Spin-extended Hartree-Fock calculations of atomic g_J factors

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g_J-factor corrections for the ground states of the first-row atoms and sodium are calculated by use of spin-extended Hartree-Fock (SEHF) wave functions. The present results are compared with Hartree-Fock values and experimental g_J factors. The theoretical SEHF g_J factors show a deviation from the experimental ones which increase very regularly from lithium to fluorine. These discrepancies are believed to arise from the neglect of correlation effects, and they indicate that the previous success of the Hartree-Fock theory in the cases of oxygen and fluorine is fortuitous. Hartree-Fock values are also presented for the g_J-factor corrections of the ground states of the second-row atoms, and for potassium, rubidium, bromine, and iodine.

I. INTRODUCTION

The prediction of the radiation correction to the electronic spin g factor g_e stimulated an increased interest in precision measurements of atomic g_J factors some 30 years ago. It was, however, not straightforward to deduce g_e from measured g_J factors since a number of rather complex corrections had to be considered. These corrections arose from relativistic and diamagnetic effects, from the departure from LS coupling, and from the motion of the atomic nucleus. Today the radiation correction to g_e is extremely well established through measurements on free electrons, and the current interest in atomic g_J factors stems from its impact on atomic structure theories. Among the relativistic and diamagnetic corrections are complex two-electron quantities which need to be computed within error limits of a few percent to cope with experimental uncertainties for the first row atoms, and even much better for some alkali metals. Needless to say, this task represents a profound test of current atomic wave functions. In several previous investigations Hartree-Fock wave functions have been used to calculate the required expectation values. For a few examples, i.e., for the oxygen ground state and the $^2P_{3/2}$ state of fluorine, the results are surprisingly good,[1,2] indicating theoretical accuracies of 0.5–1%. However, in other cases, in particular for the ^4S ground state in nitrogen and the $^2P_{1/2}$ state in fluorine, the Hartree-Fock functions are unable to provide satisfactory agreement with experiments. Even for the lithium ground state there is a clear disagreement between the Hartree-Fock results and the experimental g_J factor. In the simple case of Li Hegstrom[3] has shown that the use of a spin-extended Hartree-Fock wave function (spin-polarization) yields excellent agreement with experiment. Spin-extended Hartree-Fock (SEHF)

functions are also available for the other first-row atoms and for sodium, and the main subject of the present work is to investigate the effect of spin polarization on the g_J-factor corrections for systems more complex than Li. For atoms heavier than Li it is impractical to give SEHF functions explicitly as linear combinations of determinants, and a special formalism given by Harris[4] for computation of expectation values has to be adapted to the present problems. At least one dominant relativistic correction [cf. δH_2 of Eq. (3)] is expected to be particularly sensitive to spin polarization, and the present numerical results nicely confirm this expectation. The more accurate SEHF calculations will also allow a test of the reliability of the apparently successful Hartree-Fock predictions.

Hartree-Fock values of the g_J-factor corrections of the ground states of the heavier elements Cl, Br, I, K, and Rb are also computed and compared with precise experimental results. Finally, theoretical g_J factors are given in the Hartree-Fock approximation for the remaining second-row atoms.

II. THE ATOMIC g_J FACTOR

The standard expression for the Zeeman Hamiltonian of atoms is

$$H_Z = \mu_B \vec{B} \cdot (\vec{L} + g_e \vec{S}), \tag{1}$$

where g_e is the free electron g value including the radiation correction, $g_e = 2.002\,319\,288(14)$. For weak fields first-order theory applies, and the shifts of the energy level are given by

$$\langle LSJM_J | H_Z | LSJM_J \rangle = \mu_B B g_J M_J,$$

with the following expression for the atomic g_J factor,

$$g_J = 1 + (g_e - 1)\frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}. \tag{2}$$

Precision measurements of atomic g_J factors, however, reveal deviations from the values predicted by the simple formula Eq. (2). There are several effects which account for this discrepancy. These are the relativistic and diamagnetic corrections, departure from LS coupling, and a correction due to the motion of the atomic nucleus. The relativistic and diamagnetic corrections have been considered by several authors and given in a convenient form by Abragam and Van Vleck.[5] For the present discussion it is useful to divide the relativistic and diamagnetic contriubtions to the Hamiltonian (δH_{RD}) into five parts:

$$\delta H_{RD} = \sum_{k=1}^{5} \delta H_k,$$

the various δH_k's being given by

$$\delta H_1 = - \mu_B \vec{B} \cdot \sum_i \frac{T_i}{mc^2} \vec{l}_i,$$

$$\delta H_2 = - \mu_B \vec{B} \cdot \sum_i \frac{2T_i}{mc^2} \vec{s}_i,$$

$$\delta H_3 = - \frac{\mu_B Ze^2}{mc^2} \sum_i \left[\vec{\nabla}_i \left(\frac{1}{r_i} \right) \times \vec{A}_i \right] \cdot \vec{s}_i, \tag{3}$$

$$\delta H_4 = \frac{\mu_B e^2}{mc^2} \sum_{i,j(i\neq j)} \left[\vec{\nabla}_i \left(\frac{1}{r_{ij}} \right) \times \vec{A}_i \right] \cdot (\vec{s}_i + 2\vec{s}_j),$$

$$\delta H_5 = - \frac{e^3}{2m^2 c^3} \sum_{i,j(i\neq j)} \left(\frac{\vec{A}_i \cdot \vec{p}_j}{r_{ij}} + \frac{(\vec{r}_{ij} \cdot \vec{A}_i)(\vec{r}_{ij} \cdot \vec{p}_j)}{r_{ij}^3} \right).$$

The part of δH_4 which contains $\vec{s}_j$ is in the literature often referred to as the diamagnetic correction. For the present investigation it was found more convenient to divide δH_{RD} into one- and two-electron, spin-independent, and spin-dependent operators.

The motion of the atomic nucleus yields a correction Hamiltonian which takes the form[6]

$$\delta H_N = - \frac{e}{2mc} \frac{m}{M} \vec{B} \cdot \left(\sum_i \vec{r}_i \times \vec{p}_i + \sum_{i,j(i\neq j)} \vec{r}_i \times \vec{p}_j \right), \tag{4}$$

where M denotes the mass of the nucleus.

The effect of the departure from LS coupling on the g_J factor has been considered by Phillips,[7] with particular reference to the alkali atoms. Let the wave function of an atomic state be denoted by Ψ_0. An expansion in terms of eigenstates (ψ_k) of $\vec{L}^2$ and $\vec{S}^2$ may be written

$$\Psi_0 = c_0 \psi_0 + \sum_k c_k \psi_k,$$

and one now obtains

$$(\Psi_0, H_Z \Psi_0) = \mu_B B M_J \left(g_{J,0} + \sum_{k(k\neq 0)} |c_k|^2 (g_{J,k} - g_{J,0}) \right).$$

The expansion coefficients c_k are approximately given by $c_k = (\psi_0, H_{SO} \psi_k)/(E_0 - E_k)$, where H_{SO} denotes the spin-orbit Hamiltonian. Hence, the correction to the g_J factor arising from the departure from LS coupling is given by

$$\delta_{LS} = \sum_{k(k\neq 0)} \left| \frac{(\psi_0, H_{SO} \psi_k)}{E_0 - E_k} \right|^2 (g_{J,k} - g_{J,0}), \tag{5}$$

with $g_{J,k}$ and $g_{J,0}$ given by Eq. (2) for the respective states.

In principle one might question the use of the free-electron g value g_e in Eqs. (1) and (2). Investigations on the hydrogen atom,[8] however, indiate that the difference between the radiation corrections for free and bound electrons is very small, i.e., of the order of magnitude 10^{-8}.

III. NUMERICAL CALCULATIONS

The subject of the present paper is to carry out numerical calculations of the corrections to the g_J factor arising from Eqs. (3) and (4). The Hamiltonians of Eqs. (3) and (4) were expanded in terms of spherical tensors, which is convenient for numerical calculations since the angular part of the atomic orbitals is represented by spherical harmonics. The expansions of δH_3 and δH_4 of Eq. (3) have been given previously,[9] whereas that of δH_5 is too lengthy and complex to be reproduced here. Hartree-Fock claculations based on the formulas of Kambe and Van Vleck[10] have previously been carried out for the first-row atoms. To the knowledge of the present author no accurate Hartree-Fock calcultaions of g_J-factor corrections have been carried out so far for atoms beyond the first row, not even for the alkali ground states where the troublesome orbit-orbit part δH_5 of Eq. (3) makes no contribution. One reason for this might be that the Kambe–Van Vleck formalism seems to be rather intractable for atoms with more than one shell of p electrons.

The present work yields accurate Hartree-Fock (HF) calculations for the first and second row atoms, and in addition for the alkali metal potassium and rubidium and for the halogens bromine and iodine for which accurate HF wave functions as well as precise measurements are available. The calculations are based on the Roothaan-Hartree-Fock wave functions given by Clementi and Roetti.[11] The main purpose of the present paper is, however, to investigate the effect of spin polarization on the g_J-factor corrections. A look at the correction operator δH_2 of Eq. (3) yield in particular a motivation for such an investigation. In a spin-polarized treatment the kinetic energies T_i of spin-up and spin-down electrons of the same shell will be different, and

a contribution to the g_J factor arises even from closed shell electrons. The spin-extended Hartree-Fock wave functions (SEHF) given by Kaldor for the first-row atoms and for sodium in a series of papers[12] were used for the present calculations.

In the spin-extended Hartree-Fock method a Hartree product Φ of atomic orbitals is determined by minimizing the energy given by

$$E = (\hat{O}\Phi, H\hat{O}\Phi)/(\Phi, \hat{O}\Phi),$$

where $\hat{O}$ is a product of a spin-projection operator and an antisymmetrizer. The expectation value of a Hamiltonian δH is then given by

$$\langle \delta H \rangle = (\hat{O}\Phi, \delta H\hat{O}\Phi)/(\Phi, \hat{O}\Phi).$$

The spin-extended Hartree-Fock procedure hence yields a wave function $\psi = \hat{O}\Phi$ which is also an eigenfunction of $\vec{S}^2$, in contrast to the unrestricted Hartree-Fock method. This is obviously an indispensable requirement for computation of expectation values of spin-dependent operators such as δH_2, δH_3, and δH_4 of Eq. (3).

Explicit formulas for expectation values for spin-projected wave functions have been given by Harris[4] for one-electron and two-electron spin-independent and spin-dependent operators. Equation (187) of Harris applies to δH_1, Eq. (188) to δH_5 and δH_N, and δH_2 and δH_3 is covered by Eq. (197). Unfortunately Eq. (214) of Harris for the two-electron spin-dependent operators, which is the most complex case, is not applicable to δH_4. The reason is that the treatment of Harris is restricted to operators of the form $\sum_{i<j} b_{ij}(\vec{r})\sigma_{ij}$ where both the space factor $b_{ij}(\vec{r})$ and the spin factor σ_{ij} are assumed to be symmetric upon interchange of electrons i and j. The operator δH_4 of Eq. (3) is not of this symmetric form, but may rather be treated as two summations of the type $\sum_{i,j(i\neq j)} b_{ij}(\vec{r})\sigma_i$, where σ_i is now a one-electron spin-dependent operator. An analog to Eq. (214) of Harris was then derived for an unsymmetric space factor and expressed in terms of the simpler one-electron spin coefficients $c_k(\alpha\alpha)$, $c_k(\beta\beta)$, and $c_k(\alpha\beta)$ of Eqs. (198)–(200).

The wave function of the $^2P_{1/2}$ state (B, F, Al, Cl, Br, I) or of the $^3P_1$ state (C, O, Si, S) cannot be represented by a single determinant in the HF method or by a single projected Hartree product in the SEHF procedure. In the HF calculations one then uses the well-known trick of the invariance of the diagonal sum. This trick may also be applied to the SEHF calculations in a modified form. Since the SEHF wave functions are eigenfunctions of $\vec{S}^2$, S_z, and L_z, one has to make sure that they are also eigenfunctions of $\vec{L}^2$. The wave functions are then given in the $|LSM_LM_S\rangle$ representation, and the transformation to the $|LSJM_J\rangle$ coupling scheme is straightforward. This situation applies to the $^2P_{1/2}$ states, but unfortunately not to the $^3P_1$ states. For the present $^3P_1$ states there are three different Hartree products yielding $M_J = 1$. Only the one of these with $M_L = 0$ and $M_S = 1$ is, after antisymmetrizing and spin projection, also an eigenfunction of $\vec{L}^2$ ($L = 1$). The remaining two products, both with $M_L = 1$ and $M_S = 0$, do not represent eigenfunctions of $\vec{L}^2$, and an orbital angular momentum projector has to be applied to transform these two products to the $|LSM_LM_S\rangle$ representation. This seems to be a rather intractable procedure in the spin-polarized case with different orbitals for different spin. For the spin-dependent operators δH_2, δH_3, and δH_4 this in fact causes no problem. In the $|LSM_LM_S\rangle$ representation diagonal elements for $M_S = 0$ vanish, and the invariance of the diagonal sum yields the desired results.

The contribution to the $^3P_1$ g_J factor from the spin-independent operators δH_1, δH_5, and δH_N have to be determined in a different way. These operators all are of the general form

$$\delta H = \mu_B B A_Z,$$

where B is the external field and A_Z denotes the Z component of a spin-independent vector. A straightforward calculation now leads to the result

$$\langle LSJM_J | \mu_B B A_Z | LSJM_J \rangle = \mu_B B M_J \delta g_J,$$

with δg_J given by

$$\delta g_J = \frac{1}{M_J}(L \| A \| L)(2J + 1)$$

$$\times \sum_{M_L, M_S} M_L \begin{pmatrix} L & S & J \\ M_L & M_S & -M_J \end{pmatrix}^2, \quad (6)$$

where $(L \| A \| L)$ denotes the reduced matrix element. Hence Eq. (6) yields a simple relation between the spin-independent g_J-factor corrections of the multiplets of a spectroscopic state. For the present ^3P and ^2P states one finds

$$\delta g_{J=2} = \delta g_{J=1}, \quad \delta g_{J=1/2} = 2\delta g_{J=3/2}.$$

These simple relations of course also apply to the Hartree-Fock calculations, and they are particularly relevant to the time consuming computation of the very complex orbit-orbit correction δH_5.

IV. RESULTS

The results of the numerical calculations are given in Tables I–III. The corrections to the g_J

TABLE I. Ground-state g_J factors for the alkali atoms Li to Rb. HF means Hartree-Fock theory, SEHF means spin-extended Hartee-Fock.

Quantity		Li ^2S	Na ^2S	K ^2S	Rb ^2S
$\delta_2(10^{-5})$	HF	−2.224	−2.846	−2.814	−3.275
	SEHF	−2.612	−2.779		
$\delta_3(10^{-5})$	HF	1.839	5.885	7.975	14.303
	SEHF	1.913	5.837		
$\delta_4(10^{-5})$	HF	−1.127	−5.181	−7.383	−13.723
	SEHF	−1.139	−5.131		
g_J(HF) [a]		2.002 304 12	2.002 297 86	2.002 297 07	2.002 292 33
Previous theory [a]		2.002 300 91 [b]	2.002 293 [c]	2.002 295 [c]	2.002 295 [c]
g_J(SEHF) [a]		2.002 300 86	2.002 298 56		
g_J(expt)		2.002 301 42(80) [b]	2.002 295 63(16) [d]	2.002 294 15(16) [e]	2.002 331 09(16) [d,e]
g_J(expt)−g_J(HF)		−2.70(80)×10^{-6}	−2.17(16)×10^{-6}	−2.92(16)×10^{-6}	38.76(16)×10^{-6}
g_J(expt)−g_J(SEHF)		0.56(80)×10^{-6}	−2.89(16)×10^{-6}		

[a] Corrections due to departure from LS coupling not included.
[b] Reference 3, and Refs. therein.
[c] Reference 13.
[d] Reference 18.
[e] Reference 19.

factor arising from $\delta H_1 - \delta H_5$ and δH_N are denoted by $\delta_1 - \delta_5$ and δ_N, respectively, i.e., $\delta_k = \langle \delta H_k \rangle / \mu_B B M_J$, and δ_{LS} is given by Eq. (5). Table I lists the results for the alkali ground states Li–Rb. Experimental values and previous theoretical results are also included in the table for comparison with the present theroetical ones. The quoted theoretical results of Perl[13] for Na, K, and Rb are without exchange terms, and are in modest agreement with those of the present accurate HF calculation. On the other hand there is excellent agreement between the present SEHF value and that of Hegstrom[3] for Li. In Li the effect of spin polarization is quite considerable for the correction δ_2, and the SEHF value of g_J is in complete agreement with the experimental result. The effect of spin-polarization is not very significant for Na, and neither the HF value not the SEHF value is in satisfactory agreement with experiment. The corrections due to the departure from LS coupling are difficult to evaluate for the alkali atoms, but Vanden Bout et al.[14] have given estimates of δ_{LS} based on the theory of Phillips.[7] Their values of δ_{LS} are 2×10^{-6}, 5×10^{-6}, and 5×10^{-5} for Na, K, and Rb, respectively. Hence the inclusion of δ_{LS} would increase the discrepancy between theory and experiment for Na and K, whereas the predicted value of δ_{LS} for Rb would bring the theory into much bettér agreement with experiment. In a recent paper Flambaum et al.[15] have pointed out that the Phillips theory for δ_{LS} may not apply to heavy atoms. In the case of Cs they found that a third-order correction (second order in spin-orbit coupling, first order in Coulomb mixing of con-

figurations) dominates the fourth-order trems considered by Phillips. For the ^2S ground state of Cs their improved value is $\delta_{LS} = 3.7 \times 10^{-4}$, compared to the correction 1.4×10^{-4} estimated by Vanden Bout et al. from the Phillips theory. A similar effect might also be expected in Rb, but the present results for Rb, however, indicate that δ_{LS} is already slightly overestimated by the Phillips correction. The most plausible explanation for the discrepancy for Na and K is the insufficient electronic correlation which prevails even for the SEHF functions. This deficiency of the wave function will in particular affect the expectation values of the two-body operator δH_4.

Table II shows the computed results for the ground states of the first row atoms B, C, N, O, and F. The values of δ_{LS} are here taken from the sources cited in the table. The most prominent feature of Table II is probably the increasing effect of spin-polarization from B to F, i.e., with increasing number of electrons in the unfilled shell. This effect is, as expected, most clear for δ_2, which also in all cases represent the largest correction. For fluorine the difference between the HF and SEHF values of δ_2 amounts to almost 20%, and even for δ_4 there is an 8% difference. Since the SEHF functions should in particular yield more reliable expectation values for one-electron operators, it seems clear that the Hartree-Fock values of the g_J factors for the first-row atoms are more uncertain than previously believed.

For both B and C the SEHF values of g_J give slightly better agreement with experiments than the HF result. The experimental uncertainty is,

TABLE II. Various corrections to the ground-state g_J factors of B, C, N, O, and F. HF means that Hartree-Fock wave functions have been used, SEHF refers to calculations with spin-extended Hartree-Fock functions.

Quantity		B		C		N	O		F	
		$^2P_{3/2}$	$^2P_{1/2}$	$^3P_2$	$^3P_1$	^4S	$^3P_2$	$^3P_1$	$^2P_{3/2}$	$^2P_{1/2}$
$\delta_1(10^{-5})$	HF	-2.65	-5.30	-3.34	-3.34		-6.77	-6.77	-11.86	-23.72
	SEHF	-2.70	-5.39	-3.38	-3.38		-5.86	-5.86	-10.77	-21.54
$\delta_2(10^{-5})$	HF	-2.65	2.65	-6.68	-6.68	-19.98	-13.53	-13.53	-11.86	11.86
	SEHF	-2.82	2.82	-7.00	-7.00	-20.91	-15.32	-15.32	-14.16	14.16
$\delta_3(10^{-5})$	HF	2.15	-5.40	3.76	6.26	11.90	7.10	11.83	8.13	-20.31
	SEHF	2.21	-5.46	3.86	6.38	12.19	7.69	12.27	8.83	-20.95
$\delta_4(10^{-5})$	HF	-1.50	3.21	-2.93	-4.41	-9.33	-6.20	-6.85	-5.80	8.54
	SEHF	-1.54	3.28	-3.00	-4.51	-9.55	-6.63	-7.17	-6.30	8.86
$\delta_5(10^{-5})$	HF	-0.11	-0.23	-0.14	-0.14		-1.68	-1.68	-2.56	-5.12
	SEHF	-0.10	-0.21	-0.13	-0.13		-1.54	-1.54	-2.41	-4.83
$\delta_N(10^{-5})$	HF	-0.97	-1.95	-0.75	-0.75		-0.61	-0.61	-0.69	-1.39
	SEHF	-0.97	-1.94	-0.74	-0.74		-0.56	-0.56	-0.66	-1.32
$\delta_{LS}(10^{-5})$		0.0	0.0	-0.26[c]	0.0	-0.40[e]	-2.12[g]	0.0	0.0	0.0
$[g_J^0 - g_J(\text{HF})](10^{-5})$[a]		5.73	6.98	10.33	9.05	17.82	23.81	17.60	24.64	30.14
$[g_J^0 - g_J(\text{expt})](10^{-5})$		5.94[b]	8.36[b]	10.36[c]	9.06[c]	17.73[e]	23.72[g]	17.52[g]	24.68[i]	30.11[i]
$[g_J^0 - g_J(\text{SEHF})](10^{-5})$[a]		5.91	6.89	10.65	9.37	18.67	24.34	18.17	25.47	25.63
$[g_J^0 - g_J(\text{expt})](10^{-5})$		5.84(30)[b]	6.76(80)[b]	12.1(1.5)[d]	10.8(1.3)[d]	18.464(6)[f]	23.9(2)[h]	17.4(2)[h]	24.54(11)[j]	28.19(10)[j]
$[g_J(\text{expt}) - g_J(\text{HF})](10^{-5})$		-0.11(30)	0.22(80)	-1.7(1.5)	-1.7(1.3)	-0.645(6)	-0.05(20)	0.24(20)	0.10(11)	1.95(10)
$[g_J(\text{expt}) - g_J(\text{SEHF})](10^{-5})$		0.07(30)	0.13(80)	-1.4(1.5)	-1.4(1.3)	0.205(6)	0.48(20)	0.81(20)	0.93(11)	-2.56(10)

[a] Corrections due to departure from LS coupling are included. The meaning of g_J^0 is the uncorrected g_J factor given by Eq. (2).
[b] Reference 20.
[c] Reference 21.
[d] Reference 22.
[e] Reference 16.
[f] Reference 23.
[g] Reference 1.
[h] Reference 24.
[i] Reference 2.
[j] Reference 25.

TABLE III. g_J-factor corrections for second-row atoms and Br and I computed from Hartree-Fock wave functions.

Atom	$\delta_1+\delta_2$ (10^{-5})	δ_3 (10^{-5})	δ_4 (10^{-5})	δ_5 (10^{-5})	δ_N (10^{-5})	δ_{LS} [a] (10^{-5})	g_J(theor)	g_J(expt)
Al $^2P_{3/2}$	−4.06	3.50	−2.97	−0.26	−0.06	0.0	1.334 068	1.334 74(5) [b]
$^2P_{1/2}$	−2.03	−8.75	6.61	−0.53	−0.12	0.0	0.665 845	
Si $^3P_2$	−7.51	5.35	−4.82	−0.35	−0.06	−11.2	1.500 974	
$^3P_1$	−7.51	8.91	−7.25	−0.35	−0.06	0.0	1.501 097	
P ^4S	−14.53	15.18	−13.36			−27.2	2.001 920	
S $^3P_2$	−14.45	8.32	−7.75	−1.51	−0.10	−40.4	1.500 601	
$^3P_1$	−14.45	13.86	−10.05	−1.51	−0.10	0.0	1.501 037	
Cl $^2P_{3/2}$	−16.47	8.85	−7.13	−2.13	−0.14	0.0	1.333 936	1.333 927 5(30) [c]
$^2P_{1/2}$	−8.24	−22.13	12.91	−4.26	−0.29	0.0	0.665 674	0.665 661 9(16) [d]
Br $^2P_{3/2}$	−18.06	15.33	−13.46	−3.77	−0.05	0.0	1.333 906	1.333 921(5) [c]
$^2P_{1/2}$	−9.03	−38.32	26.59	−7.55	−0.10	0.0	0.665 610	0.665 56(2) [e]
I $^2P_{3/2}$	−17.79	19.20	−17.36	−3.90 [g]	−0.04	0.0	1.333 908	1.333 980(6) [f]
$^2P_{1/2}$	−8.89	−48.00	35.61	−7.80 [g]	−0.07	0.0	0.665 602	

[a] δ_{LS} computed by use of Hartree-Fock values of $\zeta(3p)$, Ref. 17.
[b] Reference 26.
[c] Reference 27.
[d] Reference 28.
[e] Reference 29.
[f] Reference 30.
[g] Computed by use of single zeta wave function. The deviation from the Hartree-Fock value is estimated to be $\pm 3\times10^{-6}$ and $\pm 6\times10^{-6}$, respectively, for the $^2P_{3/2}$ and $^2P_{1/2}$ corrections.

however, in both cases too large to allow any definite conclusion. The SEHF result for nitrogen clearly comes much closer to the experimental one than the HF value. The present result for N thus disproves a conclusion arrived at by Beltrán-Lόpez et al.[16] They found that the large discrepancy between HF and experimental value of g_J in N could not be attributed to the use of Hartree-Fock wave functions. Their conclusion, which was based on the results of an unrestricted Hartree-Fock calculation, is rather a warning against working with noneigenfunctions of $\hat{S}^2$.

In the cases of oxygen and fluorine the SEHF results might seem rather frustrating since the HF values represent much better agreement with experiments (except for the $^2P_{1/2}$ state of F). It is hard to find any reason why the HF functions should be better than the SEHF ones for O and F. The success of the HF calculation is probably fortuitous and due to cancellation of errors. A further discussion of this point will be given in Sec. V.

Finally, Table III shows the results of Hartree-Fock calculations for the second-row atoms Al to Cl and for bromine and iodine. The values given for δ_{LS} were obtained from Eq. (5), taking into account the spin-orbit interaction between the $^3P_2$ and $^1D_2$ levels for Si and S, and between the $^4S_{3/2}$ and $^2P_{3/2}$ levels for P. Hartree-Fock values of the spin-orbit parameter $\zeta(3p)$ were used.[17] For the $^3P_2$ states of silicon and sulfur as well

as for phosphorus δ_{LS} represents a substantial and dominant correction to the g_J factor. Precise experimental values of these g_J factors would then in fact mainly test the predicted corrections due to the departure from LS coupling.

In the case of Al the discrepancy between theoretical and expreimental value is too large to be attributed to uncertainties in the theoretical prediction. Hence, a question mark on the experimental result seems inevitable. For chlorine there is also a clear discrepancy between theory and experiment. However, in view of the present results for oxygen and fluorine these differences are not larger than what might be expected on the basis of Hartree-Fock theory. The results for bromine are more indecisive due to larger experimental uncertainties. In the case of iodine the present difference $g_{3/2}$(expt) $-g_{3/2}$(theor) $= 7.2(6)\times10^{-5}$ probably indicates that a significant effect of the departure from LS coupling has been neglected. For a heavy atom such as iodine one might also question the validity of the Pauli approximation, i.e., the convergence of the series expansion of the relativistic Zeeman Hamiltonian which to order $(\alpha Z)^2$ yields the corrections $\delta H_1-\delta H_5$ of Eq. (3).

V. CONCLUDING REMARKS

The SEHF wave functions satisfies an extension of Brillouin's theorem which means that singly

excited configurations will not interact with the ground state.[12] Hence, the SEHF procedure will in particular yield good approximations to expectation values of one-electron operators. This property also applies to the HF method, but due to the greater flexibility of the SEHF functions in the variational process they undoubtedly yield the most reliable results. The judgement between SEHF and HF results is more uncertain for two-electron properties, since even the SEHF functions include only a (small) part of the electronic correlation, i.e., double excitations are neglected in both methods. It then seems reasonable to attribute the present discrepancies between SEHF theory and experiments to inaccurate expectation values of the two-electron corrections, although significant errors in the one-electron corrections cannot be strictly ruled out. The dominant two-electron correction is δH_4, and even in the worst case ($^2P_{1/2}$ state in F) the discrepancy is less than 30% of the computed values of δ_4. For the other examples the differences range from 0 to 15% of the complex two-electron quantity δ_4. A characteristic feature of the present results is shown in Fig. 1. The difference between SEHF theory and experiment is seen to increase quite regularly with increasing number of electrons for the first-row atoms from Li to F. Hence, Fig. 1 seem to indicate that for the first-row atoms a very systematic error arises from the lack of correlation in the wave function. The great disparities of the SEHF and HF values of the one-electron quantities $\delta_1 - \delta_3$ for O and F should also be noted. Altogether the previous excellent agreement between HF theory and experiment for oxygen and the $^2P_{3/2}$ state of fluorine seems quite fortuitous and due to cancellation of errors.

The computation of accurate atomic g_J factors which are comparable with precise experimental values still represents a theoretical challenge.
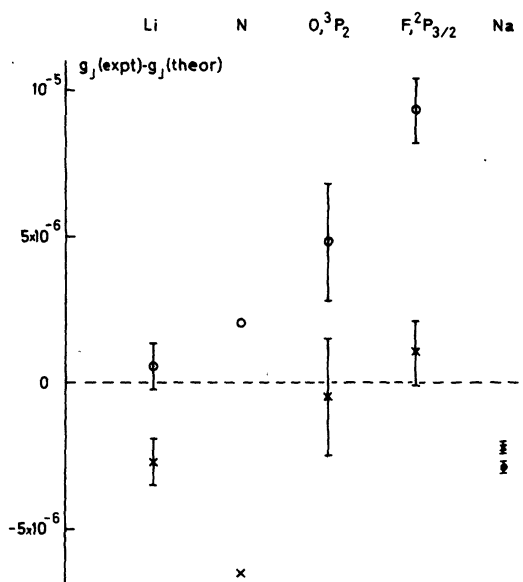

FIG. 1. The difference between experimental and theoretical g_J factors for the atoms Li, N, O, F, and Na. Hartree-Fock results are shown by crosses, whereas circles represent spin-extended Hartree-Fock calculations.

Such calculations will surely enable valuable tests of current atomic structure theories. In the case of nitrogen the experimental accuracy of the g_J factor is at present 6.4×10^{-8}. To obtain a theoretical prediction with similar accuracy one will have to pass several obstacles. First and foremost the calculations of the relativistic and diamagnetic corrections need to be improved, and this task requires an accurate wave function with a rather complete allowance for electronic correlation. Thereafter the problem will be to compute the correction due to the departure from LS coupling more accurately, and finally one might even have to consider bound-state radiative corrections.

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