

## Effect of correlation on $2p$ -row atomic $g_J$ factors

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The effect of correlation on the  $g_J$  factors of ground-state and some metastable  $2s$ - and  $2p$ -row atoms is evaluated from experimental data and theoretical values calculated within the Hartree-Fock scheme. By taking the accurate experimental  $g_J(^4S_{3/2})$  values of atomic nitrogen as reference, the effect is seen to amount to  $-1.0$  ppm per unpaired  $2l$  electron. A configuration-interaction calculation for  $g_J(\text{N}; ^4S_{3/2})$  yields a value that agrees with experiment to within  $0.24$  ppm. This also shows that the effect of correlation on  $g_J(\text{N}; ^4S_{3/2})$  is mainly due to core polarization and amounts to  $-0.94$  ppm per polarizing  $2p$  electron.

Atomic  $g_J$  factors have been investigated extensively over several decades with the purpose of testing the theory of atomic magnetism by contrasting theoretical calculations with experimental measurements of ppm accuracy. From the definition

$$g_J = \left[ \frac{\partial \langle \Phi | \mathcal{H} | \Phi \rangle}{\partial H} \right]_{H=0} / (\mu_0 M_J),$$

where  $\mathcal{H}$  is the Hamiltonian of the atom in an external magnetic field  $H$  and  $\mu_0 = e\hbar/2m_e c$ , it is seen that the main structure-dependent deviation of an atomic  $g_J$  factor from the rational Landé value is due to contributions of order  $\alpha^2$  which are due to relativistic and diamagnetic effects.<sup>1</sup> Since the validity of the relativistic Breit Hamiltonian in which the theory of this effect is based is well established by the excellent agreement obtained by Pekeris<sup>2</sup> for the energy and the ionization potentials in  $\text{He}(1s^2, ^1S_0)$ ,  $\text{He}(1s2s, ^3S_1)$ , and  $\text{He}(1s2s, ^1S_0)$  the calculation of the  $g_J$  factors to the order of  $\alpha^2$  has centered in recent years in weighing the capabilities of different methods of calculation to predict experimental atomic  $g_J$  values of varying accuracies. There are hits and misses for nearly all methods from Hartree-Fock (HF) to many-body perturbation theory (MBPT) and odd values which defy any method of calculation,<sup>3</sup> but still no well-defined idea of the effect of structure in the  $g_J$  factors. Some of this confusion can be seen to be due to the lack of precision in some of the experimental values which for several important cases rely on proton  $g_p'$  values in different samples and environments.<sup>4</sup> The very precise value measured by Hirsch *et al.*<sup>5</sup> for  $g_J(\text{N}, ^4S_{3/2})$ , however, can now be used as a reference to obtain more precise  $g_J$  values for other atoms, as well as for discerning the influence of various effects on these factors. In a recent article we used this  $g_J(\text{N}, ^4S_{3/2})$  value to remeasure  $g_J$  factors for some atomic nitrogen and oxygen states.<sup>1</sup> In this Brief Report we would like to add a comment on the effect of electron correlation on the  $g_J$  factors of first- and second-row atoms, which follows from it.

The correlation energy of a system is the difference between the energy value obtained for an exact, nonrelativistic solution of Schrödinger equation and the

Hartree-Fock energy. Since the exact solution is not generally available, the correlation energy is approximated by taking the difference between the experimental and the HF values. This difference contains other minor contributions besides electron correlation, but it will generally be a good approximation to it. With this provision we also call the effect of correlation in the  $g_J$  factor the difference  $g_J(\text{expt.}) - g_J(\text{HF})$ , except for  $g_J(\text{He}, 1s2s ^3S_1)$ , for this can be calculated accurately by using parameters derived from the completely correlated wave functions of Pekeris for the excited helium atoms.<sup>2</sup>

There are two atomic  $g_J$  factors for which the correlation effects are known precisely;  $g_J(\text{H}, ^2S_{1/2}) = g_e(1 - \alpha^2/3)$  for which obviously there are no correlation effects and  $g_J(\text{He}, 1s2s ^3S_1) = g_e[1 - (\alpha^2/3)(\langle \Phi | T | \Phi \rangle + \langle \Phi | r_{12}^{-1} | \Phi \rangle / 2)]$ ,<sup>6</sup> for which HF and electron-correlated atomic parameters and energy values are known. In these expressions  $g_e = 2.002\,319\,304\,386(20)$  is the free electron  $g$  factor<sup>7</sup> and  $T$  the kinetic-energy operator. A semiempirical value calculated from spectroscopically derived data, which should show the influence of other effects, can also be obtained by applying the virial theorem  $\langle \Phi | T | \Phi \rangle = -W_0$ ,<sup>6</sup> where  $W_0$  is the total energy. These values are listed in Table I. We see from these that neither electron correlation nor other effects should be noticeable in  $g_J(\text{He}, 1s2s ^3S_1)$  to the order of  $\alpha^2$ , or about  $0.5$  ppm, which is the limit of validity of the Breit Hamiltonian and of the theory. The experimental value, derived from a measurement of  $g_J(\text{He}, ^3S_1)/g_J(\text{H}, ^2S_{1/2})$  and the theoretical value of  $g_J(\text{H}, ^2S_{1/2})$ , agrees with these theoretical values, but it is  $1$  ppm above them if the derivation involves the  $g_p'$  value of protons in a sample of mineral oil.<sup>4</sup> The ratio  $g_J(\text{He}, ^3S_1)/g_J(\text{H}, ^2S_{1/2})$  should also show no correlation effects to the order of  $\alpha^2$ . The agreement between the HF, the correlated, and the experimental values for this ratio is also seen in Table I.

The effect of correlation can also be assessed for the  $g_J$  factor of atomic nitrogen. Its value in the  $^4S_{3/2}$  ground state is known from experiment<sup>5</sup> to about  $0.02$  ppm, or  $0.1\alpha^3$ ; i.e., it is exact for purposes of comparison with values calculated with a theory which is valid only to the

TABLE I. Theoretical values of  $g_J$  factors for  $\text{He}(1s2s, {}^3S_1)$  calculated by various methods. Experimental values are also listed.

Method of evaluation	$\langle \Phi   T   \Phi \rangle$	$\langle \Phi   r_{12}^{-1}   \Phi \rangle$	$g_J(\text{He}; 1s2s {}^3S_1)$	$g_J(\text{He}, {}^3S_1)/g_J(\text{H}, {}^2S_{1/2})$
Hartree-Fock <sup>a</sup>	2.174 251	0.268 974	2.002 23718 <sup>a</sup>	$1-23.23 \times 10^{-6}$
Complete electron correlation <sup>b</sup>	2.175 229	0.268 197	2.002 23716 <sup>b</sup>	$1-23.23 \times 10^{-6}$
Semiempirical from spectroscopic data <sup>c</sup>	2.175 325	0.268 198	2.002 23715 <sup>c</sup>	$1-23.24 \times 10^{-6}$
Experimental <sup>d</sup>			2.002 238(2) <sup>d</sup>	
			2.002 237(2) <sup>e</sup>	$1-23.23(1.0) \times 10^{-6}$

<sup>a</sup>From data in Refs. 6 and 8.

<sup>b</sup>From data in Refs. 2 and 6.

<sup>c</sup>From data in Refs. 2, 6, and 9.

<sup>d</sup>From data in Ref. 4. This value is based on a scale in which the magnetic moment of protons in a spherical sample of mineral oil is exactly  $1/657.466$  Bohr magnetons.

<sup>e</sup>From Ref. 10. This value is obtained from the experimental value of  $g_J(\text{He}, {}^3S_1)/g_J(\text{H}, {}^2S_{1/2})$  and the theoretical value of  $g_J(\text{H}, {}^2S_{1/2})$ .

order of  $\alpha^2$ . The difference between the experimental and the precise HF value is  $[g_J(\text{N}, {}^4S_{3/2})]_{\text{expt}} - [g_J(\text{N}, {}^4S'_{3/2})]_{\text{HF}} = (-6.11 \pm 0.02) \times 10^{-6} = -3.06 \pm 0.01$  ppm. For other  $2p$ -row atoms the effect of correlation  $g_J(\text{expt.}) - g_J(\text{HF})$  is known with degrees of accuracy above 1 ppm.

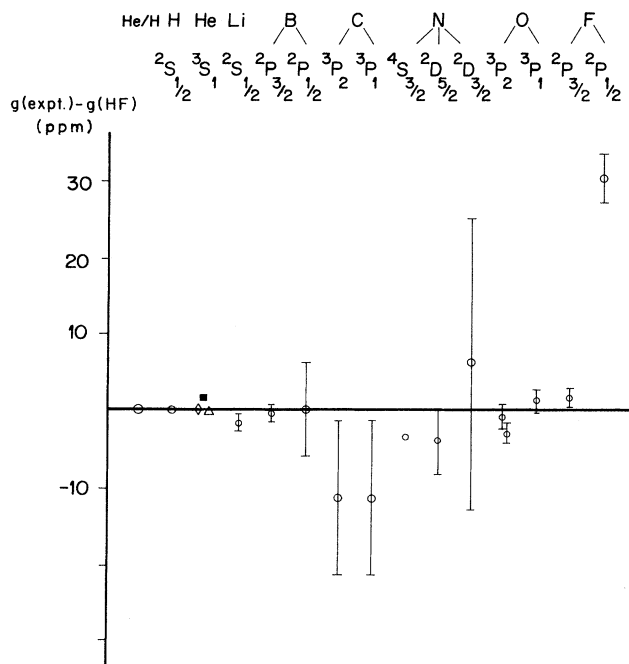


FIG. 1. The effect of correlation on the  $g_J$  factors of ground-state and metastable  $2s$  and  $2p$ -row atoms evaluated from experimental and Hartree-Fock values.  $\circ$ , from experimental and HF values.  $\blacksquare$ , based on  $\mu_p(\text{oil}) = \mu_0/657.466$ , Ref. 10.  $\blacktriangle$ , from completely correlated functions.  $\diamond$ , from experimental values of  $g_J(\text{He}; {}^3S_1)/g_J(\text{H}; {}^2S_{1/2})$  and of  $g_J(\text{H}; {}^2S_{1/2})$ .

Figure 1 shows these results for ground and excited states of the first- and second- row atoms. The absence of polarization and of the correlation effect in  $g_J(\text{He}, {}^3S_1)$ , and its general trend in the  $2p$ -row atoms suggests that it depends strongly on the polarizing effect of the unbalanced  $2p$  electrons. Disregarding the result for  $\text{F}(2p^4, {}^2P_{1/2})$  in view of its very large and unrepresentative deviation and taking an average of the remaining results for  $2p$  atoms, weighted inversely as the error bars, it is seen that the effect is negative, largest in  $\text{N}(2p^3, {}^4S_{3/2})$  and amounts to about  $-1.0$  ppm per polarizing  $2l$  electrons in  $\text{N}(2p^3, {}^4S_{3/2})$  and in  $\text{Li}(2s, {}^2S_{1/2})$ . The effect, per polarizing  $2p$  electron, is of the same size in  $\text{O}(2p^4, {}^2P_2)$  if calculated from the most recent experimental value.<sup>1</sup> Extrapolating with this estimate to  $\text{O}(3P_1)$  and  $\text{F}(2P_{3/2})$  we find that correlation effects in these atomic states should be around  $-2.0$  and  $-1.0$  ppm; whereas Fig. 1 shows values of  $+1.0$  and  $+1.5$  ppm, respectively. This difference, however, is seen to be substantially smaller by noting that the oxygen and the fluorine results are referred to the proton  $g'_p$  factor in mineral oil and this may have raised those  $g_J$  factors by as much as 4 ppm.<sup>4</sup> This upward shift is also shown by the experimental value of  $g_J(\text{He}, {}^3S_1)$  involving  $g'_p$  in its derivation. The old values of  $g_J(\text{O}, {}^2P_1)$  and  $g_J(\text{F}, {}^2P_{3/2})$  may then be smaller and of sizes consistent with our estimate of  $-1.0$  ppm per polarizing  $2p$  electrons. At any rate, the well-known good agreement of the HF calculations with the experimental values for these  $g_J$  factors seems to be well founded by these results. On the other hand, the effect of correlation in  $g_J(\text{F}, {}^2P_{1/2})$  is completely out of proportion and of sign agreement with the average of  $-1.0$  ppm per polarizing  $2p$  electron. This may be due to a very special effect in  $\text{F}(2P_{1/2})$  but, more likely, it indicates some error in either the HF calculation or the experimental value.

To further test the effect of core polarization on the  $g_J$  factors of the  $2p$ -row atoms we performed a configuration-interaction (CI) calculation of  $g_J(\text{N}, {}^4S_{3/2})$ .

Besides having the best-known experimental value<sup>5,11</sup> of  $g_J$ , nitrogen has the advantage that the effect of core polarization manifests itself in a nonzero value of its hyperfine structure constant  $a_J$ . One can thus separate the effect of core polarization from other correlation contributions to  $g_J$  by constructing the wave function using only configurations that contribute strongly to  $a_J$ .

The starting point is the orbital basis obtained by Clementi, Roothaan, and Yoshimine<sup>12</sup> in an analytical single-configuration Hartree-Fock calculation. The single excitations  $1s \rightarrow ns$ ,  $1s \rightarrow nd$ ,  $2s \rightarrow ns$ ,  $2s \rightarrow nd$ , and  $2p \rightarrow np$  were added to this ground-state configuration. The excited orbital basis is the one used by Schaefer, Klemm, and Harris<sup>13</sup> to construct the polarization wave function in their calculation of  $a_J$ . The exponents of the Slater-type orbitals of both basis sets are given in Table II. The exponents and number of basis orbitals were optimized by Schaefer, Klemm, and Harris<sup>13</sup> to assure convergence. The  $1s$ ,  $2s$ , and  $2p$  occupied orbitals are the same as those used by Clementi, Roothaan, and Yoshimine.<sup>12</sup> The  $ns$ ,  $np$ , and  $nd$  unoccupied orbitals were obtained from the basis in Table II following an orthonormalization procedure.

Each of the single excitations  $1s \rightarrow nd$ ,  $2s \rightarrow nd$ , and  $2p \rightarrow np$  give rise to only one  $^4S$  term. On the other hand, there are two different  $^4S$  terms that originate from the  $1s \rightarrow ns$  or  $2s \rightarrow ns$  excitations, and they can be labeled according to whether the unpaired core electron and the excited electron couple to form a singlet or triplet intermediate state. All  $(1sns \ ^1S)p^3 \ ^4S$ ,  $(1sns \ ^3S)p^3 \ ^4S$ ,  $(2sns \ ^1S)p^3 \ ^4S$ , and  $(2sns \ ^3S)p^3 \ ^4S$  terms were included in this work. The CI calculation was carried out with the 41  $^4S$  terms which can thus be constructed with the ground-state HF spin orbitals and the six  $ns$ , six  $nd$ , and four  $np$  excited orbitals.

TABLE II. Exponents  $\xi$  of radial wave functions.

Occupied orbitals <sup>a</sup>					
		$\xi$		$\xi$	
$1s$	6.4595	$2p$	1.1937		
$1s$	10.8389	$2p$	1.7124		
$2s$	1.4699	$2p$	3.0112		
$2s$	1.9161	$2p$	7.1018		
$2s$	3.1560				
$2s$	5.0338				
Unoccupied orbitals <sup>b</sup>					
$\xi$		$\xi$		$\xi$	
$1s$	10.0	$2p$	3.69	$3d$	23.33
$1s$	4.69	$2p$	2.42	$3d$	10.94
$2s$	3.69	$3p$	2.52	$3d$	5.17
$2s$	2.42	$3p$	1.81	$3d$	3.39
$3s$	2.52			$3d$	2.52
$3s$	1.81			$3d$	1.81

<sup>a</sup>Exponents of orbitals  $1s$ ,  $2s$ ,  $2p$  of the single-configuration Hartree-Fock calculation, Ref. 12.

<sup>b</sup>Exponents used by Schaefer, Klemm, and Harris, Ref. 13, to construct the polarization wave function.

Computer programs were written to calculate the matrix elements of the Hamiltonian between any two of these  $^4S$  terms, and a standard diagonalization procedure was followed to obtain the mixing coefficients and the energy eigenvalue of the ground-state wave function. Convergence was tested by performing the calculation for the energy and  $a_J$  with a smaller set of terms in which the  $ns$  excited orbitals were constructed from the HF basis of Clementi, Roothaan and Yoshimine.<sup>12</sup> No change was found for the energy while  $a_J$  appears to converge to a value of 10.07 MHz. The correction to  $g_J$  was obtained by calculating the expectation value of the Abragam-Van Vleck operators<sup>14</sup>

$$\begin{aligned} \delta Z_1 &= -\mu_0 \mathbf{H} \cdot \sum_i (l_i + \sigma_i) T_i / mc^2, \\ \delta Z_2 &= -(\mu_0 e^2 Z / i2mc^2) \sum_i [\nabla_i (1/r_i) \times \mathbf{A}_i] \cdot \sigma_i, \\ \delta Z_3 &= (\mu_0 e^2 / 2mc^2) \sum_{\substack{i,k \\ i \neq k}} [\nabla_i (1/r_{ik}) \times \mathbf{A}_i] \cdot \sigma_i, \\ \delta Z_4 &= (\mu_0 e^2 / 2mc^2) \sum_{\substack{i,k \\ i \neq k}} [\nabla_i (1/r_{ik}) \times \mathbf{A}_i] \cdot 2\sigma_k, \\ \delta Z_5 &= -(e^3 / 2m^2 c^3) \sum_{\substack{i,k \\ i \neq k}} [r_{ik}^{-1} (\mathbf{A}_i \cdot \mathbf{p}_k) \\ &\quad + r_{ik}^{-3} (\mathbf{r}_{ik} \cdot \mathbf{A}_i) (\mathbf{r}_{ik} \cdot \mathbf{p}_k)], \end{aligned}$$

with this polarization wave function. The nonzero matrix elements of these operators were calculated using the explicit formulas given by Beltrán-López and González.<sup>15</sup>

Table III shows a comparison of our results for the energy, for the hyperfine structure constant  $a_J$ , and for the  $g_J$  factor with the experimental values<sup>3,5,17</sup> and with results of many-body perturbation theory calculations.<sup>3,16</sup> With our polarization wave function we obtain 27% of the correlation energy, 96% of the hyperfine structure constant  $a_J$  and 92% of the difference  $g_J(\text{expt.}) - g_J(\text{HF})$ . These results show a deviation for  $g_J$  of  $-0.94$  ppm per polarizing  $2p$  electron, in close agreement with the value of  $-1.0$  ppm derived from the analysis of Fig. 1. The CI results are also in good agreement with those from MBPT, except for the correlation energy. This, however, should be expected because the CI calculation includes only the effect of core polarization, while the MBPT calculation takes into account correlation effects from double excitations also.

TABLE III. Results.

	This work	MBPT	Experimental results
$E - E(\text{HF})$ (hartree)	-0.0508	-0.1618 <sup>a</sup>	-0.1886 <sup>b</sup>
$a_J$ (MHz)	10.07	10.49 <sup>c</sup>	10.45 <sup>d</sup>
$g_J - g_J(\text{HF})$ (ppm)	-2.81	-2.70 <sup>a</sup>	-3.06 <sup>e</sup>

<sup>a</sup>Reference 3.

<sup>b</sup>Estimated from experiment: Ref. 3.

<sup>c</sup>Reference 16.

<sup>d</sup>Reference 17.

<sup>e</sup>Reference 5.

The experimental result of  $g_J - g_J(\text{HF})$  depends on the value used for the spin-orbit parameter  $\zeta_{2p}$  used for calculating the correction due to departure from  $LS$  coupling. In this work we used the basically empirical value<sup>15</sup>  $\zeta_{2p} = 70.4 \text{ cm}^{-1}$ . If one uses instead the result of a HF calculation,<sup>8</sup>  $\zeta_{2p} = 75.5$ , this correction moves the experimental value upward by 0.4 ppm, making the agreement with the present calculation even better. An

accurate experimental determination of  $\zeta_{2p}$  is, then, seen to be needed in order to carry this calculation to the level of accuracy of the experimental value. However, the agreement of the present calculation with experiment is within 0.3 ppm for any reasonable value of  $\zeta_{2p}$ . Further work is now underway to extend this CI calculation to the ground states of other  $2p$ -row atoms, and the metastable states of nitrogen.

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