p$ electron is imperfectly screened from the nucleus by the other three $2p$ electrons, and spends more time near the nucleus where potential and kinetic energy both have large absolute values.

(b) *Lamb correction.*—The Lamb correction is given for each electron by (35). We make the further simplifying assumption that

$$\rho(2) = \sum_{k \neq 1} \psi_k^*(2) \psi_k(2) \text{ has spherical symmetry.}$$

This is equivalent to replacing the probability distribution of all the electrons acting on the one under consideration (but not the probability density of this electron itself) by its average over the angles. Then $\rho(2)$

becomes a spherically symmetrical function $\rho(r_2)$. The expression (35) can be rewritten as

$$-\frac{\beta e^2}{mc^2} \left\langle \boldsymbol{\sigma}_1 \cdot \text{rot} \int \frac{\mathbf{A}(2)}{|r_1 - r_2|} \rho(2) d\tau_2 \right\rangle, \quad (39)$$

where the expectation value is to be taken over the wave function of electron one. (39) can be rewritten as

$$-(\beta e^2/mc^2) \langle \boldsymbol{\sigma}_1 \cdot \text{rot}[\mathbf{A}(1)Y/(r_1)] \rangle,$$

where the spherically symmetrical function $Y(r_1)$ is defined by:

$$Y(r) = \frac{1}{3}[V(r) + W(r)],$$

$$V(r) = \frac{1}{r^3} \int_0^r r'^4 \rho(r') dr', \quad W(r) = \int_r^\infty r' \rho(r') dr'. \quad (40)$$

If we take \mathbf{H} along the z axis, (39) becomes

$$-(e^2/mc^2)\beta H \langle \sigma_z \{ \frac{1}{6}(3 \cos^2\theta - 1)V(r) + \frac{1}{3}W(r) \} \rangle. \quad (41)$$

Here θ is the angle between \mathbf{r} and the z axis. Only the second, spherically symmetrical part of (41) was considered by Lamb.

For a $2p$ wave function, (41) is equal to

$$-\beta H \langle \sigma_z \{ \frac{1}{3}W - \frac{1}{3}(m^2 - \frac{2}{3})V \} / (137)^2 \rangle, \quad (42)$$

where V and W are to be taken in Hartree atomic units.

This leads to the following corrections:

$$\begin{aligned} \Delta g_1 &= -\frac{1}{3} \{ \bar{W} - \frac{1}{3} \bar{V} \} / (137)^2, \\ \Delta g_2 &= -\frac{1}{3} \{ \bar{W} + \frac{1}{10} \bar{V} \} / (137)^2. \end{aligned} \quad (43)$$

In (42) and (43) all the distances are expressed in atomic units. We postpone the estimate of \bar{V} and \bar{W} until after the orbit-orbit correction has been considered.

(c) *The orbit-orbit correction.*—The orbit-orbit correction is given by (36). If the density $\rho(2)$ is spherically symmetrical the second term in the large bracket is easily seen to vanish. Then (36) yields:

$$-(e^3/2m^2c^3) \int \psi_1^*(1) [\mathbf{H} \times \mathbf{r}_1] \cdot Y(r_1) \mathbf{p}_1 \psi_1(r) d\tau_1, \quad (44)$$

where Y is defined by (40).

The expression (44) can be rewritten as

$$-(\beta e^2/mc^2) \mathbf{H} \cdot \langle \mathbf{I} \rangle. \quad (45)$$

This results in the following corrections for g_1 and g_2 :

$$\Delta g_1 = \Delta g_2 = -\frac{1}{6} (\bar{V} + \bar{W}) / (137)^2. \quad (46)$$

To estimate \bar{V} and \bar{W} , we use Slater's wave functions. We find for \bar{V} and \bar{W} expressed in atomic units:

$$\bar{V} = 1.27, \quad \bar{W} = 2.2.$$

In Table II we recapitulate all the corrections from the beginning.

TABLE II. Corrections to g_1 and g_2 .

| Type of correction | Corrections in units of 10^{-6} | |
|---------------------------------|-----------------------------------|--------------|
| | Δg_1 | Δg_2 |
| Departures from R-S coupling | 0 | -21 |
| Orbital moment (nuclear motion) | +2 | +2 |
| Breit-Margenau from (37) | -130 | -156 |
| Lamb from (43) | -28 | -42 |
| Orbit-orbit from (46) | -31 | -31 |
| Total | -187 | -248 |

The totality of corrections added to (8) gives

$$g_1 = 1.500958, \quad g_2 = 1.500897.$$

For comparison the experimental values are [see Eq. (7)]

$$g_1 = 1.500971, \quad g_2 = 1.500905.$$

The agreement is excellent, but doubtless partly accidental. The smoothing due to the neglect of exchange matrix elements and averaging over the angles of the density ρ has probably reduced the difference between Δg_1 and Δg_2 .

Beringer's experimental measurements can hence be regarded as essentially a confirmation of, or at least, in good accord with, the Schwinger electro-dynamical corrections. It is instructive to express the results in the form of a theoretical g factor inclusive of only the electro-dynamical correction, and experimental values correspondingly corrected for everything but the electro-dynamical effect. The Schwinger theory then gives [see Eq. (8)]

$$g_1 = g_2 = 1.501145,$$

and experiment gives

$$g_1 = 1.501158, \quad g_2 = 1.501153.$$

It is, of course, the deviations from the simple Landé value 1.5 which are significant.

The agreement could presumably be improved by more accurate numerical calculations. Notably we have omitted the exchange terms in certain places [see remarks following Eq. (31)] and we have used only crude wave functions to evaluate (40). A subtle and difficult refinement would be to base the calculations on wave functions for groups of electrons rather than simply additively from unpolarized single electron wave functions in the usual Hartree-Fock fashion.

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