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Atomic Bethe-Goldstone Calculations of Term Splittings, Ionization Potentials, and Electron Affinities for B, C, N, O, F, and Ne.
II. Configurational Excitations

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Term splittings, ionization potentials, and electron affinities of states in the lowest configurations of atoms with Z from 5 to 10 have been computed. Correlation-energy terms are obtained from variational solution of one- and two-particle Bethe–Goldstone equations, formulated in terms of *configurational* virtual excitations. This procedure differs from previous calculations (which used *orbital* virtual excitations) in that LS eigenfunctions are obtained at each stage of the hierarchy of computations. The present procedure makes it possible to compute correlation energies for multideterminantal LS states. Computed results are in reasonable agreement with experiment, but are less satisfactory than results obtained previously with *orbital* virtual excitations, including three-particle terms.

I. INTRODUCTION

In a previous paper[1] (hereafter referred to as I) we presented the results of calculations of ionization potentials, electron affinities, and term splittings for states of the lowest electronic configurations of first-row atoms, with Z from 5 to 10. These results represent energy differences made up from two separately computed contributions: (i) Hartree–Fock and (ii) correlation terms. The latter were computed by variational solution of orbital-excitation Bethe–Goldstone equations. The computational procedure has been described in detail elsewhere.[2] In a few cases, three-particle correlation effects were computed, so that quantitative estimates could be made of the importance of these terms in the physical excitation processes of interest here. The states considered in I were limited to those for which the state with $M_L = L$ and $M_S = S$ can be represented by a single Slater determinant in the Hartree–Fock approximation.

We pointed out in I that it would be desirable to make parallel calculations of the energy differences considered there, using the alternative technique of configurational virtual excitations[3] to define the hierarchy of variational Bethe–Goldstone equations. Because some three- and four-particle *orbital* excitations are included in the definition of one- and two-particle *configurational* excitations, the possibility exists that the entire effect of virtual orbital excitations of more than two particles would be adequately described by one- and two-particle configurational excitations. The work reported here is a test of this hypothesis. It also includes some states, represented in the Hartree–Fock approximation by more than one Slater determinant, that could not be tested by the simpler orbital-excitation method of I.

The only previously published results comparable to those reported here are calculations of Weiss[4] on F and Ne. The results obtained here will be compared with those of Weiss in the discussion given below. This discussion also applies to recent work on O by Marchetti *et al.*[5]

II. CALCULATIONS

The use of configurational excitation in Bethe–Goldstone calculations has been described previously.[3] Here we give some additional details required to compute correlation energies of multideterminantal LS eigenstates.

The first step of each calculation is to carry out an open-shell matrix Hartree–Fock calculation[6] for a single Slater determinant selected from the configuration appropriate to the atomic state under consideration. If there are other Slater determinants with the same M_L and M_S values in this configuration, a zeroth-order Bethe–Goldstone calculation is required, to diagonalize the Hamiltonian over this set of Slater determinants. This defines a variational Hilbert space [0], and a gross energy increment ΔE_0, considered as a correction to the single-determinant Hartree–Fock energy.[3]

The hierarchy of variational equations then follows in the usual way, but virtual excitations and not energy increments are referred to [0] rather than just to the reference Slater determinant.

The total energy is given by

TABLE I. Energy contributions for C (^3P), in a.u. (Hartree units).

	Calculation (a)	Calculation (b)	Calculation (c)
E_0	−37.6886	−37.6310	−37.6310[a]
ΔE_0		−0.0563	−0.0916
ϵ_{2s}	−0.0387	−0.0373	−0.0180
ϵ_{2p}		−0.0011	−0.0079
ϵ_{2s2s}	−0.0303	−0.0307	−0.0147
ϵ_{2s2p}	−0.0204	−0.0218	−0.0214
ϵ_{2p2p}	−0.0099	−0.0098	−0.0083
Total	−37.7879	−37.7880	−37.7858

[a] Approximate Hartree-Fock energy of reference determinant.

$$E=E_0+\Delta E_0+\sum_i \epsilon_i+\sum_{ij} \epsilon_{ij}+\cdots , \tag{1}$$

where E_0 is the single-determinant Hartree–Fock energy, and net energy increments are defined by

$$\begin{aligned} \epsilon_i &= \Delta E_i - \Delta E_0 , \\ \epsilon_{ij} &= \Delta E_{ij} - \Delta E_0 - \epsilon_i - \epsilon_j . \end{aligned} \tag{2}$$

Here ΔE_i, ΔE_{ij} denote the directly computed gross energy increments, defined as eigenvalues of a Hamiltonian matrix whose diagonal elements represent virtual excitation energies relative to E_0.[2,3]

These definitions can be illustrated by an example, the ^3P ground state of neutral carbon. Table I lists individual contributions to the total energy of this state using configurational virtual excitations and either a single or multideterminant representation of the reference state. All three calculations have a common orbital basis set: the double ζ basis set of Clementi[7] augmented by s, p, d, f functions with powers of r up to quantum number $n=5$. This orbital basis has been used for earlier calculations.[8]

Calculation (a), in Table I, is a standard calculation using the single-determinant reference state det[(closed shells)$2p_0^\alpha\, 2p_1^\alpha$]. This is a ^3P eigenstate with $L=M_L=1$, $S=M_S=1$. Calculation (b) uses $(2p_{-1}^\beta\, 2p_1^\alpha)$ as reference determinant, constructing a ^3P eigenstate in the form

$$1.0(2p_{-1}^\beta 2p_1^\alpha) - 1.0(2p_1^\beta\, 2p_{-1}^\alpha) - 0.0(2p_0^\beta\, 2p_0^\alpha) . \tag{3}$$

ΔE_0 in this case is computed as an eigenvalue of the 3×3 matrix corresponding to Hilbert space [0], spanned by the three Slater determinants indicated in Eq. (3). The net energy increments are given by the usual formulas:

$$\begin{aligned} &\epsilon_{2s}=\Delta E_{2s}-\Delta E_0 , \quad \epsilon_{2p}=\Delta E_{2p}-\Delta E_0 , \\ &\epsilon_{2s,2s}=\Delta E_{2s,2s}-\Delta E_0-\epsilon_{2s} , \\ &\epsilon_{2s,2p}=\Delta E_{2s,2p}-\Delta E_0-\epsilon_{2s}-\epsilon_{2p} , \\ &\epsilon_{2p,2p}=\Delta E_{2p,2p}-\Delta E_0-\epsilon_{2p} . \end{aligned} \tag{4}$$

Calculation (c) represents a further extension of the formalism. To account for the near-degeneracy effect of interaction between configurations $2s^2 2p^2$ and $2p^4$, it is convenient to include $2p^4$ in the reference Hilbert space [0]. In fact, any configuration suspected of having a substantial effect can be included in [0]. So long as these configurations are included in all of the virtually excited variational spaces, the general argument leading to definition of net energy increments as in Eqs. (4) still is valid.[3] To illustrate this point, calculation (c) includes both $1s^2 2p^4$ and $1s^2 2s 3d 2p^2$ in [0]. The former is quite important (coefficient ~0.15) but the latter is less so (coefficient ~0.03).

The data in Table I show that the total energy computed in (a) or (b) is practically identical, although there are slight differences in the energy subdivision among the various net increments. The total energy in calculation (c) is somewhat smaller, by about 0.002 a.u., but ΔE_0, which contains the $2p^4 : 2s^2 2p^2$ near-degeneracy effect in this case, is much larger than in calculation (b). In calculations (a) and (b) the near-degeneracy effect represents a major contribution to the $2s2s$ net increment. The configuration $1s^2 2s 3d 2p^2$ contributes to the $2s$ net increment in calculations (a) and (b) but not in (c), where its effect is included in ΔE_0.

In a basis of Slater determinants, the configuration-interaction matrices for configurational excitations are much larger than the corresponding matrices for orbital excitations. Since a procedure for constructing symmetry-adapted functions prior to the matrix eigenvalue computation has not yet been implemented in the computer programs used here, the size of these matrices and the resulting large computation times are serious limiting factors. In the worst case considered, the calculation of $\Delta E_{2s,2p}$ for O(^1S) was terminated without satisfactory convergence. Such practical considerations led us to omit calculations of the KL intershell correlation energies. In orbital excitation calculations,[1] these terms were found to be small, and to make very small contributions to the energy differences of interest here.

With the present computer programs, it would be quite out of the question to compute three-particle terms, using configurational excitations.

III. RESULTS AND DISCUSSION

Table II lists the various computed contributions to the total energy. Only L-shell correlation energies are included, so the "total" energy given here cannot be compared directly with experiment. As indicated in the table, results for the $2p^4(^1S)$ state of N⁻ and O are somewhat uncertain due to inadequate convergence of the $\Delta E_{2s,2p}$ eigenvalue calculation. The expected error is less than 0.001

TABLE II. Contributions to total energies (a.u.), with all signs reversed.

Atom (state)	E_0	ΔE_0	ϵ_{2s}	ϵ_{2p}	$\epsilon_{2s,2s}$	$\epsilon_{2s,2p}$	$\epsilon_{2p,2p}$	Total
B(^2P)	24.5291		0.0218		0.0409	0.0088		24.6006
B$^-$(^3P)	24.5192		0.0258		0.0296	0.0246	0.0110	24.6102
B$^-$(^1D)	24.4905		0.0217	0.0023	0.0317	0.0263	0.0180	24.5905
B$^-$(^1S)	24.4768^a	0.0009^b	0.0003	0.0011	0.0257	0.0277	0.0384	24.5709
C(^3P)	37.6886		0.0387		0.0303	0.0204	0.0099	37.7879
C(^1D)	37.6313		0.0355	0.0037	0.0309	0.0222	0.0145	37.7344
C(^1S)	37.6031^a	0.0063^b	0.0011	0.0010	0.0104	0.0237	0.0370	37.6826
C$^-$(^4S)	37.7088		0.0389		0.0174	0.0372	0.0301	37.8324
C$^-$(^2D)	37.6425		0.0350	0.0045	0.0192	0.0385	0.0383	37.7780
C$^-$(^2P)	37.6411^a	−0.0194^b	0.0166	0.0046	0.0167	0.0398	0.0518	37.7512
C II (^2P)	37.2922		0.0256		0.0488	0.0087		37.3753
N(^4S)	54.4009		0.0496		0.0149	0.0329	0.0289	54.5272
N(^2D)	54.2962		0.0459	0.0053	0.0157	0.0346	0.0361	54.4338
N(^2P)	54.2956^a	−0.0336^b	0.0220	0.0042	0.0123	0.0353	0.0516	54.3874
N$^-$(^3P)	54.3219		0.0309	0.0064	0.0159	0.0540	0.0767	54.5058
N$^-$(^1D)	54.2669		0.0299	0.0054	0.0166	0.0538	0.0817	54.4543
N$^-$(^1S)	54.2367^a	−0.0147^b	0.0015	0.0006	0.0155	0.0546^c	0.1014	54.3956^c
N II (^3P)	53.8880		0.0438		0.0332	0.0202	0.0097	53.9949
N II (^1D)	53.8074		0.0408	0.0041	0.0336	0.0209	0.0143	53.9211
N II (^1S)	53.7673^a	0.0008^b	0.0014	0.0009	0.0079	0.0218	0.0386	53.8387
O(^3P)	74.8094		0.0378	0.0059	0.0140	0.0493	0.0756	74.9920
O(^1D)	74.7292		0.0365	0.0062	0.0144	0.0493	0.0804	74.9160
O(^1S)	74.6887^a	−0.0254^b	0.0020	0.0005	0.0122	0.0511^c	0.1023	74.8314^c
O$^-$(^2P)	74.7895		0.0185	0.0051	0.0139	0.0688	0.1316	75.0274
O II (^4S)	74.3726		0.0549		0.0140	0.0312	0.0286	74.5013
O II (^2D)	74.2333		0.0514	0.0056	0.0145	0.0329	0.0357	74.3734
F(^2P)	99.4093		0.0217	0.0050	0.0127	0.0637	0.1314	99.6438
F$^-$(^1S)	99.4594				0.0118	0.0831	0.1960	99.7503
F II (^3P)	98.8316		0.0417	0.0057	0.0133	0.0466	0.0756	99.0145
Ne(^1S)	128.5470				0.0112	0.0775	0.1964	128.8321
Ne II (^2P)	127.8170		0.0238	0.0050	0.0122	0.0605	0.1317	128.0502

[a] Approximate Hartree-Fock energy of reference determinant.

[b] Configuration $1s^2 2p^{n+2}$ included with $1s^2 2s^2 2p^n$ in [0].

[c] Incomplete convergence of diagonalization.

a.u. The reference determinant for C(^1S) is $2p_0^{\beta} 2p_0^{\alpha}$. Configuration $1s^2 2p^{n+2}$ is included in the Hilbert space [0] for the ^1S and ^2P terms indicated in the table.

KL intershell correlation energies were not computed in detail. In Table III we give a few examples of net energy increments obtained with a restricted orbital basis. Quantitatively, the *KL* correlation energy computed in this approximation is only half that obtained previously with the full orbital basis set used here.[1] Nevertheless, the energy differences relevant to excitation processes are nearly the same.

In Table IV we compare total *LL* correlation energies obtained by *orbital* excitation and by *configurational* excitation. With the exception of C II(^2P) and N II(^3P) the correlation energy obtained by configurational excitation is always smaller than that obtained by orbital excitation. This result is expected, since explicit three-particle terms are neglected in both cases. Configurational excitations indexed by two particles contain certain three-particle virtual excitations implicitly, and the expected effect of these terms is to compensate for an excess of correlation energy computed for pair excitations only.[1,2]

As shown in Table IV, results of the two methods are significantly different. For neutral atoms, the difference is generally small, ranging from 2 or 3% in N I to 10% in O I. For negative ions, the

TABLE III. *KL* intershell net energy increments (a.u.), signs reversed.

Atom (state)	C (^3P)	C (^1D)	C (^1S)	C$^-$ (^4S)
$\epsilon_{1s,2s}$	0.0022	0.0030	0.0018	0.0020
$\epsilon_{1s,2p}$	0.0030	0.0029	0.0025	0.0037
Total	0.0052	0.0059	0.0043	0.0057

TABLE IV. Comparison of orbital- and configurational-excitation formalism. Total *LL* correlation energies (a.u.), signs reversed.

Atom (state)	Orb.	Config.
$\mathrm{B}^-(^3P)$	0.0970	0.0910
$\mathrm{B}^-(^1D)$	0.1118	0.1000
$\mathrm{B}(^2P)$	0.0721	0.0715
$\mathrm{C}^-(^4S)$	0.1344	0.1236
$\mathrm{C}^-(^2D)$	0.1514	0.1355
$\mathrm{C}(^3P)$	0.0999	0.0993
$\mathrm{C}(^1D)$	0.1106	0.1031
$\mathrm{C\,II}(^2P)$	0.0826	0.0831
$\mathrm{N}^-(^3P)$	0.2136	0.1839
$\mathrm{N}^-(^1D)$	0.2229	0.1874
$\mathrm{N}(^4S)$	0.1292	0.1263
$\mathrm{N}(^2D)$	0.1417	0.1376
$\mathrm{N\,II}(^3P)$	0.1050	0.1069
$\mathrm{N\,II}(^1D)$	0.1162	0.1137
$\mathrm{O}^-(^2P)$	0.2899	0.2379
$\mathrm{O}(^3P)$	0.1935	0.1826
$\mathrm{O}(^1D)$	0.2041	0.1868
$\mathrm{O\,II}(^4S)$	0.1289	0.1287
$\mathrm{O\,II}(^2D)$	0.1416	0.1401
$\mathrm{F}^-(^1S)$	0.3694	0.2909
$\mathrm{F}(^3P)$	0.2612	0.2345
$\mathrm{F\,II}(^3P)$	0.1892	0.1829
$\mathrm{Ne}(^1S)$	0.3315	0.2851
$\mathrm{Ne\,II}(^2P)$	0.2516	0.2332

differences are greater, ranging from 10% in B^- to 25% in F^-. These differences parallel the expected effect of three-particle terms, which have been shown to be larger in negative ions than in neutral atoms, and to increase in importance as the $2p$ subshell is filled.[1] Higher-order terms are expected to be smaller, but we have no detailed quantitative estimate.[2]

Computed energy differences for the ionization or excitation processes considered here are given in Table V. Two sets of results are given: the "complete" orbital basis set (i), and one with the highest energy unoccupied s and p orbital removed (ii). The energy difference for process $A \rightarrow B$ is defined as in I,

$$\Delta E_{AB} = E_B - E_A \, . \tag{5}$$

Experimental results as well as results of other calculations are included in the final column of the table.

Comparison of results (i) and (ii) indicates that there is no appreciable difference in the results if a slightly truncated orbital basis set is used.

TABLE V. Computed and observed ionization energies, electron affinities, and term splittings (eV).

Process	(i)	(ii)	Expt.[a]
$\mathrm{B}(^2P)\rightarrow\mathrm{B}^-(^3P)$	−0.261	−0.248	−0.33[b]
$\mathrm{B}^-(^3P)\rightarrow\mathrm{B}^-(^1D)$	0.536	0.536	0.53[c] 0.52[d]
$\mathrm{B}^-(^3P)\rightarrow\mathrm{B}^-(^1S)$	1.069	1.069	1.16[c] 1.31[d]
$\mathrm{C}(^3P)\rightarrow\mathrm{C}(^1D)$	1.456	1.355	1.26[g]
$\mathrm{C}(^3P)\rightarrow\mathrm{C}(^1S)$	2.865	2.865	2.68[g]
$\mathrm{C}(^3P)\rightarrow\mathrm{C}^-(^4S)$	−1.211	−1.211	−1.24[b]
$\mathrm{C}^-(^4S)\rightarrow\mathrm{C}^-(^2D)$	1.480	1.486	1.36[c] 1.29[d] 1.30[e] 1.25[f]
$\mathrm{C}^-(^4S)\rightarrow\mathrm{C}^-(^2P)$	2.210	2.209	1.89[c] 1.46[d] 1.99[e] 1.85[f]
$\mathrm{C}(^3P)\rightarrow\mathrm{C\,II}(^2P)$	11.227	11.227	11.27[g]
$\mathrm{N}(^4S)\rightarrow\mathrm{N}(^2D)$	2.541	2.550	2.38?[g]
$\mathrm{N}(^4S)\rightarrow\mathrm{N}(^2P)$	3.804	3.812	3.58?[g]
$\mathrm{N}(^4S)\rightarrow\mathrm{N\,II}(^3P)$	14.484	14.514	14.55[g]
$\mathrm{N\,II}(^3P)\rightarrow\mathrm{N\,II}(^1D)$	2.008	1.984	1.89[g]
$\mathrm{N\,II}(^3P)\rightarrow\mathrm{N\,II}(^1S)$	4.250	4.223	4.05[g]
$\mathrm{N}(^4S)\rightarrow\mathrm{N}^-(^3P)$	0.582	0.591	−0.05?[b]
$\mathrm{N}^-(^3P)\rightarrow\mathrm{N}^-(^1D)$	1.401	1.404	1.11[c] 1.28[d] 1.04[e] 1.22[f]
$\mathrm{N}^-(^3P)\rightarrow\mathrm{N}^-(^1S)$	2.999	3.023	2.40[c] 2.60[d] 2.36[e] 2.58[f]
$\mathrm{O}(^3P)\rightarrow\mathrm{O}(^1D)$	2.068	2.073	1.95[g]
$\mathrm{O}(^3P)\rightarrow\mathrm{O}(^1S)$	4.370	4.432	4.18[g]
$\mathrm{O}(^3P)\rightarrow\mathrm{O}^-(^2P)$	−0.963	−1.039	−1.47[g]
$\mathrm{O}(^3P)\rightarrow\mathrm{O\,II}(^4S)$	13.352	13.341	13.62[g]
$\mathrm{O\,II}(^4S)\rightarrow\mathrm{O\,II}(^2D)$	3.480	3.491	3.33[g]
$\mathrm{O\,II}(^4S)\rightarrow\mathrm{O\,II}(^2P)$		5.241	5.02[g]
$\mathrm{F}(^2P)\rightarrow\mathrm{F}^-(^1S)$	−2.898	−2.922	−3.50[b] −3.47[h]
$\mathrm{F}(^2P)\rightarrow\mathrm{F\,II}(^3P)$		17.115	17.43[g]
$\mathrm{F\,II}(^3P)\rightarrow\mathrm{F\,II}(^1D)$		2.682	2.59[g]
$\mathrm{F\,II}(^3P)\rightarrow\mathrm{F\,II}(^1S)$		5.777	5.53[g]
$\mathrm{Ne}(^1S)\rightarrow\mathrm{Ne\,II}(^2P)$		21.251	21.56[g] 21.52[h] 21.55[i]

[a] Includes other calculations.

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TABLE VI. Net energy increments in F, F$^-$, Ne, Ne II (a.u.), signs reversed.

	$\epsilon_{2s,2s}$		$\epsilon_{2s,2p}$		$\epsilon_{2p,2p}$	
Atom	a	This work	a	This work	a	This work
F	0.0106	0.0127	0.0590	0.0637	0.1465	0.1314
F$^-$	0.0110	0.0118	0.0793	0.0831	0.2315	0.1960
Ne II	0.0106	0.0122	0.0546	0.0605	0.1420	0.1317
Ne	0.0105	0.0112	0.0721	0.0775	0.2161	0.1964

[a] Reference 4, Table V.

The present results for electron affinities are qualitatively similar to those given in Table IV of I (results including three-particle terms). In particular, from the present one- and two-particle configurational excitation calculations, N$^-$(^3P) is not bound relative to N(^4S). In I, using orbital excitations, these states appeared in the opposite order unless three-particle terms were included.

The results of I are in better quantitative agreement with experiment than those given here. This implies that the effect of three-particle (and higher) terms is not fully accounted for by use of one- and two-particle configurational excitations.

For the processes Ne → Ne$^+$ and F → F$^-$, the present results can be compared with those of Weiss,[4] given as Ref. h in Table V. Weiss uses *LS* eigenstates throughout his calculations, but subdivides the Hilbert space of virtual excitations according to different electron-pair coupling schemes rather than just according to subshell occupancy as done here. For example, correlation energy due to xy/p^2 virtual excitation of a p^6 subshell is computed by Weiss as three separate energy increments: $((p^4)^3P(xy)^3P)^1S$; $((p^4)^1D(xy)^1D)^1S$; and $((p^4)^1S(xy)^1S)^1S$. In the present work these coupling schemes are all included together, contributing to $\epsilon_{2p,2p}$. Since matrix elements of the electronic Hamiltonian connect states belonging to different coupling schemes, the present results and those of Weiss would differ even for a complete orbital basis. Repetition of our work with the orbital basis of Weiss gives no significantly different results. This shows that the substantially better agreement with experiment of the results of Weiss, compared with the present results, must be attributed to the use by Weiss of independent electron-pair coupling schemes to define pair-correlation energies. Comparative results are shown in Table VI. For the $(2s, 2s)$ and $(2s, 2p)$ energy contributions, the differences are negligible, but the $(2p, 2p)$ energies are quite different. The difference between $(2p, 2p)$ results for the closed-shell configuration of F$^-$ and Ne is apparently much larger than for the $2p^5$ configuration of F and Ne$^+$.

The calculations reported here and in I truncate the virtual orbital expansion at $l = 3$, as does the work of Weiss.[4] A previous calculation on the ^1S ground state of Ne, which included orbitals with $l \leq 6$, obtained 105.2% of the empirical correlation energy, using orbital-excitation Bethe–Goldstone equations.[9] This represents a substantial increase over the correlation energy, 98.0% of the empirical value, obtained by orbital-excitation calculations with $l \leq 3$, comparable to the present work.[8] The largest change in net energy increments occurred for $(2p, 2p)$ energies.[9] Since virtual orbitals with $l > 3$ might be expected to have a relatively greater effect on virtual excitations of occupied p orbitals than on s orbitals, a significant part of this increase of correlation energy for Ne(^1S) must be attributed to lack of convergence of the spherical harmonic expansion in the $l \leq 3$ calculation.

In order to test this point, $\epsilon_{2p,2p}$ has been recomputed, using configurational excitations, with one g orbital added to the basis set used here. For F$^-$(^1S) the revised value of $\epsilon_{2p,2p}$ in a.u. is −0.2004, compared with −0.1960 in Table II, and for Ne(^1S) the revised value is −0.2011, compared with −0.1964 in Table II. The change of $\epsilon_{2p,2p}$ is −0.120 and −0.128 eV, respectively. This change is approximately a quarter of the discrepancy between present results and experiment for the process F(^2P) → F$^-$(^1S), noted in Table V. The full correction for angular completeness will, of course, be greater than that obtained with a single virtual orbital (whose exponent was not optimized). If the effect is relatively greater for the $2p^6$ closed shell than for $2p^5$, it would tend to bring the present results into closer agreement with experiment. A similar effect, in the work of Weiss, could bring the results out of agreement with experiment.

In view of this question of angular completeness, which can only be resolved by more elaborate calculations than those reported here or by Weiss,[4] final conclusions cannot yet be drawn about the ultimate accuracy of configurational-excitation calculations.

While a fortuitous cancellation of errors cannot be ruled out, it should be pointed out that a recent calculation of the electron affinity of atomic oxygen,[5] following exactly the procedure used by Weiss for fluorine, is in very good agreement with experiment. The result shown here, in Table V, differs from experiment by 0.5 eV.

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N^{14} $^4S_{3/2}$ g_J Factor Measured by an Atomic-Beam Universal-Detector Technique*

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The atomic-beam magnetic-resonance technique has been used to measure the g-factor ratio of the ground state of nitrogen to the ground state of potassium. The result is $g_J(N^{14}, {}^4S_{3/2})/g_J(K^{39}, {}^2S_{1/2}) = 0.9999196(20)$, where the quoted error represents the 90% confidence level. Combining this result with that of other researchers, we find the absolute g_J factor for nitrogen to be $g_J(N^{14}, {}^4S_{3/2}) = 2.002\,134(5)$. This value is in much better agreement with the result of a recent calculation carried out according to the theory of Kambe and Van Vleck than is the earlier measured value, which was obtained by electron paramagnetic resonance. The discrepancy between experiment and theory is reduced from 13.5 ± 2 to 4 ± 2.5 ppm. The atomic nitrogen was generated in an electrodeless discharge and detected with a new mass-spectrometer universal detector; this latter instrument is described in some detail.

I. INTRODUCTION

In the last few years, several calculations of atomic g_J factors have been made using the theory of Kambe and Van Vleck and high-accuracy Hartree-Fock wave functions.[1] The theoretical g_J factors calculated for the $^3P_1$ and $^3P_2$ states of atomic oxygen, as well as for the $^2P_{3/2}$ state of fluorine, were found to agree with experiment to within 1 ppm or better[2]; this result fostered the hope that such accuracy could be obtained for all states of first-row atoms for which Hartree-Fock wave functions of comparable accuracy were available. Recent theoretical results for nitrogen, however, did not encourage this hope; for the $^4S_{3/2}$, $^2D_{5/2}$, and $^2D_{3/2}$ states the discrepancies with measured g_J values were found to be 13.5 ± 2, 30 ± 8.5, and 15 ± 25 ppm, respectively.[3] The contrast between such exact agreement in fluorine and oxygen and such striking discrepancies in nitrogen suggested that a remeasurement of these latter g_J values was in order. The results of the remeasurement of the g_J value of the $^4S_{3/2}$ state are reported here.

II. THEORY OF EXPERIMENT

The ground configuration of nitrogen is $1s^22s^22p^3$, giving rise to three multiplets: the $^4S_{3/2}$ ground state, the $^2D_{5/2,3/2}$ states, and the $^2P_{3/2,1/2}$ states, which are 19 230 and 28 840 cm^{-1} above the ground state, respectively.[4] The Hamiltonian describing the hyperfine structure (hfs) and Zeeman effect of the $^4S_{3/2}$ ground state of nitrogen is[5]

$$\mathcal{H} = ah\vec{I}\cdot\vec{J} + bh\frac{3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - I(I+1)J(J+1)}{2I(2I+1)J(2J+1)} + g_J\mu_B(\vec{J}\cdot\vec{H}) - g_I\mu_B(\vec{I}\cdot\vec{H}) , \qquad (1)$$

where a is the hfs magnetic-dipole interaction constant, b the nuclear-quadrupole interaction constant, $I\hbar$ the nuclear angular momentum, $J\hbar$ the electronic angular momentum, $g_I = \mu_I/I$ and $g_J = -\mu_J/J$ the corresponding g factors (where μ_I and μ_J are measured in μ_B and $I = 1$ for N^{14}), and $\vec{H}$ the magnetic field. The energy levels for any value of H are obtained by diagonalizing this Hamiltonian on the set of hyperfine states (I, J, F, M_F) associated with the electronic state of interest. Because the dominant configuration contains no unpaired s electrons, the hfs magnetic-dipole constant a is quite small. Owing to the spherical symmetry of the half-filled p shell (S state), the quadrupole coupling constant is very nearly zero in the ground state.

The operation of an atomic-beam apparatus has been adequately described elsewhere.[5] Here it suffices to note that the apparatus used in this experiment is of the "flop-in" variety; thus, in order to be observable, transitions must change the sign of the projection of the magnetic moment along the direction of the magnetic field, and also satisfy the usual selection rules for magnetic-dipole transitions between Zeeman-split hyperfine levels.

The two transitions between hyperfine levels of the $^4S_{3/2}$ ground state of N^{14} studied in this experiment are designated α and β; see Fig. 1. They connect states characterized by the low-field quantum numbers (F, M_F) given by

$$\alpha: \ (2.5, -0.5) \longleftrightarrow (2.5, -1.5),$$