[9] S. Sengupta and A. Mukherji, J. Chem. Phys. 47, 260 (1967).

[10] See, for example, D.W. Davies, *The Theory of the Electric and Magnetic Properties of Molecules* (John Wiley & Sons, New York, 1967), Chap. 6.

[11] J. Frenkel, *Wave Mechanics, Advanced General Theory* (Dover Publications, Inc., New York, 1950), p. 436.

[12] See, for example, J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. 2, Chap. 17.

[13] Arnold Sommerfeld, *Optics* (Academic Press, Inc., New York, 1954), p. 105.

[14] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, England, 1932), p. 367.

[15] The functions were obtained from E. Clementi, J. Chem. Phys. 38, 996 (1963).

[16] H. Radt, Ph. D. dissertation, State University of New York at Buffalo, (1969), (unpublished).

[17] J. D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, Inc., New York, 1962), p. 66.

[18] See, for example, H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Mass., 1950), p. 33.

[19] Experimental first-transition frequencies obtained from Charlotte E. Moore, Nat. Bur. Std. (U.S.), Circ. No. 467 (1949), Vol. 1.

[20] C. Cuthbertson and M. Cuthbertson, Proc. Roy. Soc. (London) A135, 40 (1932).

[21] H. J. Kolker and H. H. Michels, J. Chem. Phys. 43, 1027 (1965).

[22] A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. (London) A259, 424 (1960).

[23] J. Lahiri and A. Mukherji, J. Phys. Soc. Japan 21, 1178 (1966).

[24] A. Dalgarno and H. A. J. McIntyre, Proc. Phys. Soc. (London) 85, 47 (1965).

[25] H. P. Kelly, Phys. Rev. 136, B896 (1964).

[26] H. B. Levine and H. S. Taylor, J. Chem. Phys. 41, 1367 (1964).

Calculation of the Magnetic Moment of Atomic Fluorine

V. Beltrán-López*
Reactor, Centro Nuclear, Comisión Nacional de Energía Nuclear, México, D. F., México

and

E. Ley Koo†
Instituto de Fisica, Universidad Nacional Autónoma de México, México, D. F., México

and

N. Segovia
Comisión Nacional de Energía Nuclear, México, D. F., México

and

E. Blaisten
Facultad de Ciencias, Universidad Nacional Autónoma de México, México, D. F., México

(Received 15 January 1968)

The atomic g_J factors for the two levels composing the lowest term of atomic fluorine have been calculated utilizing the theory of Kambe and Van Vleck and wave functions resulting from Hartree-Fock treatments of varying accuracy. For the high-accuracy wave functions, the results of our calculation are in exact agreement with the measured $g_J(\mathrm{F}^{19}; {}^2P_{\frac{3}{2}})/g_J(\mathrm{H}^1; {}^2S_{\frac{1}{2}}) = \frac{2}{3} - (497 \pm 1) \times 10^{-6}$, to within the experimental error. The contribution to $g_J(\mathrm{F}^{19}; {}^2P_{\frac{3}{2}})$ arising from the Breit interaction is found to amount to 49×10^{-6}. This sizeable contribution, and the excellent agreement obtained, substantiate the validity of the theory and, in particular, of the Breit interaction to the order of α^2. For the upper level, the value $g_J(\mathrm{F}^{19}; {}^2P_{\frac{1}{2}}) = \frac{2}{3} - (1072 \pm 2) \times 10^{-6}$ is obtained. For this, no experimental test of adequate sensitivity has been made.

I. INTRODUCTION

The various effects affecting the simple atomic Landé g_J factors have been considered by several authors.[1-7] The corrections which are produced arise from the anomalous magnetic moment of the electron,[1,3,8] isotopic effects caused by the motion of the nucleus,[4,5] relativistic and diamagnetic effects,[5,9] and departures from Russell-Saunders coupling.[6] The anomalous magnetic moment is known to the order of α^2, therefore its inclusion in the calculation is readily accomplished. The theories for the isotopic and departures from L-S coupling effects are well established and can be calculated to the accuracy permitted by the available wave functions. Concerning the so-called relativistic and diamagnetic effects, it is convenient to make the following remarks. Abragam and Van Vleck[5] have shown how these effects can be derived from the Darwin-Breit Hamiltonian,[10] which, as it is well known, is of an approximate nature and can be used only in a first-order perturbation calculation. This makes the corresponding corrections amenable to calculation to the order of α^2, and should make the results accurate up to the order of α^3, i.e., a few tenths of a ppm. This has been accomplished unquestionably in the case of helium,[11] but in this case the magnitudes of the corrections due to the Breit interaction are comparable to the minimum errors in the calculation itself, so that this is not a very stringent test for the theory. The contribution from the Breit interaction is expected to be larger in more complex atoms and detailed calculations have been made for oxygen. In the first of these[7] the calculated g values for the two lowest levels were in fair agreement with experiment. However, several algebraical errors were detected in a later work[12] with the result that the calculated g values deviated from experiment by as much as 10×10^{-6}. This can be blamed on several facts not related to the theory, such as the use of low-accuracy wave functions or the neglect of effects which might produce corrections of a magnitude of a few ppm. The aim of this work is to test the theory of atomic magnetism to the above-mentioned accuracy by comparing the results of a calculation based on high-accuracy wave functions with g_J factors which have been measured to within 1 ppm or better. Oxygen and fluorine are among these.[13,14] Fluorine was chosen because departures from L-S coupling are expected to be very small and inaccuracies resulting from the lack of knowledge of wave functions of excited configurations are less likely to vitiate our results. The present calculation proves this to be the case. All the integrals in this calculation have been evaluated with wave functions obtained by three different groups of authors[15–17] which we shall henceforth identify as K-A, C-R-Y, and Brown, respectively. The first two are very precise solutions of the Hartree-Fock equations and are believed to have three-decimal-place accuracy or better for the orbitals. The Brown wave functions are less accurate.

The numerical results of this calculation are in excellent agreement with experiment. Provided that correlation effects are not important, this is the first succesful test for the Kambe and Van Vleck theory of atomic magnetism.

II. CALCULATIONS

The lowest term of atomic fluorine is an inverted $2p^5\,P$ doublet with the $^2P_{1/2}$ level some 400 cm^{-1} above the ground $^2P_{3/2}$ level. All other terms lie more than 10^5 cm^{-1} above the ^2P term.[18] The simple Landé g_J factors for the two levels are given by the expressions:

$$g_{\frac{3}{2}}=\tfrac{2}{3}g_l+\tfrac{1}{3}g_S,\quad g_{\frac{1}{2}}=\tfrac{4}{3}g_l-\tfrac{1}{3}g_S. \tag{1}$$

The corrections to these values which arise from the various effects referred to in Sec. I are calculated as follows.

Spin-Factor Anomaly

We account for this effect by inserting the value[3,8] $g_S=2\times(1.001\,159\,622)$ into Eqs. (1). The increments produced over the Landé values $\frac{4}{3}$ and $\frac{2}{3}$ are respectively:

$$(\delta g_{\frac{3}{2}})_{sfa}=+773.1\times10^{-6},\quad (\delta g_{\frac{1}{2}})_{sfa}=-773.1\times10^{-6}. \tag{2}$$

Isotopic Effect

The correction to the g_J value which arises from the finite mass of the nucleus has been treated by Phillips,[4] and applied by Abragam and Van Vleck[5] to the case of atoms with s and p electrons in closed shells and only p electrons outside closed shells. Their results are given in the two equivalent forms:

$$\delta g_L=-(m/M)\{1+\tfrac{2}{3}\textstyle\sum_n[\int P_{2p}(d/dr)(P_{ns}/r)rdr](\int P_{2p}P_{ns}rdr)\} \tag{3}$$

$$\delta g_L=-(m/M)[1-\tfrac{2}{3}\textstyle\sum_n(\int P_{ns}P_{2p}rdr)^2(E_{2p}-E_{ns})]. \tag{4}$$

In these equations P_{ns} and $P2p$ are the radial parts of the wave functions for the ns and $2p$ electrons, normalized in the sense of $\int(P_{ns})^2dr=1$. In Eq. (4) E_{ns} and E_{2p} are the total energies of the ns and $2p$ one-electron states. The summation is over occupied s states, and each orbital state is counted once only. The quantities pertinent to the evaluation of Eqs. (3) and (4) are listed in Table I.

By using the values from Table I in Eqs. (3) and (4), and substituting in Eqs. (1), we obtain the isotopic corrections shown in Table II.

Relativistic and Diamagnetic Effects

The corrections which are due to relativistic and diamagnetic effects arise from velocity-dependent interactions. Abraham and Van Vleck[5] have shown how these corrections can be obtained from the Darwin-Breit Hamiltonian. The part of this which is of interest to our calculation is conveniently separated into the following contributions:

$$\begin{aligned}
&\delta Z_1=-\beta\vec{\mathrm{H}}\cdot\textstyle\sum_i(\vec{l}_i+\vec{\sigma}_i)T_i/mc^2,\quad \delta Z_2=-(\beta e^2Z/2mc^2)\textstyle\sum_i[\nabla_i(1/r_i)\times\vec{\mathrm{A}}_i]\cdot\vec{\sigma}_i,\\
&\delta Z_3=(\beta e^2/2mc^2)\textstyle\sum_{i\neq k}[\nabla_i(1/r_{ik})\times\vec{\mathrm{A}}_i]\cdot\vec{\sigma}_i,\quad \delta Z_4=(\beta e^2/2mc^2)\textstyle\sum_{i\neq k}[\nabla_i(1/r_{ik})\times\vec{\mathrm{A}}_i]\cdot 2\vec{\sigma}_k,\\
&\delta Z_5=-(e^3/2m^2c^3)\textstyle\sum_{i\neq k}[r_{ik}^{-1}(\vec{\mathrm{A}}_i\cdot\vec{\mathrm{p}}_k)+r_{ik}^{-3}(\vec{\mathrm{r}}_{ik}\cdot\vec{\mathrm{A}}_i)(\vec{\mathrm{r}}_{ik}\cdot\vec{\mathrm{p}}_k)].
\end{aligned} \tag{5}$$

Table I. Quantities involved in the evaluation of the isotopic corrections. The values for the E's are those of the energy parameters $\epsilon_{ns,ns}$ and $\epsilon_{2p,2p}$ of the respective Hartree-Fock treatments expressed in atomic units.

	K-A	C-R-Y	Brown
$\int P_{2p}P_{1s}rdr$	0.09798	0.09653	0.082
$\int P_{2p}P_{2s}rdr$	1.01640	1.01493	−1.069
$\int P_{2p}\frac{d}{dr}\left(\frac{P_{1s}}{r}\right)rdr$	−2.30060	−2.30334	−2.127
$\int P_{2p}\frac{d}{dr}\left(\frac{P_{2s}}{r}\right)rdr$	−0.72065	−0.72205	+0.682
E_{1s}	−26.3875	−26.3830	−26.540
E_{2s}	−1.57835	−1.57255	−1.200
E_{2p}	−0.73445	−0.7300	−0.505

Table II. Correction due to the isotopic effect. The upper indices I and II refer to the values obtained by using Eqs. (3) and (4), respectively.

	K-A	C-R-Y	Brown
$\delta g_{3/2}{}^{\mathrm{I}}$	-6.9×10^{-6}	-7.0×10^{-6}	-7.6×10^{-6}
$\delta g_{3/2}{}^{\mathrm{II}}$	−4.9	−5.0	−7.4
$\delta g_{1/2}{}^{\mathrm{I}}$	−13.9	−14.0	−15.3
$\delta g_{1/2}{}^{\mathrm{II}}$	−9.8	−10.0	−14.8

Kambe and Van Vleck[7] have reduced the expectation value of these contributions to the nlm_sm_l scheme. Application of their results to the case of the fluorine atom gives the following contributions to the g_J factors:

$$(\delta g_{3/2})_1 = -\tfrac{4}{3}\alpha^2\langle 2p|-\tfrac{1}{2}\nabla^2|2p\rangle,\quad (\delta g_{3/2})_2 = (2/15)Z\alpha^2\langle 2p|1/r|2p\rangle,$$

$$(\delta g_{3/2})_3 = \alpha^2\{-(4/15)F^0(2p,2p)+(1/75)F^2(2p,2p)+\textstyle\sum_n[-(4/15)F_>{}^0(2p,ns)+(1/45)G^1(ns,2p)]\},$$

$$(\delta g_{3/2})_4 = \alpha^2\{-\tfrac{2}{5}F^0(2p,2p)+(4/25)F^2(2p,2p)+\textstyle\sum_n[-4/9)F_>{}^0(ns,2p)+(4/45)F_>{}^2(2p,ns)+(2/45)G^1(ns,2p)]\},$$

$$\begin{aligned}(\delta g_{3/2})_5 = \alpha^2\{-\tfrac{1}{3}[F^0(2p,2p)+F^2(2p,2p)]+\textstyle\sum_n[-(4/9)F_>{}^0(ns,2p)-(4/9)F_>{}^2(2p,ns)\\ +\tfrac{1}{9}G^{-1}(ns,2p)+(7/45)G^1(ns,2p)+(2/45)G^3(ns,2p)+\tfrac{1}{3}R(ns,2p)]\}.\end{aligned} \tag{6}$$

$$(\delta g_{1/2})_1 = \tfrac{1}{2}(\delta g_{3/2})_1,\quad (\delta g_{1/2})_2 = -\tfrac{5}{2}(\delta g_{3/2})_2,\quad (\delta g_{1/2})_5 = 2$$

$$\begin{aligned}(\delta g_{3/2})_5, (\delta g_{1/2})_3 + (\delta g_{1/2})_4 = \alpha^2\{\tfrac{2}{3}F^0(2p,2p)-(8/15)F^2(2p,2p)\\ +\textstyle\sum_n[\tfrac{2}{3}F_>{}^0(2p,ns)-(8/9)F_>{}^2(2p,ns)+(4/9)F_>{}^0(ns,2p)+\tfrac{1}{3}G^1(ns,2p)]\}.\end{aligned} \tag{7}$$

In these equations, the integrals F and G are of the usual Condon and Shortley[19] type, whereas $F_>$ and R are those defined by Kambe and Van Vleck. In Table III we list the values of all the integrals appearing in Eqs. (6) and (7).

The very important value for the kinetic energy of a $2p$ electron has been evaluated by direct integration of the corresponding operator, and also by expressing this kinetic energy in terms of the difference between the total energy $\epsilon_{2p,2p}$ parameter for the $2p$ electron and the potential energy in which it finds itself. The relevant equation is:

$$\langle 2p|T|2p\rangle = \epsilon_{2p,2p} + 9\langle 2p|1/r|2p\rangle - 4F^0(2p,2p) + (8/25)F^2(2p,2p) + \textstyle\sum_n[-2F^0(ns,2p)+\tfrac{1}{3}G^1(ns,2p)]. \tag{8}$$

By substituting the values for the integrals into Eqs. (6) and (7) we obtain the corrections shown in Table IV.

Departures from L-S Coupling

Phillips has shown[6] that the mixing of excited configurations with the ground state leads to a correction in the atomic g value given by:

$$(\delta g)_{LS} = \textstyle\sum_{\ell k} V_{0\ell}{}^2\xi_{\ell k}{}^2\Delta g_{0k}/E_{0\ell}{}^2E_{0k}{}^2. \tag{9}$$

Here $V_{0\ell}$ and $\xi_{\ell k}$ are the matrix elements of the electrostatic and spin-orbit interactions, respectively; E_{0k} and Δg_{0k} are the energy and g_J factor differences between the kth level and the ground-state level. The configuration $(2p)^4(3p)$ is the nearest one which can be admixed with the ground level ${}^2P_{3/2}$. The electrostatic interaction connects the unperturbed ${}^2P_{3/2}({}^1S)$ level and the ${}^2P_{3/2}({}^{2s+1}L)$ levels of the excited configuration. These levels and the corresponding matrix elements are listed in Table V.

Table III. Integrals involved in the computation of the relativistic and diamagnetic corrections to g_J.

	K-A	C-R-Y	Brown
$\langle 2p\|-\frac{1}{2}\nabla^2\|2p\rangle$	3.3378	3.3402	3.03
$\langle 2p\|T\|2p\rangle^{a}$	3.3378	3.3436	3.046
$\langle 2p\|1/r\|2p\rangle$	1.27022	1.27163	1.2160
$F_>{}^0(1s,2p)$	0.03990	0.03976	0.03948
$F_>{}^0(2s,2p)$	0.4469	0.4472	0.4468
$F_>{}^0(2p,1s)$	1.2165	1.2154	1.2145
$F_>{}^0(2p,2s)$	0.4333	0.4340	0.4329
$F_>{}^2(2p,1s)$	0.1434	0.1429	0.1431
$F_>{}^2(2p,2s)$	0.1983	0.1985	0.1975
$F^0(2p,2p)$	0.8568	0.8599	0.8563
$F^2(2p,2p)$	0.3788	0.3800	0.3776
$G^{-1}(1s,2p)$	0.3908	0.3935	0.3901
$G^{-1}(2s,2p)$	1.1928	1.1931	1.1935
$G^1(1s,2p)$	0.1254	0.1251	0.1248
$G^1(2s,2p)$	0.5328	0.5340	0.5320
$G^3(1s,2p)$	0.0684	0.0676	0.0676
$G^3(2s,2p)$	0.3070	0.3065	0.3051
$R(1s,2p)$	0.2306	0.2297	0.2643
$R(2s,2p)$	-0.2129	-0.2127	-0.2051

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

Table IV. Relativistic and diamagnetic corrections to g_J. Results based on the values of $\langle 2p|-\frac{1}{2}\nabla^2|2p\rangle$ of Table III.

	K-A	C-R-Y	Brown
$\delta g_{3/2}$	$-4.505\alpha^2$	$-4.509\alpha^2$	$-4.15\alpha^2$
$\delta g_{1/2}$	$-5.393\alpha^2$	$-5.414\alpha^2$	$-5.03\alpha^2$

Table V. Matrix elements of the electrostatic interaction between the unperturbed ${}^2P_{3/2}({}^1S)$ level and the ${}^2P_{3/2}({}^{2S+1}L)$ levels of the excited $(2p)^4 3p$ configuration. The arguments for the integrals F and G are those in $F(2p^{\mathrm{I}},2p^{\mathrm{I}},2p^{\mathrm{II}},3p^{\mathrm{II}})$, where I and II designate the ground and excited configurations, respectively, in which case $F_0=G_0$, $F_2=G_2$.

${}^2P_{3/2}({}^{2S+1}L)$	V_{0i}
${}^2P_{3/2}({}^1S)$	$-\frac{1}{6}[F_0+G_0+10(F_2+G_2)]$
${}^2P_{3/2}({}^3S)$	$\sqrt{\frac{1}{12}}[F_0-G_0+10(F_2-G_2)]$
${}^2P_{3/2}({}^1P)$	$\sqrt{\frac{1}{12}}[F_0-G_0-5(F_2-G_2)]$
${}^2P_{3/2}({}^3P)$	$-\frac{1}{2}[F_0+G_0-5(F_2-G_2)]$
${}^2P_{3/2}({}^1D)$	$-\frac{1}{6}\sqrt{5}[F_0+G_0+(F_2+G_2)]$
${}^2P_{3/2}({}^3D)$	$\sqrt{\frac{5}{12}}[F_0-G_0+(F_2-G_2)]$

Table VI. Matrix elements of the spin-orbit interaction between levels of the excited configuration, and differences in g_J value. The matrix elements ξ_{ik} are in units of $\zeta(2p)$, the spin-orbit parameter for the electrons in the $2p$ shell.

i	k	ξ_{ik}	Δg_{0k}
${}^2P_{3/2}({}^3S)$	${}^4P_{3/2}({}^3S)$	$-\frac{1}{3}\sqrt{5}$	$\frac{2}{5}$
${}^2P_{3/2}({}^1P)$	${}^2D_{3/2}({}^1P)$	$\frac{1}{4}\sqrt{5}$	$-8/15$
${}^2P_{3/2}({}^3P)$	${}^4S_{3/2}({}^3P)$	$\frac{1}{3}\sqrt{2}$	$\frac{2}{3}$
${}^2P_{3/2}({}^3P)$	${}^4P_{3/2}({}^3P)$	$-\frac{1}{6}\sqrt{5}$	$\frac{2}{5}$
${}^2P_{3/2}({}^3P)$	${}^2D_{3/2}({}^3P)$	$-\frac{1}{12}\sqrt{5}$	$-8/15$
${}^2P_{3/2}({}^3P)$	${}^4D_{3/2}({}^3P)$	$-\frac{1}{6}\sqrt{5}$	$-2/15$
${}^2P_{3/2}({}^1D)$	${}^2D_{3/2}({}^1D)$	$\frac{3}{4}$	$-8/15$
${}^2P_{3/2}({}^3D)$	${}^4P_{3/2}({}^3D)$	$\frac{1}{6}\sqrt{5}$	$\frac{2}{5}$
${}^2P_{3/2}({}^3D)$	${}^2D_{3/2}({}^3D)$	$-\frac{1}{4}$	$-8/15$
${}^2P_{3/2}({}^3D)$	${}^4D_{3/2}({}^3D)$	$-\frac{1}{2}$	$-2/15$

Table VII. Total corrections to $g_J(F^{19};\,{}^2P_{3/2})$ and $g_J(F^{19};\,{}^2P_{1/2})$ computed with wave functions from different authors. The indices I and II have the same meaning as in Table II.

	K-A	C-R-Y	Brown
$\delta g_{3/2}{}^{\mathrm{I}}$	526.3×10^{-6}	526.0×10^{-6}	545.5×10^{-6}
$\delta g_{3/2}{}^{\mathrm{II}}$	528.3	528.0	545.7
$\delta g_{1/2}{}^{\mathrm{I}}$	-1074.2	-1075.4	-1056.2
$\delta g_{1/2}{}^{\mathrm{II}}$	-1070.1	-1071.4	-1055.7

Table VIII. Calculated values for the ratio of $g_J(F^{19};\,{}^2P_{3/2})/g_J(H^1;\,{}^2S_{1/2})$, computed with wave functions from different authors. The indices I and II have the same meaning as in Table II.

	K-A	C-R-Y	Brown
I	$\frac{2}{3}-497.5\times10^{-6}$	$\frac{2}{3}-497.7\times10^{-6}$	$\frac{2}{3}-488\times10^{-6}$
II	$\frac{2}{3}-496.5\times10^{-6}$	$\frac{2}{3}-496.7\times10^{-6}$	$\frac{2}{3}-488\times10^{-6}$

In Table VI we list the levels of the excited configuration which can be connected via the spin-orbit interaction with the ground-state configuration. We also list the matrix elements of this interaction and the values of Δg_{0k}. With the values of Tables V and VI and Eq. (9) we obtain

$$(\delta g_{\frac{3}{2}})_{LS} = \zeta^2(2p)2F_2(2F_2-F_0)/E^4. \tag{10}$$

We evaluated the integrals F_0 and F_2 by using the Slater-type[20] wave functions

$$P_{2p}{}^{\mathrm{I}}(r) = 12.58r^2e^{-2.6r},\quad P_{2p}{}^{\mathrm{II}}(r) = 14.88r^2e^{-2.78r},\quad P_{3p}{}^{\mathrm{II}}(r) = 0.594r^2(1-0.315r)e^{-0.63r} \tag{11}$$

The resulting values are $F_0 = 0.211$ and $F_2 = 0.0046$.

Taking the values for the spin-orbit parameter[21] $\zeta(2p) = 260\ \mathrm{cm}^{-1}$ and the energy of the levels of the excited configuration[18] $E = 1.1\times 10^5\ \mathrm{cm}^{-1}$, we obtain

$$(\delta g_{\frac{3}{2}})_{LS} = -4.1\times 10^{-8} \tag{7}$$

The total corrections to the g_J factors

$$\delta g_J = (\delta g_J)_{sfa} + (\delta g_J)_{\mathrm{iso}} + (\delta g_J)_{\mathrm{rd}} + (\delta g_J)_{LS}$$

can now be obtained with the values of Eq. (2) and Tables II and IV. The value for the fine-structure constant has been taken as[22] $\alpha^{-1} = 137.0388$. The correction due to departures from L-S coupling need not be included, as it is two orders-of-magnitude smaller than the required approximation. The results are listed in Table VII.

For comparison with experiment we divide the corrected $g_{3/2}$ values based on Table VII by the theoretical $g_J(\mathrm{H}^1, {}^2S_{\frac{1}{2}}) = 2(1-\alpha^2/3)$ obtaining the results shown in Table VIII. These values are to be compared with the experimentally[14] obtained $\frac{4}{3} - (497\pm 1)\times 10^{-6}$.

III. CONCLUSIONS

The results of our calculations based on the K-A and C-R-Y wave functions are indeed in very good agreement with the experimental value, although correlation effects have not been taken into account. The slight inconsistency shown by these wave functions upon calculation of the isotopic effect gives rise to an uncertainty not bigger than 1×10^{-6}, which is within the accuracy to which the theory is expected to be valid. This seems to indicate that correlation effects are negligible in this case, and our results can be taken as the first successful test of the theory of atomic magnetism to the order of α.[2]

Concerning the quality of the wave functions: The consistency of the Hartree-Fock treatment, from which they were obtained, should have been apparent in the calculation of the quantum mechanically equivalent terms in Eqs. (3) and (4), and also in the calculation of the average kinetic energy of a $2p$ electron by the two methods mentioned in Sec. II. An examination of Table III indicates that the values for the kinetic energy are equal to within 1×10^{-4}, 3×10^{-3}, and 15×10^{-3} for the K-A, C-R-Y, and Brown wave functions, respectively. Table II shows that the values of the correction due to the isotopic effect found by the two different methods differ by 2×10^{-6}, 2×10^{-6}, and 0.2×10^{-6} when calculated with the K-A, C-R-Y, and Brown wave functions, respectively. Given that the contribution of the kinetic energy to g_J is two orders-of-magnitude larger than that of the isotopic effect, the results based on the K-A and C-R-Y wave functions are more reliable than those based on Brown's. This is further supported by the fact that in all tables the values from K-A and C-R-Y are consistent with each other. The contribution to g_J arising from the Breit interaction is obtained from the parts δZ_4 and δZ_5 of Eqs. (5). For $J = \frac{3}{2}$, this contribution is found to amount to $(\delta g_{3/2})_4 + (\delta g_{3/2})_5 = -0.918\alpha^2 = -48.8\times 10^{-6}$, which is considerably larger than in the case of He[11] where it is only 2.3×10^{-6}. It appears then that the theory of the corrections to g_J can give agreement with experiment to within 1×10^{-6}, provided that wave functions as accurate as those of K-A and C-R-Y are used.

Other calculations have been reported previously[14,23] for $g_J(F, {}^2P_{\frac{3}{2}})$. These were made with the theory of Abragam and Van Vleck,[5] which neglects contributions from exchange integrals. We see that the agreement of those calculations with experiment is due to an accidental cancellation of the neglected exchange terms with the effect of using a wrong value for $\langle T\rangle_{2p}$. Specifically, if the K-A value for $\langle T\rangle_{2p}$ from Table I is used in the calculation of Ref. 14, we obtain $\delta g_{3/2} = -261\times 10^{-6}$, which compares much better, as it should, with the correction to g_J arising from only the direct terms in our calculation. In the K-A case, this contribution amounts to $(\delta g_J)_{\mathrm{rd}} = -264\times 10^{-6}$. It should also be pointed out that agreement obtained with a theory which neglects exchange terms is not to be trusted, as the exchange terms amount to 23×10^{-6} in this case, and are therefore by no means negligible. Another important point refers to the isotopic effect. This was calculated to be negligible in the two references cited above, whereas in the present work it is seen to amount to 5×10^{-6}. The accuracy of this calculation can be trusted to 1×10^{-6}. The only part where crude wave functions were used is in the contribution to g_J from breakdown of L-S coupling. However, in the case of fluorine this correction is only 4×10^{-8}. The use of better wave functions for the excited configuration will not change the calculated value by two orders of magnitude. In other atoms this contribution can be quite important, and may require accurate wave functions for the perturbing terms.

In summary, the calculations based on the Kambe-Van Vleck theory and accurate wave functions can give results accurate to within 1×10^{-6}, provided correlation effects are negligible. It will be worthwhile to re-examine the calculations for other atoms, such as oxygen, where a discrepancy[12] of 10×10^{-6} still remains.

---

*Work supported in part by Facultad de Ciencias, Universidad Nacional Autónoma de México, México D. F., México.

†Work supported in part by Comisión Nacional de Energía Nuclear, México D. F., México.

[1] J. W. Schwinger, Phys. Rev. 73, 416 (1947).

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

[3] C. Sommerfield, Phys. Rev. 107, 328 (1957).

[4] M. Phillips, Phys. Rev. 76, 1803 (1949).

[5] A. Abragam and J. H. Van Vleck, Phys. Rev. 92, 1448 (1953).

[6] M. Phillips, Phys. Rev. 88, 202 (1952).

[7] K. Kambe and J. H. Van Vleck, Phys. Rev. 96, 66 (1954).

[8] D. T. Wilkinson and H. Crane, Phys. Rev. 130, 852 (1963).

[9] W. Lamb, Phys. Rev. 60, 817 (1941).

[10] G. Breit, Phys. Rev. 34, 553 (1929).

[11] W. Perl and V. W. Hughes, Phys. Rev. 91, 842 (1953).

[12] F. R. Innes and C. W. Ufford, Phys. Rev. 111, 194 (1957).

[13] H. E. Radford and V. W. Hughes, Phys. Rev. 114, 1274 (1959).

[14] H. E. Radford, V. W. Hughes, and V. Beltrán-López, Phys. Rev. 123, 153 (1961).

[15] A. M. Karo and L. C. Allen, J. Chem. Phys. 31, 968 (1959).

[16] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. 127, 1618 (1962).

[17] F. W. Brown, Phys. Rev. 44, 214 (1933).

[18] R. F. Bacher and S. A. Goudsmit, *Atomic Energy Levels* (McGraw-Hill Book Co., Inc., New York, 1932).

[19] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935).

[20] J. C. Slater, *The Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., Inc., New York, 1960), Vol. I.

[21] P. O. Löwdin, *Quantum Theory of Atoms, Molecules, and the Solid State* (Academic Press, Inc., New York, 1966).

[22] W. E. Cleland, J. M. Bailey, M. Eckhause, V. W. Hughes, R. M. Mobley, R. Prepost, and J. E. Rothberg, Phys. Rev. Letters 13, 202 (1964).

[23] J. S. M. Harvey, R. A. Kamper, and K. R. Lea, Proc. Phys. Soc. (London) 76, 979 (1960).

Correlation Coefficients for Electronic Wave Functions

Werner Kutzelnigg
Lehrstuhl für Theoretische Chemie der Universität, Göttingen, Germany

and

Giuseppe Del Re
Gruppo Chimica Teorica, Consiglie Nazionale della Ricerche, Roma, Italy

and

Gaston Berthier
Laboratoire de Chimie Quantique, Université de Paris, France

(Received 2 January 1968; revised manuscript received 1 May 1968)

Electron correlation in atoms and molecules can be analyzed in terms of correlation coefficients similar to those used in probability theory and mathematical statistics. Different correlation coefficients can be defined for angular, radial, and momentum correlation in atoms and for axial (left-right), equatorial, and radial (in-out) correlation in molecules. The correlation coefficients are closely related to certain coefficients of the so-called natural expansion of the wave function. Nonvanishing correlation coefficients are obtained for the Fermi correlation in the independent-particle model as well as for electron correlation proper. Numerical examples show that the correlation coefficients for atoms are of the order of −0.05, suggesting that the correlation is usually small and negative, as compared with ±1 for "perfect" correlation. However, positive correlation coefficients may occur, in particular for excited states. Correlation in supersystems consisting of two nonoverlapping systems at large distances, and the distinction between interorbital and intraorbital correlation, are also discussed.

1. INTRODUCTION

The term "electron correlation", introduced by Wigner and Seitz[1] into the quantum mechanics of electron systems, is apparently borrowed from probability theory and mathematical statistics, where correlation is a well-defined concept referring to nonindependent variables. Curiously enough, the formalism used in probability theory to study distributions of correlated variables does not seem to have been applied to electron correlation. We discuss here, both formally and by numerical examples, the introduction of *correlation coefficients* in this field and their connection with more usual concepts. These quantities may provide a useful tool for analyzing electronic wave functions, especially those going beyond the Hartree-Fock method, and for assessing the importance of correlation in many-particle systems.

2. ONE- AND TWO-ELECTRON DISTRIBUTION FUNCTIONS

Given a normalized n-particle wave function $\Psi(1, 2, \cdots, n)$, the one- and two-particle distribution functions $\rho(1)$ and $\pi(1, 2)$ in ordinary space[2] (which are equal to the diagonal elements of the corresponding one- and two-particle density matrices) are defined by[2,3]