Improved Theory of the Zeeman Effect of Atomic Oxygen

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The previous calculations of Abragam and Van Vleck on the g factors of the $2p^4 \, ^3P$ terms of atomic oxygen are refined by including exchange, using better wave functions, and not assuming that the charge distribution in which a $2p$ electron moves is spherically symmetric. In Sec. 2, a general technique is developed for calculating the relativistic and diamagnetic corrections to the g factors of complex atoms (Breit-Margenau and Lamb terms, etc.) by an expansion in spherical harmonics which is an extension of the well-known Slater procedure for computing the angular dependence of electrostatic energy. The integrals encountered are usually either of the Condon and Shortley F, G type, or variants thereof. The most important members are computed by means of the wave functions of Hartree, Hartree, and Swirles, based on a Fock self-consistent field, but some of the minor contributions are estimated with Slater wave functions improved by introducing slightly different screening constants for the $2s$ and $2p$ terms. When all corrections are comprised, including also the Schwinger electrodynamic shift, motion of nucleus, and deviations from Russell-Saunders coupling, the calculated values of the g factors for the $^3P_1$ and $^3P_2$ terms are, respectively, 1.500974, 1.500913, in excellent agreement with Rawson and Beringer's experimental determinations 1.500971, 1.500905.

I. INTRODUCTION

THE gyromagnetic ratios or g values have been measured quite accurately for a number of atoms by molecular beam or microwave techniques in several laboratories.[1] The precision is high enough to detect perceptible departures from the values given by simple vector-coupling theory. The deviations arise from a variety of causes, *viz.* (I) the Schwinger quantum-electrodynamical effect, (II) motion of the nucleus, (III) departures from Russell-Saunders coupling, (IV) relativistic or diamagnetic corrections, including modulation by the magnetic field of spin orbit and the velocity dependent part of the orbit-orbit interaction. The theory has been given for the helium atom by Perl and Hughes,[2] and extended to the n-electron case by Perl.[3] Abragam and Van Vleck[4] have independently developed the theory with particular reference to the oxygen atom. The reader is referred to the latter paper, henceforth called AVV for detailed explanation of the mechanisms underlying the various corrections (I)–(IV) mentioned above. Abragam and Van Vleck made certain approximations, *viz.*, they neglected exchange terms, and in treating the Zeeman contribution of a given electron, they assumed that the charge distribution of the remaining electrons is centro-symmetric, whereas in complex atoms such as oxygen it is not. Also in some places they used rather crude Slater wave functions. It is the purpose of the present article to refine their theory by not making these approximations. A general procedure will be presented in Sec. II, which is not confined to the

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[1] P. Kusch and A. M. Foley, Phys. Rev. 74, 250 (1948); Koenig, Prodell, and Kusch, Rev. Rev. 88, 191 (1952); E. B. Rawson and R. Beringer, Phys. Rev. 88, 677 (1952); Hughes, Tucker, Rhoderick, and Weinreich, Phys. Rev. 91, 828 (1953); Brix, Eisinger, Lew, and Wessel, Phys. Rev. 92, 647 (1953).

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

[3] W. Perl, Phys. Rev. 91, 852 (1953).

[4] A. Abragam and J. H. Van Vleck, Phys. Rev. 92, 1448 (1953), referred to as AVV.

particular case of the oxygen atom. It does not duplicate Perl's theory, as he was concerned mainly with deriving the basic Hamiltonian function [our Eq. (1)] and with applications to systems with only one valence electron. Our analysis in Sec. II furnishes an expansion in spherical harmonics applicable to arbitrary complex atoms.

II. MATRIX ELEMENTS IN THE nlm_lm_s SCHEME

Abragam and Van Vleck have shown that the relativistic and diamagnetic corrections are given by the expectation value of the Hamiltonian operator

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

The explanation of the notation used in Eq. (1) is given in AVV, and will not be repeated here, as the various symbols have their usual significance. We take the magnetic field along the z axis, whence

$$ A_x = -\tfrac{1}{2}yH, \quad A_y = \tfrac{1}{2}xH, \quad A_z = 0. $$

As shown in AVV the first term of (1), proportional to the kinetic energy T, is the relativistic correction proper; the second and third terms derive from spin orbit, the fourth from the spin-other orbit, and the fifth from the magnetic orbit-orbit interaction. The sum of the first three terms is called the Breit-Margenau, the fourth the Lamb correction.

We will show that it is possible to follow a procedure analogous to that in the theory of complex spectra. This analogy is not explicitly brought out in AVV, but is very helpful. The operators involved in (1) are

generalizations of a quantity either of type F or G in the terminology of Condon and Shortley's book[5] (henceforth called TAS). Matrix elements of δZ in the $nlm_l m_s$ scheme can be calculated by making expansions which are similar to those in TAS, but usually considerably more complicated. Transformation to the $SLJM$ scheme will be made in Sec. 3 by the method of diagonal sums.

In the $nlm_l m_s$ scheme a state A can be specified by a complete ordered set a^1, a^2, $\cdots a^N$ of one-electron quantum numbers, where a^i stands for a set of four quantum numbers $nlm_l m_s$. The corresponding orbital function is $R(nl)\Theta(lm_l)\Phi(m_l)$. The first two terms of (1) are of one-electron type, and so easy to evaluate. One readily finds that

$$(A|\delta Z_1|A) = -(\beta H/mc^2)\sum_i(m_l{}^i+2m_s{}^i)(n^il^i|T|n^il^i),\tag{2}$$

$$(A|\delta Z_2|A) = \frac{\beta HZe^2}{mc^2}\sum_i\left(n^il^i\left|\frac{1}{r}\right|n^il^i\right)\frac{[l^i(l^i+1)-1+(m_l{}^i)^2]m_s{}^i}{(2l^i-1)(2l^i+3)}.\tag{3}$$

Here, $(n^il^i|T|n^il^i)$ denotes the kinetic energy of a single n^il^i electron. The contributions from a closed shell to (2) or (3) vanish.

The third and fourth term of δZ will be treated simultaneously. Their combined diagonal element is

$$(A|\delta Z_3+\delta Z_4|A) = (\beta e^2/2mc^2)\sum_{i\neq k}[(2m_s{}^i+4m_s{}^k)J(a^ia^k;a^ia^k)+6m_s{}^i\delta(m_s{}^i,m_s{}^k)J(a^ia^k;a^ka^i)],\tag{4}$$

where

$$J(ab;cd) = (ab|[\nabla_i(1/r_{ik})\times\mathbf{A}_i]_z|cd).\tag{5}$$

The spin dependence of (4) is such that the contributions from interactions within closed shells cancel out, but this is not true of the interactions between closed shells and valence electrons. We calculate the requisite values of (5) in the following way. We first note that

$$\left[\nabla_1\left(\frac{1}{r_{12}}\right)\times\mathbf{A}_1\right]_z = \frac{H}{2}\left[r_1\sin^2\theta_1\frac{\partial}{\partial r_1}+\cos\theta_1\sin\theta_1\frac{\partial}{\partial\theta_1}\right]\left(\frac{1}{r_{12}}\right),\tag{6}$$

and then make the standard expansion (notation as in TAS):

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty}\frac{r_<{}^k}{r_>{}^{k+1}}\frac{4\pi}{2k+1}\sum_{m=-k}^{k}\Theta_1(km)\Theta_2(km)\Phi_1(m)\Phi_2{}^*(m).\tag{7}$$

By appropriate recursion formulas (TAS p. 53), we express $\sin^2\theta_1\Theta_1(km)$, and $\cos\theta_1\sin\theta_1\partial\Theta_1/\partial\theta_1$ as linear combinations of $\Theta_1(k+2m)$, $\Theta_1(km)$, and $\Theta_1(k-2m)$. We thus obtain the result,

$$\left[\nabla_1\left(\frac{1}{r_{12}}\right)\times\mathbf{A}_1\right]_z = \frac{H}{2}\sum_{k=0}^{\infty}\frac{r_<{}^k}{r_>{}^{k+1}}\frac{4\pi}{2k+1}\sum_{m=-k}^{k}\left\{\mp\frac{(k\pm1)(k+1\pm1)+m^2}{2k+1\pm2}\Theta_1(km)\right.$$
$$\left.\pm\frac{(2k+1)}{(2k+1\pm2)}\left(\frac{[(k\pm1)^2-m^2][(k+1\pm1)^2-m^2]}{(2k-1\pm2)(2k+3\pm2)}\right)^{\frac{1}{2}}\Theta_1(k\pm2m)\right\}\Theta_2(km)\Phi_1(m)\Phi_2{}^*(m).\tag{8}$$

Here the upper or lower choice of sign applies according as $r_1>r_2$ or $r_1<r_2$. The integrations over φ involved in taking the expectation values are elementary. Those over θ lead to the well-known expressions of Condon and Shortley, viz.,

$$C^k(lm_l,l'm_l') = [2/(2k+1)]^{\frac{1}{2}}\int_0^{\pi}\Theta(km_l-m_l')\Theta(lm_l)\Theta(l'm_l')\sin\theta d\theta,\tag{9}$$

whose numerical values are tabulated in TAS, p. 178. The radial integrals involved in the direct in distinction from exchange terms are of the form

$$F_>{}^k(nl,n'l') = \int_0^{\infty}dr_1\int_0^{r_1}\frac{r_2{}^k}{r_1{}^{k+1}}R_1{}^2(nl)R_2{}^2(n'l')dr_2.\tag{10}$$

Our expressions $F_>{}^k$ are somewhat different from the Condon and Shortley integrals F^k, which can be defined in terms of the $F_>{}^k$ as follows:

$$F^k(nl,n'l') = F_>{}^k(nl,n'l')+F_>{}^k(n'l',nl).$$

[5] E. V. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), referred to as TAS.

For the special case $n'=n$, $l'=l$, this relation becomes

$$F_>^k(nl,nl)=\tfrac{1}{2}F^k(nl,nl).\tag{11}$$

We find

$$J(ab\,;ab)=\tfrac{1}{2}H\sum_{k=0}^{\infty}\frac{(k+1)(k+2)}{(2k+3)}[F_>^k(n^al^a,n^bl^b)C^k(l^bm_l{}^b,l^bm_l{}^b)$$
$$+F_>^{k+2}(n^bl^b,n^al^a)C^{k+2}(l^bm_l{}^b,l^bm_l{}^b)][C^{k+2}(l^am_l{}^a,l^am_l{}^a)-C^k(l^am_l{}^a,l^am_l{}^a)].\tag{12}$$

In a similar fashion we find that the exchange integrals are given by the following expressions:

$$J(ab\,;b'a)=\frac{H}{4}\sum_{k=0}^{\infty}\sum_{\pm}G^k(n^al^a;n^bl^b)\left\{\frac{2(m_l{}^a-m_l{}^b)^2-(2k^2+2k-1)}{(2k-1)(2k+3)}C^k(l^am_l{}^a,l^bm_l{}^b)\right.$$
$$\left.\pm\left(\frac{[(k\pm1)^2-(m_l{}^a-m_l{}^b)^2][(k+1\pm1)^2-(m_l{}^a-m_l{}^b)^2]}{(2k+1\pm2)^2}\right)^{\tfrac{1}{2}}C^{k\pm2}(l^am_l{}^a,l^bm_l{}^b)\right\}C^k(l^am_l{}^a,l^bm_l{}^b),\tag{13}$$

where G^k is defined as in Condon and Shortley. [There is no need to introduce also an exchange integral $G_>^k$ analogous to (10), as $G_>^k=\tfrac{1}{2}G^k$.] In (13) and elsewhere the symbol $\sum_{\pm}$ means that there is to be a summation sign over both sign choices.

The calculation of the fifth or orbit-orbit term of δZ is based on the same general sort of procedure as for the other terms, but is considerably more laborious. The final result is[6]

$$(A\,|\,\delta Z_5\,|\,A)=-(\beta e^2/mc^2\hbar)\sum_{i\neq k}[M(a^ia^k;a^ia^k)-\delta(m_s{}^i,m_s{}^k)M(a^ia^k;a^ka^i)],\tag{14}$$

with

$$M(ab\,;ab)=\tfrac{1}{2}\hbar H\sum_{k=1}^{\infty}[F_>^{k-1}(n^al^a,n^bl^b)+F_>^{k+1}(n^bl^b,n^al^a)]\left[\frac{k(k+1)(2l^b+1)}{(2k+1)^2(2l^b-1)}\right]^{\tfrac{1}{2}}[\sum_{\pm}\pm C^{k\pm1}(l^am^a,l^am^a)]$$

$$\times[\sum_{\pm}\pm(l^b\mp m_l{}^b)^{\tfrac{1}{2}}(l^b\mp m_l{}^b-1)^{\tfrac{1}{2}}C^k(l^bm_l{}^b,l^b-1m_l{}^b\pm1)],\tag{15}$$

$$M(ab\,;ba)=\tfrac{1}{8}\hbar H\sum_{k=0}^{\infty}(\sum_{\pm}G^{k\pm1}(n^al^a,n^bl^b))$$

$$\times\left\{\sum_{\pm}(m_l{}^a-m_l{}^b\pm2)\left[l_a\frac{(l^a\pm m_l{}^a+1)(l^a\pm m_l{}^a+2)}{(2l^a+1)(2l^a+3)}(C^k(l^a+1m_l{}^a\pm1,\,l^bm_l{}^b))^2\right.\right.$$

$$+\left(\frac{(l^a\mp m_l{}^a-1)(l^a\mp m_l{}^a)(l^a\pm m_l{}^a+1)(l^a\pm m_l{}^a+2)}{(2l^a-1)(2l^a+1)^2(2l^a+3)}\right)^{\tfrac{1}{2}}C^k(l^a+1m_l{}^a\pm1,\,l^bm_l{}^b)C^k(l^a-1m_l{}^a\pm1,\,l^bm_l{}^b)$$

$$\left.-(l^a+1)\frac{(l^a\mp m_l{}^a-1)(l^a\mp m_l{}^a)}{(2l^a-1)(2l^a+1)}(C^k(l^a-1m_l{}^a\pm1,\,l^bm_l{}^b))^2\right]$$

$$+2(m_l{}^a-m_l{}^b)\left[l_a\frac{(l^a+1-m_l{}^a)(l^a+1+m_l{}^a)}{(2l^a+1)(2l^a+3)}(C^k(l^a+1m_l{}^a,\,l^bm_l{}^b))^2\right.$$

$$-\left(\frac{(l^a-m_l{}^a)(l^a+m_l{}^a)(l^a+1-m_l{}^a)(l^a+1+m_l{}^a)}{(2l^a-1)(2l^a+1)^2(2l^a+3)}\right)^{\tfrac{1}{2}}C^k(l^a+1m_l{}^a,\,l^bm_l{}^b)C^k(l^a-1m_l{}^a,\,l^bm_l{}^b)$$

$$\left.\left.-(l^a+1)\frac{(l^a-m_l{}^a)(l^a+m_l{}^a)}{(2l^a-1)(2l^a+1)}(C^k(l^a-1m_l{}^a,\,l^bm_l{}^b))^2\right]\right\}$$

$$+\tfrac{1}{2}\hbar H(m_l{}^a-m_l{}^b)\sum_{k=0}^{\infty}\left\{\int_0^{\infty}\int_0^{\infty}\left[\frac{(1-k)}{2k+1}r_1r_2\frac{r_<{}^k}{r_>{}^{k+1}}+r_2{}^2\frac{r_<{}^{k+1}}{r_>{}^{k+2}}-\frac{k+4}{2k+5}r_1r_2\frac{r_<{}^{k+2}}{r_>{}^{k+3}}\right]\right.$$

$$\left.\times R_1(n^al^a)R_1(n^bl^b)R_2(n^bl^b)\frac{d}{dr_2}\frac{R_2(n^al^a)}{r_2}dr_1dr_2\right\}[C^{k+1}(l^am_l{}^a,l^bm_l{}^b)]^2.\tag{16}$$

In concluding the present section, it should be mentioned that the sums over k in the various expressions which we have derived do not really involve an infinite number of terms and instead in any practical case are limited to a few terms, as is usual for spherical harmonic expansions in atomic spectra. The reason that this is true is that $C^k(lm,l'm')$ vanishes unless k, l, and l' satisfy the so-called triangular condition $k+l+l' = 2q$ (q integral), $|l-l'| \leq k \leq l+l'$.

III. APPLICATION TO THE OXYGEN ATOM

The preceding section gives the general technique for calculating matrix elements in the nlm_sm_l system of representation. The application to oxygen proceeds by specializing the results to the configuration $2p^4$. In addition, it is necessary to transform the results to the $LSJM$ system of representation. This is accomplished by using the invariance of the diagonal sum, together with the fact that the transformation properties of all the first-order Zeeman terms under rotations are such that they must be proportional to the magnetic quantum number M. This feature or trick is explained in AVV and so need not be described here. Some of the manipulations involved in δZ_5 are fairly complicated, and as a check on the accuracy of the calculations they have been reduced to the final form by grouping the integrals in two different ways in the intermediate steps, of which we omit the details.

The final forms for the corrections to the g factors of the $^3P_1$ and $^3P_2$ terms, which as in AVV we denote by Δg_1 and Δg_2, prove to be[6]

$$\Delta g_1 = (8mc^2)^{-1}\{-12\langle T\rangle_{\mathrm{Av}}+2Z\langle 1/r\rangle_{\mathrm{Av}}-[5F^0(2p,2p)-(11/5)F^2(2p,2p)$$

$$+\sum_{n=1,2}(4F_>^2(2p,ns)+(16/3)F_>^0(ns,2p)-(8/5)F_>^2(2p,ns))]$$

$$-2[F^0(2p,2p)+F^2(2p,2p)+\sum_{n=1,2}(4/3)(F_>^0(ns,2p)+F_>^0(2p,ns)$$

$$-(7/20)G^1(2p,ns)-\tfrac{1}{4}G^{-1}(2p,ns)-(1/10)G^3(2p,ns)-\tfrac{3}{4}R(2p,ns))]\}, \quad (17)$$

$$\Delta g_2 = \Delta g_1-(5mc^2)^{-1}\{(Z/2)\langle 1/r\rangle_{\mathrm{Av}}-[\tfrac{3}{4}F^0(2p,2p)+\tfrac{3}{4}F^2(2p,2p)$$

$$+\sum_{n=1,2}(-F_>^0(2p,ns)+(4/3)F_>^2(2p,ns)-G^1(2p,ns)]\}. \quad (18)$$

Here, $\langle T\rangle_{\mathrm{Av}}$ and $\langle 1/r\rangle_{\mathrm{Av}}$ denote the mean values of the kinetic energy and $1/r$ for a $2p$ electron, and G^{-1} is the exchange integral G^k for $k=-1$. The definition of $R(2p,ns)$ is

$$R(2p,ns)=\tfrac{1}{3}\int_0^\infty\int_0^\infty\left(r_1r_2\frac{1}{r_>}+r_2^2\frac{r_<}{r_>^2}-\tfrac{4}{5}r_1r_2\frac{r_<^2}{r_>^3}\right)R_1(2p)R_1(ns)\left(R_2(2p)\frac{d}{dr_2}\frac{R_2(ns)}{r_2}-R_2(ns)\frac{d}{dr_2}\frac{R_2(2p)}{r_2}\right)dr_1dr_2. \quad (19)$$

In Table I we give the numerical values which we use for the various integrals, and also the methods by which these values are calculated. A few comments on the latter are in order. Many of the integrals have already been computed in the paper of Hartree, Hartree, and Swirles[7] (henceforth abbreviated to HHS), or can be estimated quite accurately from data in it. More of the integrals are given in an earlier article by Hartree and Black[8] (HB), which does not, however, include the Fock exchange terms. It is not consistent to calculate some integrals with wave functions which include exchange, and others with functions which do not, but the relatively minor modifications caused by exchange can be extrapolated by comparing the results for the integrals which have been computed by both methods. Some integrals such as G^1 are so small or have such

TABLE I. The numerical values of $\langle T\rangle_{\mathrm{Av}}$ and various radial integrals involved in the expressions for Δg_1 and Δg_2. (All values are in atomic units.)

Integral	Numerical value	Integral	Numerical value
	$13^5\times10^{-6}$		1.11[a]
$F^0(2s,2p)$	0.773[b]	$F^0(1s,2p)$	1.099[c]
$F^0(2p,2p)$	0.754[b]	$F_>^0(2p,1s)$	1.089[d]
$F^2(2p,2p)$	0.336[b]	$F_>^0(2p,2s)$	0.409[e]
$G^1(1s,2p)$	0.092[f]	$F_>^2(2p,1s)$	0.207[d]
$G^1(2s,2p)$	0.472[b]	$F_>^2(2p,2s)$	0.179[e]
$G^{-1}(2p,1s)$	0.173[g]	$G^{-1}(2p,2s)$	1.354[g]
$G^3(2p,1s)$	0.032[g]	$G^3(2p,2s)$	0.291[g]
$R(2p,1s)$	−0.123[g]	$R(2p,2s)$	−0.042[g]

[a] Calculated by numerical integration of the HHS wave function, and also by integration of the Löwdin analytical function. The value 1.11 is obtained in both cases.
[b] Calculated by Hartree, Hartree, and Swirles.
[c] Extrapolated from HB by assuming $F^0(1s,2p) =F^0(1s,2p)_{\mathrm{HB}}+\langle 1/r\rangle_{\mathrm{HHS}}-\langle 1/r\rangle_{\mathrm{HB}}$.
[d] Calculated by the formula $F_>^k(2p,1s) =\langle r^k\rangle_{1s}\langle r^{-k-1}\rangle_{2p}-F_>^{-k-1}(1s,2p)$. The first term is computed with Löwdin functions, while the second is small and is adequately calculated with the modified Slater functions.
[e] Derived from HHS by making a rough estimate of the small difference $F_>^k(2p,2s)-\tfrac{1}{2}F^k(2p,2p)$.
[f] Calculated by D. R. Hartree and M. M. Black.
[g] Calculated from the modified Slater functions.

[6] Mimeographed pages of the algebraic details of the derivation of Eqs. (13)–(18) can be obtained by writing to Miss Esther Reynolds, Librarian, Lyman Laboratory, Harvard University, Cambridge, Massachusetts. This supplementary material is also available as Document with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number 4326 and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.
[7] Hartree, Hartree, and Swirles, Trans. Roy. Soc. (London) A238, 229 (1939), referred to as HHS.
[8] D. R. Hartree and M. M. Black, Proc. Roy. Soc. (London) A139, 311 (1933), referred to as HB.

small coefficients that the distinction between HHS and HB is immaterial. There are also available the elaborate analytical wave functions of Löwdin,[9] which are quite accurate analytical descriptions of the wave functions obtained numerically by HHS, but it is too laborious to calculate anything but one-electron integrals by means of them. When no other method is available, we have utilized a modified form of Slater wave function. The modification consists in using slightly different, rather than identical exponents, for the $2s$ and $2p$ wave functions, viz.,

$$R(2s) = Br^2 e^{-2.195r}, \quad R(2p) = B'r^2 e^{-2.075r}. \quad (20)$$

The exponents have been determined so as to yield the same values of $F^0(2s,2s)$ and $F^0(2p,2p)$ as those obtained numerically with HHS wave functions. Fortunately, all the terms which must be estimated only by means of the modified Slater functions are relatively minor, so that the absence of high precision therein will not vitiate our results.

By far the most important integral or expectation value to know accurately is that involving the mean kinetic energy. This has been calculated by the following three methods, which agree to within one percent:

(a) Direct integration of the kinetic energy operator with Löwdin wave functions.

(b) A method which utilizes the conservation of energy, and which expresses T as a difference between the total energy and an appropriate potential energy. The relevant formula is

$$\langle T \rangle_{Av} = -\tfrac{1}{2}\epsilon_{2p,2p} + Z\langle 1/r \rangle_{Av} - 2F^0(2p,1s) - 2F^0(2p,2s)$$

$$-3F^0(2p,2p) + (3/10)F^2(2p,2p)$$

$$+\tfrac{1}{3}G^1(2p,1s) + \tfrac{1}{3}G^1(2p,2p), \quad (21)$$

where $\epsilon_{2p,2p}$ is the energy parameter of HHS (the

TABLE II. Calculated and observed corrections Δg_1 and Δg_2 to the g factors of the $2p^4 \, ^3P_1$ and $^3P_2$ terms of oxygen. (The uncorrected value is $g=1.5$ for both terms.)

Correction		Δg_1 KVV[a]	AVV[b]	Δg_2 KVV[a]	AVV[b]
$\langle \delta Z_1 \rangle$		-203 ⎫		-203 ⎫	
$\langle \delta Z_2 \rangle$		$+118$ ⎬	-158[c]	$+71$ ⎬	-198[c]
$\langle \delta Z_3 + \delta Z_3 \rangle$	(direct)	-71 ⎭		-70 ⎭	
$\langle \delta Z_3 + \delta Z_3 \rangle$	(exchange)	$+2$	$\cdots$	$+8$	$\cdots$
$\langle \delta Z_5 \rangle$	(direct)	-34	-31	-28	-31
$\langle \delta Z_5 \rangle$	(exchange)	$+15$	$\cdots$	$+9$	$\cdots$
Relativistic and diamagnetic		-173	-189	-213	-229
Motion of nucleus		$+2$	$+2$	$+2$	$+2$
Departure from Russell-Saunders coupling		0	0	-21	-21
Schwinger-Karplus-Kroll		$+1145$	$+1145$	$+1145$	$+1145$
TOTAL		974	958	913	897
Observed		971		905	

[a] Kambe and Van Vleck (present work).
[b] Abragam and Van Vleck (see reference 4).
[c] Sum of the Breit-Margenau and Lamb corrections which is $\langle \delta Z_1 + \delta Z_2 \rangle + \langle \delta Z_3 + \delta Z_4 \rangle$ (direct) in the present calculation. The contribution of the Breit-Margenau corrections (without exchange) is
-142×10^{-6} (for Δg_1), -164×10^{-6} (Δg_2) (K. & V.V.)
-130×10^{-6} (Δg_1), -156×10^{-6} (Δg_2) (A. & V.V.)

[9] P. O. Löwdin, Phys. Rev. 90, 120 (1953).

quantity conserved according to their wave equation— not to be confused with a physical ionization energy). The various integrals in this formula are calculated as shown in the table, mainly with the numerical data of HHS.

(c) A generalized virial theorem. Because of the Fock exchange terms, the virial theorem does not have its usual elementary form, but from the HHS wave equation one deduces that

$$\langle T \rangle_{Av} = \tfrac{1}{2}Z\langle 1/r \rangle_{Av} - F_>^0(2p,1s) - F_>^0(2p,2s)$$

$$-\tfrac{3}{4}F^0(2p,2p) + (3/40)F^2(2p,2p)$$

$$+ (1/6)[G'(1s,2p) + G'(2s,2p)] + \tfrac{1}{3}\sum_{n=1,2}$$

$$\times \int_0^\infty Y_1(ns,2p)R_1(ns)(dR_1(2p)/dr_1)dr_1, \quad (22)$$

where

$$Y_1(ns,2p) = \int_0^{r_1} (r_2/r_1)R_2(ns)R_2(2p)dr_2$$

$$+ \int_{r_1}^\infty (r_1^2/r_2)R_2(ns)R_2(2p)dr_2. \quad (23)$$

The agreement of the mean kinetic energy as obtained from (b) and (c) is a check on the accuracy of the HHS wave functions. This comparison is of interest for this reason quite irrespective of the application to oxygen, and furnishes a method of checking the accuracy of wave functions based on Hartree-Fock fields for other atoms than oxygen.[10] This is one reason why we have included formula (22). The numerical check is, of course, only on the numerical accuracy with which the equations are integrated, and supplies no information concerning the physical soundness of the mathematical model itself.

The values of $\langle T \rangle_{Av}$ obtained by methods (a), (b), and (c) are, respectively, 136, 135, and 133×10^{-6}.

IV. COMPARISON WITH EXPERIMENT FOR OXYGEN

In Table II we list the various corrections to the g factor which we have calculated. The earlier values obtained in AVV are appended for comparison. We also tabulate the various other corrections which must be included and are the same as given in AVV. The new grand total is seen to agree well with the measurements of Rawson and Beringer. The discrepancy is less than either the experimental or theoretical error.

The one fact which is a little disconcerting is that the difference $\Delta g_1 - \Delta g_2$ is not given with higher precision than the absolute values themselves, viz.,

$$\Delta g_1 - \Delta g_2 = 61 \times 10^{-6} \text{ (calc)}, \quad \Delta g_1 - \Delta g_2 = 66 \times 10^{-6} \text{ (obs)}.$$

Experimentally, $\Delta g_1 - \Delta g_2$ can probably be measured more accurately than g_1 or g_2, and this should also be

[10] Our formulas (21) and (22) are specialized to the configuration $2p^4$, but there are analogous expressions in other cases.

true of the theoretical calculations. In fact, the orbit-orbit corrections (as well as the more certain electrodynamical corrections and those for the motion of the nucleus) cancel out entirely from $\Delta g_1 - \Delta g_2$ [see Eq. (18)], and these were the only corrections in which we had to resort to modified Slater wave functions. The deviations from Russell-Saunders coupling are involved solely in the difference $\Delta g_1 - \Delta g_2$, and it is natural to blame them for the discrepancy. However, the spin-orbit parameter involved therein can be estimated quite accurately by extrapolation from atomic spectra [unless perchance, the nondiagonal element $(^3P_2|\zeta_{2p}|^1D_2)$ differs markedly from the diagonal elements[11] $(^1P|\zeta_{2p}|^1P)$ or $(^3P|\zeta_{2p}|^3P)$]. In any case, a discrepancy of only 5×10^{-6} is, after all, very small. Complete reliance cannot be placed on even the most perfect Hartree-Fock wave functions used to compute F^k, etc., because of

approximations basic to the self-consistent field model. The HHS wave functions, for instance, give a spin-orbit parameter about 10 percent too high. (The discrepancy in $\Delta g_1 - \Delta g_2$ would, incidentally, disappear almost completely if we used the HHS rather than spectroscopic value of ζ_{2p} in calculating the deviations from Russell-Saunders coupling, but there appears to be no logical grounds for so doing.) We are hence probably hoping for too much precision, and it certainly does not seem repaying to push further any calculations based on the Hartree-Fock model. The experimental measurements of Rawson and Beringer were originally essayed to see whether there was experimental evidence for the Schwinger electrodynamical corrections in complex atoms. As a result of the present paper we can certainly say that these corrections are confirmed in oxygen, though of necessity with less precision than in atoms with a single valence electron.

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[11] G. W. King and J. H. Van Vleck, Phys. Rev. 56, 464 (1939), find that the diagonal and off-diagonal elements of ζ are appreciably different in mercury, but in light atoms like oxygen the difference may not be as great.

Decay Scheme of I¹³²*

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The radiations of 2.33-hr I¹³² have been investigated with magnetic lens and scintillation spectrometers. Beta rays of 2.12 (18 percent), 1.53 (24 percent), 1.16 (23 percent), and 0.9 (20 percent) Mev have been identified. Gamma rays of 0.528 (25 percent), 0.624 (6 percent), 0.673 (100 percent), 0.777 (75 percent), 0.96 (20 percent), 1.16 (8 percent), 1.40 (11 percent), 1.96 (5 percent), and 2.2 (2 percent) Mev have been observed, and their coincidences are tabulated. A possible decay scheme is proposed which is consistent with the experimental data.

INTRODUCTION

THE routine production[1] of 77-hr Te¹³² — 2.33-hr I¹³² has made available high purity, high specific activity I¹³² sources for the first time. Previous investigations reported β rays[2] with maximum energies of 2.2 and 0.9 Mev, and γ rays[3] of 0.67, 1.41, and 1.99 Mev. A γ ray of energy greater than 2.23 Mev was reported[4] since photoneutron production in D_2O was observed.

In view of the uncertainty in the existing information, it seemed advisable to undertake the present investigation.

Source Preparation

The radioactive Te was separated with carrier Te from pile-irradiated U by a series of hydrolytic precipitations of TeO_2 alternated with precipitation of elemental Te by means of $NaHSO_3$ solution. The final solution consisted of Na_2TeO_3 in NaOH.

Since the half-life of I¹³² is short, it was desirable to use a Te¹³² — I¹³² equilibrium source for the β-ray energy measurements. This source was prepared by evaporating a small aliquot of the above solution on 0.1 mg/cm² nylon one week after the initial Te separation; the I which had grown in during the one-week delay was driven off during the evaporation. Sufficient time was then allowed for the I¹³² to attain equilibrium with the Te¹³² before the measurements were begun. The one-week delay before the separation of Te from I allowed

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[1] Stang, Tucker, Banks, Doering, and Mills, Nucleonics (to be published).

[2] Novey, Sullivan, Coryell, Newton, Sleight, and Johnson, in *Radiochemical Studies: The Fission Products* (McGraw-Hill Book Company, Inc., New York, 1951), Paper No. 135, National Nuclear Energy Series, Plutonium Project Record, Vol. 9, Book 2, part 5, p. 958.

[3] Maienschein, Bair, and Baker, Phys. Rev. 83, 477 (1951).

[4] L. S. Goldring, Brookhaven National Laboratory Quarterly Progress Report, July 1–September 30, 1951 (unpublished); Brookhaven National Laboratory Report BNL-132 (S-11) (unpublished).