

Letters 28, 279 (1968).

³⁸D. Jenkins, R. Kunselman, M. Simmons, and T. Yamazaki, Phys. Rev. Letters 17, 1 (1966); D. Jenkins and R. Kunselman, Phys. Letters 17, 1148 (1966); D. Jenkins and K. Crowe, Phys. Rev. Letters 16, 637 (1966).

³⁹C. Wiegand and D. Mack, Phys. Rev. Letters 18,

685 (1967).

⁴⁰B. R. Riley, J. Fetkovich, J. McKenzie, and I. Wang, Bull. Am. Phys. Soc. 14, 51 (1969); (private communication).

⁴¹J. R. Rook, Nucl. Phys. 9, 441 (1968).

⁴²E. H. S. Burhop, Nucl. Phys. 1, 438 (1967).

Magnetic Moments of Five Levels in the Ground-State Configuration of Ni and O II

V. Beltrán-López and Teodoro González E.

Reactor, Comisión Nacional de Energía Nuclear, México, D. F., México

and

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

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The atomic g_j factor for the ${}^2D_{5/2, 3/2}$, ${}^2P_{3/2, 1/2}$, and ${}^4S_{3/2}$ levels of p^3 configurations of Ni and O II have been calculated with precise Hartree-Fock wave functions. These values are compared with available experimental results. The observed discrepancies are seen to be too large to be attributable to the use of Hartree-Fock wave functions.

I. CALCULATIONS

Five levels arise from the three Russell-Saunders terms of a p^3 configuration. These are ${}^4S_{3/2}$, ${}^2D_{5/2, 3/2}$, and ${}^2P_{3/2, 1/2}$. The Landé g_J factors for these levels are affected by various corrections which have been discussed in several papers.¹⁻⁵ Of these, the so-called relativistic and diamagnetic corrections are calculated by taking the expectation value of the Hamiltonian^{4, 5}

$$\delta Z = \delta Z_1 + \delta Z_2 + \delta Z_3 + \delta Z_4 + \delta Z_5,$$

where

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

In the case of single-determinant wave functions of atomic states, this expectation value has been reduced to radial integrals by Kambe and Van Vleck.⁵ The corresponding value for other states can often be obtained by using a diagonal-rule procedure. In the case of the p^3 configuration however, this procedure is possible for evaluating the corrections of only the ${}^2D_{5/2}$ and ${}^4S_{3/2}$ levels. For the ${}^2D_{3/2}$ and ${}^2P_{1/2}$ levels one must calculate the expectation value directly with the LS -coupled wave functions. If we designate with the letters A , B , C , D , and E the

Slater determinants $(1^+, 1^-, 0^+)$, $(1^+, 0^+, 0^-)$, $(1^+, 1^-, -1^+)$, $(1^+, 1^-, 0^-)$, and $(1^+, 0^-, -1^+)$, respectively, the LS -coupled functions of interest are

$$\begin{aligned} {}^2D_{5/2}^{5/2} &= A, \quad {}^2D_{5/2}^{3/2} = (1/\sqrt{10}) (2B - 2C - \sqrt{2} D), \\ {}^2D_{3/2}^{3/2} &= (1/\sqrt{10}) (B - C + \sqrt{8} D), \\ {}^2P_{3/2}^{3/2} &= (1/\sqrt{2}) (B + C), \quad {}^4S_{3/2}^{3/2} = E. \end{aligned} \quad (2)$$

It is clear, then, that except for the ${}^2D_{5/2}$ and ${}^4S_{3/2}$ levels, it is necessary to calculate the matrix elements of δZ between determinants differing in the quantum numbers of one or two electrons. We have obtained formulas for the matrix elements of δZ_1 and δZ_2 between determinants S and S' differing in the m_s , m_l values of one electron. These formulas are

$$\begin{aligned} \langle S | \delta Z_1 | S' \rangle &= -(-1)^P (\beta H / mc^2) \delta(l, l') \delta(m_s, m'_s) \\ &\quad \times \langle nl | T | n'l' \rangle (m'_l + 2m'_s), \end{aligned} \quad (3)$$

$$\begin{aligned} \langle S | \delta Z_2 | S' \rangle &= -(-1)^P (\beta e^2 Z / 2mc^2) \delta(m_l + m_s, m'_l + m'_s) \\ &\quad \times [m'_s / (2l + 1) (2l + 3)] \\ &\quad \times \{ (l \pm m_l + 1) (l \mp m'_l + 1) [(l + 1)^2 - (m'_l)^2] \}^{1/2} \\ &\quad + [m_s / (2l - 1) (2l + 1)] \\ &\quad \times \{ (l \pm m'_l) (l \mp m_l) [l^2 - (m_l)^2] \}^{1/2}. \end{aligned} \quad (4)$$

In Eqs. (3) and (4) the double signs before m and m' refer to m_s and m'_s ; i. e., the upper sign in m is chosen if $m_s = +\frac{1}{2}$ and the lower if $m_s = -\frac{1}{2}$.

The matrix elements of $\delta Z_{3,4}$ between determinants differing by the quantum numbers of one or two electrons can be obtained from the usual formulas⁶ for two-particle operators if one knows the matrix elements between pairs of electrons with

different quantum numbers. We have obtained these matrix elements for electrons with quantum numbers characterized by the letters a, b, c, d , with the restriction that $l_a = l_b = l_c = l_d$. These elements are given by the expression

$$\begin{aligned} \langle ab | \delta Z_3 | cd \rangle = & \frac{\beta e^2 H}{8mc^2} \delta(m_{s_b}, m_{s_d}) \left\{ \delta(m_{s_a}, m_{s_c}) \delta(m, m_a - m_c) \delta(m, m_a - m_b) \sum_{k=0}^{\infty} c^k(lm_{i_d}, lm_{i_b}) \right. \\ & \times \left[\left(-\frac{[(k-m)(k+m)(k-m+1)(k+m-1)]^{1/2}}{2k-1} c^{k-2}(lm_{i_d}, lm_{i_c}) + \frac{k(k-1)+m^2}{2k+1} c^k(lm_{i_d}, lm_{i_c}) \right) \right. \\ & \times R_{>}^k(dc, ba) + \left(-\frac{(k+1)(k+2)+m^2}{2k+3} c^k(lm_{i_d}, lm_{i_c}) \right. \\ & \left. \left. + \frac{[(k-m+1)(k-m+2)(k+m+1)(k+m+2)]^{1/2}}{2k+3} c^{k+2}(lm_{i_d}, lm_{i_c}) \right) R_{>}^k(ab, cd) \right] \\ & - \left[\sum_{\pm} \delta(m_{s_a}, m_{s_c} \mp 1) \delta(m, m_a - m_b) \delta(m, m_a - m_c \mp 1) \right] \\ & \times \sum_{k=0}^{\infty} c^k(lm_{i_d}, lm_{i_b}) \left[-\frac{[(k-m+1)(k-m+2)(k-m+3)(k+m+1)]^{1/2}}{2k+3} \right. \\ & \times c^{k+2}(lm_{i_d}, lm_{i_c}) R_{>}^k(ab, cd) + [(k-m+1)(k+m)]^{1/2} c^k(lm_{i_d}, lm_{i_c}) \\ & \left. \left. \times \left(\frac{k-m}{2k-1} R_{>}^k(dc, ba) + \frac{k+m+1}{2k+3} R_{>}^k(ab, cd) \right) - \frac{[(k-m)(k+m+2)(k+m-1)(k+m)]^{1/2}}{2k-1} R_{>}^k(dc, ba) \right] \right\}, \end{aligned} \quad (5)$$

where

$$R_{>}^k(ab, cd) = \int_0^{\infty} dr_1 \int_0^{r_1} (r_2^k / r_1^{k+1}) P_1(n_a l_a) P_1(n_c l_c) P_2(n_b l_b) P_2(n_d l_d) dr_2.$$

The matrix elements for δZ_4 can be obtained if we multiply by 2 and make the interchanges $m_{s_a} \leftrightarrow m_{s_b}$ and $m_{s_c} \leftrightarrow m_{s_d}$ in Eq. (4).

The matrix elements of δZ_5 off-diagonal in the determinants B, C, D of Eqs. (2) can be seen to vanish due to the spin independence and invariance of δZ_5 under rotations over the z axis. Using then our results and those contained in Ref. 5, we can obtain expressions for the relativistic and diamagnetic corrections g_{rd} to the g_j factors of the levels. The resulting expressions are

$$\begin{aligned} \delta g_{rd}(^2D_{5/2}) = & \alpha^2 \left\{ -\frac{8}{5} \langle T \rangle_{2p} + \frac{1}{25} Z \langle 1/r \rangle_{2p} + \sum_n \left[-\frac{4}{5} F_{>}^0(ns, 2p) - \frac{2}{25} F_{>}^0(2p, ns) - \frac{16}{25} F_{>}^2(2p, ns) + \frac{2}{15} G^{-1}(2p, ns) \right. \right. \\ & \left. \left. + \frac{23}{75} G^1(2p, ns) + \frac{4}{75} G^3(2p, ns) - \frac{2}{5} R(2p, ns) \right] - \frac{2}{5} F_0(2p, 2p) - \frac{23}{125} F_2(2p, 2p) \right\}, \\ \delta g_{rd}(^2D_{3/2}) = & \alpha^2 \left\{ -\frac{4}{5} \langle T \rangle_{2p} + \frac{2}{75} Z \langle 1/r \rangle_{2p} + \sum_n \left[-\frac{8}{15} F_{>}^0(ns, 2p) - \frac{4}{75} F_{>}^0(2p, ns) - \frac{32}{75} F_{>}^2(2p, ns) + \frac{1}{5} G^{-1}(2p, ns) \right. \right. \\ & \left. \left. + \frac{2}{75} G^1(2p, ns) + \frac{2}{25} G^3(2p, ns) - \frac{3}{5} R(2p, ns) \right] - \frac{1}{10} F_0(2p, 2p) - \frac{32}{125} F_2(2p, 2p) \right\}, \\ \delta g_{rd}(^2P_{3/2}) = & \alpha^2 \left\{ -\frac{4}{3} \langle T \rangle_{2p} + \frac{2}{15} Z \langle 1/r \rangle_{2p} + \sum_n \left[-\frac{8}{9} F_{>}^0(ns, 2p) - \frac{4}{15} F_{>}^0(2p, ns) - \frac{16}{45} F_{>}^2(2p, ns) + \frac{1}{9} G^{-1}(2p, ns) \right. \right. \\ & \left. \left. + \frac{2}{9} G^1(2p, ns) + \frac{2}{45} G^3(2p, ns) - \frac{1}{3} R(2p, ns) \right] - \frac{1}{2} F_0(2p, 2p) - \frac{2}{25} F_2(2p, 2p) \right\}, \\ \delta g_{rd}(^2P_{1/2}) = & \alpha^2 \left\{ -\frac{2}{3} \langle T \rangle_{2p} - \frac{1}{3} Z \langle 1/r \rangle_{2p} + \sum_n \left[-\frac{4}{9} F_{>}^0(ns, 2p) + \frac{2}{3} F_{>}^0(2p, ns) + \frac{2}{9} G^{-1}(2p, ns) + \frac{4}{9} G^1(2p, ns) \right. \right. \\ & \left. \left. + \frac{4}{45} G^3(2p, ns) - \frac{1}{3} R(2p, ns) \right] - \frac{2}{15} F_0(2p, 2p) - \frac{3}{5} F_2(2p, 2p) \right\}, \\ \delta g_{rd}(^4S_{3/2}) = & \alpha^2 \left\{ -2 \langle T \rangle_{2p} + \frac{1}{3} Z \langle 1/r \rangle_{2p} + \sum_n \left[-\frac{4}{3} F_{>}^0(ns, 2p) - \frac{2}{3} F_{>}^0(2p, ns) + \frac{1}{3} G^{-1}(2p, ns) \right] - F_0(2p, 2p) + \frac{1}{5} F_2(2p, 2p) \right\}. \end{aligned} \quad (6)$$

In these equations $\langle T \rangle_{2p}$ and $\langle 1/r \rangle_{2p}$ are the average values of the kinetic energy and the inverse radius of a $2p$ electron, F and G are the usual Slater integrals, and F_2 and R are those defined by Kambe and Van Vleck.⁵

Besides the corrections arising from the relativistic and diamagnetic effects, others arise from the effect of the motion of the nucleus (isotopic effect), the spin-factor anomaly, and the departures from LS coupling. These have been extensively discussed in previous calculations,^{1,2,4,5} and the first two are easily taken into account. Their contributions to the g_J factors are

$$\begin{aligned}\delta g_{\text{sta}}(^2D_{5/2}) &= -\delta g_{\text{sta}}(^2D_{3/2}) = \frac{1}{5}\delta g_s, \\ \delta g_{\text{sta}}(^2P_{3/2}) &= -\delta g_{\text{sta}}(^2P_{1/2}) = \frac{1}{3}\delta g_s, \\ \delta g_{\text{sta}}(^4S_{3/2}) &= \delta g_s,\end{aligned}\quad (7)$$

where^{7,8}

$$\delta g_s = 2319.24 \times 10^{-6},$$

and

$$\begin{aligned}\delta g_{\text{iso}}(^2D_{5/2}) &= \frac{4}{5}\delta g_L, \quad \delta g_{\text{iso}}(^2D_{3/2}) = \frac{6}{5}\delta g_L, \\ \delta g_{\text{iso}}(^2P_{3/2}) &= \frac{1}{2}\delta g_{\text{iso}}(^2P_{1/2}) = \frac{2}{3}\delta g_L, \\ \delta g_{\text{iso}}(^4S_{3/2}) &= 0,\end{aligned}\quad (8)$$

where⁴

$$\delta g_L = -(m/M) \left[1 - \frac{2}{3} \sum_n \left(\int P_{ns} P_{2p} r dr \right)^2 (E_{2p} - E_{ns}) \right]$$

and E_{2p} , E_{ns} are the total energies of the ns and $2p$ electron states.

The corrections arising from the departures of the wave functions from LS coupling are due to the admixing of states of different symmetry with the state under consideration. If all the states belong to the same configuration, the admixture results mainly from spin-orbit interaction. In the case of a p^3 configuration these corrections are

$$\begin{aligned}\delta g_{LS}(^2D_{5/2}) &= 0, \quad \delta g_{LS}(^2D_{3/2}) = \frac{2}{3}(\zeta_{2p}/PD)^2, \\ \delta g_{LS}(^2P_{1/2}) &= 0, \\ \delta g_{LS}(^2P_{3/2}) &= \frac{2}{3}[(\zeta_{2p}/PS)^2 - (\zeta_{2p}/PD)^2], \\ \delta g_{LS}(^4S_{3/2}) &= -\frac{2}{3}(\zeta_{2p}/PS)^2,\end{aligned}\quad (9)$$

where $PS = E(^2P_{3/2}) - E(^4S_{3/2}) \simeq 28880 \text{ cm}^{-1}$, $PD = E(^2P_{3/2}) - E(^2D_{3/2}) \simeq 9653 \text{ cm}^{-1}$, and ζ_{2p} is the spin-orbit parameter of a $2p$ electron in the p^3 configuration.

The numerical evaluation of the radial integrals in δg_{rad} and δg_{iso} has been made with the wave functions of Clementi, Roothaan, and Yoshimine.⁹ Their values expressed in atomic units are shown in Table I. With these and Eqs. (6)–(8) we can obtain the numerical values of the corrections to $g_J(^2D_{5/2})$

and $g_J(^2P_{1/2})$. For the other levels we need also the corrections given by Eqs. (9), the spin-orbit parameter ζ_{2p} is not well known. The reason being that it cannot be obtained from first-order splittings in spectroscopic data, as the diagonal elements of the spin-orbit interaction vanish in a p^3 configuration. Its value has been estimated by extrapolation from neighboring configurations¹⁰ to be 69 cm^{-1} and accurately calculated¹¹ at 72.4 cm^{-1} . Taking the mean ($\zeta_{2p} = 70.4 \text{ cm}^{-1}$) as the true value, we can obtain all the corrections to the g_J factors of the five levels in the p^3 configuration of atomic nitrogen with a Hartree-Fock approximation. These corrections are shown in Table II together with the experimental^{12,13} data and the corresponding differences.

II. DISCUSSION

The calculated values of Table II are seen to differ considerably from the experimental ones. This is somewhat disturbing in view of the excellent agreement obtained in the cases of O ($^3P_{1,2}$) and F ($^2P_{3/2}$). One would first be inclined to attribute the discrepancies to the use of Hartree-Fock (HF) wave functions, particularly in an atom where such wave functions are known to fail in predicting the value of certain parameters such as the hyperfine-structure constant.^{14–16} However, a wave function which correctly predicts the hfs constant necessarily has the symmetry of the corresponding HF wave function and cannot directly alter the g_J values significantly.² This can only occur if wave functions of a different symmetry are allowed to admix. In a configuration-interaction (CI) picture, a possible mechanism for this admixture would be as follows: The wave function $\Psi_0(S, L, J)$ of the ground-state configuration is admixed by electrostatic repulsion with the wave function $\Psi_1(S, L, J)$ of a state of the same symmetry in an excited configuration. This wave function in turn may have an admixture, via spin-orbit interaction of a state $\Psi_1(S', L', J)$ of a different symmetry which can contribute to the g_J factor of the true ground state. The amount of this contribution has been calculated¹⁷ by a perturbation theory which is valid when the electrostatic repulsion between configurations is small compared to their unperturbed electrostatic energy separation. There is no excited configuration in this case, for nitrogen, which could contribute a correction of the size that is needed, on account of the large energy separations. If the electrostatic repulsion between configurations is large compared to their unperturbed energy difference, the contribution to g_J is calculated by degenerate perturbation theory, and it turns out to be fairly independent of the perturbed energy separations, its size being determined mostly by the square of the coupling coefficient of the levels in the excited configuration, i. e., the

TABLE I. Integrals involved in the computation of the relativistic and diamagnetic corrections to g_J .

	Ni			O II		
	$4s$	$2D$	$2P$	$4s$	$2D$	$2P$
$(2p T 2p)$	1.8765	1.8230	1.7893	3.0443	2.9825	2.9420
$(2p 1/r 2p)$	0.9577	0.9421	0.9315	1.2257	1.2118	1.2025
$F_2^0(1s, 2p)$	0.0274	0.0266	0.0262	0.0416	0.0408	0.0403
$F_2^0(2s, 2p)$	0.3398	0.3305	0.3244	0.4503	0.4420	0.4363
$F_2^0(2p, 1s)$	0.9203	0.9056	0.8957	1.1689	1.1558	1.1474
$F_2^0(2p, 2s)$	0.3289	0.3318	0.3336	0.3904	0.3936	0.3956
$F_2^0(2p, 1s)$	0.1036	0.1009	0.0991	0.1468	0.1440	0.1421
$F_2^0(2p, 2s)$	0.1530	0.1526	0.1521	0.1873	0.1874	0.1873
$F_2^0(2p, 2p)$	0.3284	0.3210	0.3160	0.4269	0.4203	0.4159
$F_2^0(2p, 2p)$	0.1479	0.1435	0.1405	0.1958	0.1918	0.1891
$G^{-1}(1s, 2p)$	0.2725	0.2651	0.2603	0.4064	0.3982	0.3930
$G^{-1}(2s, 2p)$	0.9230	0.9152	0.9091	1.0935	1.0902	1.0872
$G^1(1s, 2p)$	0.0870	0.0846	0.0831	0.1305	0.1279	0.1262
$G^1(2s, 2p)$	0.4122	0.4065	0.4024	0.5166	0.5128	0.5099
$G^3(1s, 2p)$	0.0473	0.0460	0.0452	0.0711	0.0697	0.0687
$G^3(2s, 2p)$	0.2373	0.2337	0.2310	0.3016	0.2989	0.2970
$R(1s, 2p)$	-0.1621
$R(2s, 2p)$	0.1489
$I(1s, 2p)$	0.1208	0.1190	0.1178	0.1171	0.1158	0.1149
$I(2s, 2p)$	1.3458	1.3510	1.3534	1.0697	1.0753	1.0787
$E(1s, 2p)$	-1.6885	-1.6625	-1.6423	-2.1913	-2.1592	-2.1615
$E(2s, 2p)$	-0.5731	-0.5838	-0.5904	-0.6030	-0.6182	-0.6222

square of $\alpha = \xi/[E_1(SLJ) - E_1(S'L'J')]$, where ξ is the spin-orbit matrix element between the levels of the excited configuration. We have examined the effect of the $1s^2 2s 2p^3 3s$ configuration. This is a good candidate, as it accounts for 85% of the hfs constant¹⁴ indicating that its unperturbed energy lies close to the ground-state configuration and its effect on the g_J factor is of the second type discussed above. Further, this configuration gives rise to, among others, a $^4S_{3/2}$ level which can spin-orbit couple to a $^4P_{3/2}$ and $^2P_{3/2}$ states. The contribution of these to g_J ($^4S_{3/2}$) in the ground state is proportional to $g'_J - g_J$, where g'_J is the g_J factor of the spin-orbit coupled state and g_J that of a $^4S_{3/2}$ level. The contribution is then negative, i. e., in the right direction to correct g_J ($^4S_{3/2}$). It can also be shown that g_J ($^2D_{5/2}$) would receive positive contributions from $^4D_{5/2}$ and $^4P_{5/2}$ states, which are again in the right direction to correct g_J ($^2D_{5/2}$). The size of

TABLE II. Total correction to the g_J factors of the five levels of the ground-state configurations of Ni and O II.

Level	Ni			O II
	$\delta g_J(\text{calc.})$ ($\times 10^{-6}$)	$\delta g_J(\text{expt.})$ ($\times 10^{-6}$)	$\delta g_J(\text{calc. - expt.})$ ($\times 10^{-6}$)	$\delta g_J(\text{calc.})$ ($\times 10^{-6}$)
$^4S_{3/2}$	2142	2114	27	2026
$^2D_{5/2}$	323	360 ± 10	-36 ± 10	245
$^2D_{3/2}$	-522	-510 ± 20	-12 ± 20	-504
$^2P_{3/2}$	611			394
$^2P_{1/2}$	-916			-1005

these corrections is, however, much too small in view of the following. By utilizing Van Vleck's theorem¹⁸ it can be readily seen that the energy separations between the spin-orbit coupled states are of the size¹⁹ of $G_1(2s, 2p) = 0.47 \text{ a. u.} \approx 10^5 \text{ cm}^{-1}$, while the spin-orbit parameter ζ_{2p} in the excited configuration cannot differ much from ζ_{2p} in the ground state. The magnitude of α^2 then turns out to be about 0.5×10^{-6} . This argument is given further support by looking at other atoms in the same isoelectronic sequence. In these, the $1s^2 2s 2p^3 3s$ configuration is pulled down from the continuum by the increasing nuclear charge²⁰ and the term separations can be seen to be around 10^5 cm^{-1} ; for instance in Ne IV, 4S and 2P in the excited configuration are separated²¹ by $99,800 \text{ cm}^{-1}$. These relative positions are roughly constant along the members of the isoelectronic sequence,²⁰ thus indicating that our calculated values for the term separations in $1s^2 2s 2p^3 3s$ are reasonable.

A non-HF function can also change the calculated value of g_J by changing the values of the radial integrals in Eqs. (6). These changes are, however, much too small to account for the differences. We have, for instance, used wave functions resulting from an unrestricted Hartree-Fock (UHF) treatment of the nitrogen atom¹⁵ to calculate g_J ($^4S_{3/2}$) within an UHF picture; i. e., Eqs. (6) have to be modified to account for the fact that in such a picture $P_{ns}^+ \neq P_{ns}^-$. The resulting value for the relativistic and diamagnetic corrections δg_{rd} ($^4S_{3/2}$) = $170. \times 10^{-6}$, which makes slightly worse the disagreement with

the experimental value.

It is then hard to see how the large differences between experimental and calculated values can be removed by using a wave function which can be expanded in terms of the solutions to the HF average field. A further test of this can be afforded by measurements of the g_J factors in other members of the nitrogen isoelectronic sequence. In these, the interaction with $1s^2 2s 2p^3 ns$ -type configurations

should be different and probably smaller. We would then expect fairly constant differences between calculated and experimental values if our arguments are correct. With this possibility in mind we have calculated the g_J values in the five levels of OII, for which good HF wave functions are available.²² The calculated values are given in Table II, and the necessary integrals computed with good HF wave functions²² in Table I.

¹V. Beltrán-López, E. Ley-Koo, N. Segovia, and E. Blaisten, *Phys. Rev.* **172**, 44 (1968).

²V. Beltrán-López, E. Blaisten, N. Segovia, and E. Ley-Koo, *Phys. Rev.* **177**, 432 (1969).

³J. S. M. Harvey, *Phys. Rev.* **181**, 1 (1969).

⁴A. Abragam and J. H. Van Vleck, *Phys. Rev.* **92**, 1448 (1953).

⁵K. Kambe and J. H. Van Vleck, *Phys. Rev.* **96**, 66 (1954).

⁶E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U. P., Cambridge, England, 1953).

⁷C. Sommerfield and N. M. Kroll, *Phys. Rev.* **77**, 536 (1950).

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

⁹E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.* **127**, 1618 (1962).

¹⁰C. W. Ufford and R. M. Gilmour, *Astrophys. J.* **111**, 580 (1950).

¹¹M. Blume and R. E. Watson, *Proc. Roy. Soc. (London)* **A270**, 127 (1962).

¹²M. A. Heald and R. Beringer, *Phys. Rev.* **96**, 645 (1954).

¹³H. E. Radford and K. M. Evenson, *Phys. Rev.* **168**, 70 (1968).

¹⁴N. Bessis-Maxloun and H. Lefebvre-Brion, *Compt. Rend.* **251**, 648 (1960).

¹⁵D. A. Goodings, *Phys. Rev.* **123**, 1706 (1961).

¹⁶H. F. Schaefer III, R. A. Klemm, and F. E. Harris, *Phys. Rev.* **176**, 49 (1968).

¹⁷M. Phillips, *Phys. Rev.* **88**, 202 (1952).

¹⁸J. C. Slater, *The Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vols. I and II.

¹⁹Calculated with the Slater-type approximate wave functions $P_{2s} = 7.87 [1.19 r \exp(-6.7r) - r^2 \exp(-2.125r)]$, $P_{2p} = 7.6r^2 \exp(-2.125r)$. The value of $G_1(2S, 2p)$ is 0.484. Its value from Ref. 18 is 0.464.

²⁰R. N. Zare, *J. Chem. Phys.* **45**, 1966 (1966).

²¹*Atomic Energy Levels*, Natl. Bur. Std. (U. S.) Circ. No. 467. (U. S. GPO, Washington, D. C., 1949), Vol. I.

²²C. C. J. Roothaan and P. S. Kelly, *Phys. Rev.* **131**, 1177 (1963).

$W^3\Delta_u - X^1\Sigma_g^+$ System of N_2 †

K. A. Saum and W. M. Benesch

Institute for Molecular Physics, University of Maryland, College Park, Maryland 20742

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Bands of $W^3\Delta_u - X^1\Sigma_g^+$, a new system of molecular nitrogen, have been identified in absorption from their locations as predicted by the spectroscopic constants obtained in infrared emission. Three bands have been observed and measured, the (5,0), (6,0), and (7,0). A Deslandres table with Franck-Condon factors is presented, which indicates that the system will occur most readily below 2500 Å. The relevant potential energy curves for the system are given with the observed transitions displayed.

The $W^3\Delta_u$ state of molecular nitrogen was first identified in the course of a series of experiments which measured the infrared emission spectrum from discharges through nitrogen^{1,2} and oxygen³ 1–5- μ wavelength. A group of 15 bands of the system $W^3\Delta_u \leftrightarrow B^3\Pi_g$ have thus far been identified, comprising eight of the mode $W \rightarrow B$ and seven of the mode $W \rightarrow B$, all in emission. This array of data, developed from spectra of moderate resolution,

yields a set of spectroscopic constants among which ω_e is good to 1%.

These constants form the basis for the generation of potential curves for the state in question, the $W^3\Delta_u$, as well as Deslandres tables and Franck-Condon factors for band systems involving all other known electronic states of the molecule. One of these tables, containing band frequencies and Franck-Condon factors, has been given previously