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Calculation of the Magnetic Moment of Atomic Oxygen

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A precision calculation has been made for the atomic g_J factors of the $(2p^4)^3P_1$ and $(2p^4)^3P_2$ terms of atomic oxygen. The results are in exact agreement with the experimental values to within the experimental error.

In a previous paper[1] we have shown that the g_J value of atomic fluorine as calculated with the theory developed by Kambe and Van Vleck[2] is in exact agreement with experiment to within the experimental error of 1 ppm. No such agreement had been obtained previously for similar calculations in atoms heavier than helium. In particular, the g_J values in the lowest ^3P term of atomic oxygen have been calculated by several authors.[2-4] The results of these calculations are in disagreement with experiment[5] by 6 to 7 ppm. A revision of these calculations was thus desirable in order to find out if these discrepancies originate on limitations of the theory or of the wave functions employed. For a meaningful comparison with the results obtained for fluorine, we have used in the present calculation Hartree-Fock (HF) wave functions of the same accuracy as those employed in the case of atomic fluorine.

The corrections to the simple Landé g_J factors have been extensively discussed by several authors.[2-4] We shall thus give only a succinct account of our results as follows.

SPIN FACTOR ANOMALY

The corrections due to this effect are obtained by inserting the value[6] $g_S = 2\times 1.001\,159\,622$ into the expressions

$$g_1(^3P_1) = g_2(^3P_2) = \tfrac{1}{2}(g_l + g_s)$$

for the Landé factors of the $^3P_1$ and $^3P_2$ levels. The numerical values of these corrections are then

$$(\delta g_1)_{sfa} = (\delta g_2)_{sfa} = \tfrac{1}{2}\delta g_s = 1159.6\times 10^{-6}. \qquad (1)$$

RELATIVISTIC AND DIAMAGNETIC EFFECTS

The corrections due to relativistic and diamagnetic effects in oxygen have been reduced to radial integrals by Kambe and Van Vleck[2] and later by Innes and Ufford[4] who detected minor but significant algebraical errors. The values for the radial integrals were obtained by Kambe and Van Vleck with wave functions of varying accuracy. We have recalculated these integrals with the wave functions of Clementi, Roothaan, and Yoshimine[7] which are believed to have three-decimal-place accuracy. In Table I we list the values of all integrals pertinent to our calculation. Substituting these values into the correct expressions for the relativistic and diamagnetic corrections we obtain

$$(\delta g_1)_{rd} = -(3.185\pm 0.004)\alpha^2 = -(169.6\pm 0.2)\times 10^{-6},$$
$$(\delta g_2)_{rd} = -(3.952\pm 0.004)\alpha^2 = -(210.4\pm 0.2)\times 10^{-6}. \qquad (2)$$

The value for the fine-structure constant has been taken as[8] $\alpha^{-1} = 137.0388$. The uncertainty in these corrections arises from the two values obtained for the kinetic energy of a $2p$ electron, one by direct integration of the kinetic-energy operator and the other from the Hartree-Fock equation for that electron.

ISOTOPIC EFFECT

The correction to g_1 which arises from the motion of the nucleus is calculated by evaluating the two equivalent expressions given by Abragam and Van Vleck[3] [Eqs. (3) and (4) of Ref. 1]. Substitution of these values into the expressions for the Landé factors gives the results

$$(\delta g_1)_{\text{iso}} = (\delta g_2)_{\text{iso}} = \tfrac{1}{2}\delta g_L = -(5.6\pm 0.5)\times 10^{-6}. \qquad (3)$$

The uncertainty arises from the two values obtained for δg_L.

DEPARTURES FROM LS COUPLING

The effect of breakdown of LS coupling on the atomic oxygen g_J factors, which arises from

TABLE I. Integrals involved in the evaluation of the corrections to g_1 and g_2.

$\langle 2p \| 1/r \| 2p\rangle$	1.1111
$\langle 2p \| -\frac{1}{2}\nabla^2 \| 2p\rangle^a$	2.5385
$\langle 2p \| -\frac{1}{2}\nabla^2 \| 2p\rangle$	2.5332
$F_>{}^0$ $(1S, 2p)$	0.033 61
$F_>{}^0$ $(2S, 2p)$	0.3917
F_0 $(2p, 2p)$	0.7553
$F_>{}^0$ $(2p, 1s)$	1.0651
$F_>{}^0$ $(2p, 2s)$	0.3827
$F_>{}^2$ $(2p, 1s)$	0.1229
$F_>{}^2$ $(2p, 2s)$	0.1761
F_2 $(2p, 2p)$	0.3366
G^{-1} $(2p, 1s)$	0.3316
G^{-1} $(2p, 2s)$	1.0566
G^1 $(2p, 1s)$	0.1059
G^1 $(2p, 2s)$	0.4727
G^3 $(2p, 1s)$	0.0576
G^3 $(2p, 2s)$	0.2719
R $(2p, 1s)$	− 0.1948
R $(2p, 2s)$	0.1773
$\int r\, P_{2p}P_{1s}dr$	0.1070
$\int r\, P_{2p}P_{2s}dr$	1.1584
$\int P_{2p}(d/dr)(P_{1s}/r)dr$	1.9909
$\int P_{2p}(d/dr)(P_{2s}/r)dr$	− 0.6506
E_{1s}	−20.6686
E_{2s}	− 1.2443
E_{2p}	− 0.6319

[a] Value based on the Hartree-Fock equations.

levels within the ground-state configuration, is[3]

$$(\delta g_2)_{LS} = -\frac{1}{2}\left(\frac{\zeta_{2p}}{E(^3P_2)-E(^1D_2)}\right)^2 = -21.2\times10^{-6}. \quad (4)$$

The perturbation arising from levels in excited configurations is calculated with the formula given by Phillips[9] [Eq. (9) in Ref. 1]. The levels which are more likely to perturb g_1 and g_2 are shown in Fig. 1 together with the matrix elements of interest to our calculation. The radial integral $R_0(2p, 2p, 2p, 3p)$ has been evaluated with the approximate Slater-type[10] wave functions

$$P_{2p}{}^{\mathrm{I}}(r) = 14.7r^2 e^{-2.77r},$$

$$P_{2p}{}^{\mathrm{II}}(r) = 34.2r^2 e^{-2.45r},$$

$$P_{3p}{}^{\mathrm{II}}(r) = 0.15(1-0.61r)r^2 e^{-0.58r}$$

The resulting value is $R_0 = 0.11$ a.u. The value of R_2 is at least one order of magnitude smaller and will be neglected. The corrections to g_1 and g_2 are then seen to be

$$\delta g_1 = 1.23[\tfrac{1}{4}(\zeta_{3p}/86.6)^2 - \tfrac{1}{9}(\zeta_{2p}/127)^2]\times10^{-7}, \quad (5)$$

$$\delta g_2 = 5.4\delta g_1,$$

where the spin-orbit parameters are to be expressed in cm^{-1}.

The value for ζ_{2p} can be taken as[11] 146.6 cm^{-1}; the value for ζ_{3p} should be considerably smaller. At any rate the influence of ζ_{3p} is opposite to that of ζ_{2p}, so a reasonable upper limit for these corrections can be reached by neglecting ζ_{3p}. By doing this we obtain the maximum values:

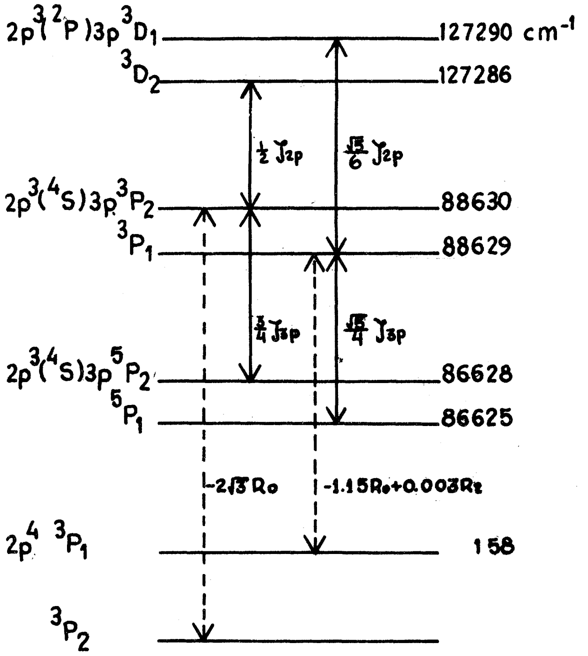

FIG. 1. States of the excited configurations which more strongly perturb the values of g_1 and g_2. The dashed lines join states connected by electrostatic interactions, and the continuous lines refer to spin-orbit interactions.

$$\delta g_1 = -0.18\times10^{-7}, \quad \delta g_2 = -0.98\times10^{-7}.$$

We therefore conclude that the effect of excited configurations is negligible, and the corrections arising from breakdown of LS coupling are only those caused by levels of the ground-state configurations.

The resulting values are then, from Eqs. (1)–(4),

$$g_1 = (1.500\,984\,4 \pm 0.7)\times10^{-6},$$

$$g_2 = (1.500\,922\,4 \pm 0.7)\times10^{-6},$$

which are to be compared with the experimental values[5]

$$g_1 = (1.500\,986 \pm 2)\times10^{-6},$$

$$g_2 = (1.500\,921 \pm 2)\times10^{-6}.$$

These excellent results, together with those obtained for atomic fluorine, seem to indicate that the Kambe-Van Vleck theory is correct to the order of approximation of these calculations, i.e., to first-order perturbation theory of the Breit interaction. It remains to make clear what is the significance of these results as far as the wave functions are concerned. It has been shown[12] that a single-determinant HF wave function cannot account for the observed hyperfine interaction in O^{17}.

For this it has been necessary to construct extended Hartree-Fock wave functions giving s and p polarization. However, it has been demonstrated[12,13] that, to first-order corrections, these wave functions can be obtained from a configuration interaction (CI) function built on a one-determinant HF function and all singly excited $s \leftrightarrow s'$ and $p \leftrightarrow p'$ functions with the symmetry (same S and L) of the HF determinant. Therefore, corrections to g_J cannot be produced with such wave functions. The atomic g factors test only the HF function upon which the CI is built.

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ERRATUM

New Theory of Electron Drift Velocity in Gases, G. Cavalleri and G. Sesta [Phys. Rev. 170, 286 (1968)]. We are very grateful to Professor Skullerud for having pointed out an error in Eq. (25), which must read

$$W = \int_0^\infty w(c_0)T(c_0)f(c_0)dc_0 \Big/ \int_0^\infty T(c_0)f(c_0)dc_0 \; .$$