attendant on Stark broadening (damping) constants from this method are typically ±10–20% for the resonance lines of atomic (ionic) species whose ionization potentials are close to that of hydrogen (ionized helium). Conversely, the optically thick profiles of vuv resonance lines whose damping constants and oscillator strengths are known can be used to determine the temperature of a plasma without recourse to absolute intensity measurements.

Note added in proof: For O I and C II a curve of growth analysis has be been used to determine the product of oscillator strengths and Stark widths of some vuv lines [J. C. Morris and R. L. Garrison, Phys. Rev. 188, (1969)].

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†Supported by National Aeronautics and Space Administration and National Science Foundation.

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PHYSICAL REVIEW A VOLUME 2, NUMBER 5 NOVEMBER 1970

Relativistic Hartree-Fock Hyperfine-Structure Calculations for the Scandium, Copper, Gallium, and Bromine Atoms

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(Received 10 April 1970)

The magnetic dipole and electric quadrupole hyperfine constants have been calculated for the $^2D_{3/2}$ and $^2D_{5/2}$ states of scandium and copper and the $^2P_{1/2}$ and $^2P_{3/2}$ states of gallium and bromine atoms. Both restricted and unrestricted numerical relativistic Hartree-Fock calculations have been carried out; the relativistic core-polarization contribution to the hyperfine constants is studied in comparison with the nonrelativistic results.

I. INTRODUCTION

In a recent paper,[1] the contribution of the relativistic effects to the hyperfine structure of atoms with the $(4p)^n$ ground-state configuration was investigated using Dirac-Slater wave functions. These effects were studied within the relativistic Hartree-Fock framework, i.e., by substituting a four-component spinor for each one-electron spin orbital in the expression of the nonrelativistic wave function in j-j coupling. The relativistic radial functions were calculated by a numerical solution of the variational equations, using the Slater approximation[2] for the exchange terms. Moreover, as long as one uses the relativistic method within the restricted scheme, the closed shells do not contribute to the hyperfine constants, i.e., only the relativistic contribution of the open shell is considered and, up to now, core-polarization effects have to be obtained apart from the nonrelativistic framework. It is then desirable to inquire whether a relativistic treatment of core-polarization effects would lead to any substantial improvement to the nonrelativistic results.

In the present paper, the hyperfine structure of the ${}^2D_{3/2}$ and ${}^2D_{5/2}$ states of scandium and copper and of the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states of gallium and bromine is investigated. For these states, the wave functions in j-j coupling are single determinants, and restricted Dirac relativistic Hartree-Fock (DHF) as well as unrestricted relativistic Hartree-Fock (DUHF) hyperfine-structure calculations have been carried without any approximation for the exchange terms. Relativistic results are studied in comparison with the nonrelativistic ones calculated from the nonrelativistic restricted Hartree-Fock (HF) and unrestricted Hartree-Fock (UHF) methods.

II. CALCULATIONS

A. Nonrelativistic Core-Polarization Effects

In the nonrelativistic theory, the hyperfine magnetic dipole $a(J)$ and electric quadrupole $b(J)$ constants are obtained for single determinantal wave function from the following expressions[1,3]:

$$a(J) = a_c(J) + a_l(J) + a_d(J),$$

where

$$a_c(J) = 2\beta_e\left(\frac{\mu}{I}\right)\frac{1}{J}\sum_i \tfrac{2}{3} m_{s_i} |R_i(0)|^2 \qquad (m_{s_i} = \pm\tfrac{1}{2}),$$

$$a_l(J) = 2\beta_e\left(\frac{\mu}{I}\right)\frac{1}{J}\sum_i m_{l_i}\left\langle R_i(r)\frac{1}{r^3}R_i(r)\right\rangle,$$

$$a_d(J) = 2\beta_e\left(\frac{\mu}{I}\right)\frac{1}{J}\sum_i \frac{2m_{si}[l_i(l_i+1) - 3m_{li}^2]}{(2l_i+3)(2l_i-l)} \times\left\langle R_i(r)\frac{1}{r^3}R_i(r)\right\rangle, \tag{1}$$

$$b(J) = -e^2 Q\sum_i \frac{2[l_i(l_i+1) - 3m_{li}^2]}{(2l_i+3)(2l_i-1)}\left\langle R_i(r)\frac{1}{r^3}R_i(r)\right\rangle.$$

In these expressions, the spin orbitals are of the usual central form $|\phi_i\rangle = R_i(r)|l_i m_{l_i} m_{s_i}\rangle$; $\beta_e = e\hbar/2mc$ is the Bohr magneton; μ and Q are the magnetic dipole and electric quadrupole moments of the nucleus of spin I; and J is the total angular momentum of the electrons. It is by now well known that s orbitals ($l=0$) make a zero contribution to $a_l(J)$, $a_d(J)$, and $b(J)$ while the others ($l\neq 0$) make a zero contribution to $a_c(J)$. In the restricted HF framework, the contribution of the closed shells to all constants is zero.

The UHF wave functions used to introduce the polarization of closed shells are obtained, for each state $J = L + S$ with projection of spin $M_S = S$ and projection of angular momentum $M_L = L$ maximum, in allowing all the spin orbitals to have different radial parts. Indeed, it has been shown[3] that for configurations $(nl)^x$ with $l\neq 0$, it is important to include not only spin but also orbital polarization effects. A numerical program written by Froese-Fischer and Bagus has been used to calculate the functions as well as all the radial integrals $\langle R_i(r)|r^{-3}|R_i(r)\rangle$, each of them depending on the values of the four quantum-number values $(nlm_l m_s)$ of the UHF spin orbitals.

As is well known, the UHF wave function is only defined unambiguously from the single determinantal HF wave function, i.e., for the states $J = L+S$. Although the UHF functions are not strictly eigenfunctions of L^2, S^2, and J^2 operators, we have assumed the validity of the usual relations for calculating the hyperfine constants $a(J)$ and $b(J)$ of all J states arising from the same (L, S) term as a function of the partial constants calculated for the state $J = L+S$. The following relations are used[1,3] for the ${}^2D$ state:

$$a(\tfrac{3}{2}) = -a_c(\tfrac{5}{2}) + \tfrac{3}{2}a_l(\tfrac{5}{2}) - \tfrac{7}{2}a_d(\tfrac{5}{2}), \qquad b(\tfrac{3}{2}) = \tfrac{7}{10}b(\tfrac{5}{2}); \tag{2}$$

for the ${}^2P$ state

$$a(\tfrac{1}{2}) = -a_c(\tfrac{3}{2}) + 2a_l(\tfrac{3}{2}) - 10a_d(\tfrac{3}{2}).$$

B. Relativistic Effects

1. *Relativistic Wave Functions*

The relativistic one-electron wave functions are conveniently expressed in the four-component spinor form

$$\varphi_{nljm} = \begin{pmatrix} r^{-1}P(r)\chi_{ljm} \\ ir^{-1}Q(r)\chi_{\bar{l}jm}\end{pmatrix} = \begin{pmatrix} r^{-1}P(r)\chi_{km} \\ ir^{-1}Q(r)\chi_{-km}\end{pmatrix} = \varphi_{nkm}, \tag{3}$$

where the spin angular functions χ_{km} are two-component spinors which are eigenfunctions of the single-particle operators l^2, j^2, j_z, and $K = \beta(\vec{\sigma}'\cdot\vec{1}+1)$ with $l(l+1)$, $j(j+1)$, m, and k, respectively, as eigenvalues such that

$$j = |k| - \tfrac{1}{2}, \quad l = |k+\tfrac{1}{2}| - \tfrac{1}{2}, \quad \bar{l} = |-k+\tfrac{1}{2}| - \tfrac{1}{2}.$$

We have used the matrices

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I\end{pmatrix}, \quad \vec{\sigma}' = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma}\end{pmatrix},$$

where σ_x, σ_y, σ_z, and I are, respectively, the three Pauli matrices and the unit matrix of second order.

The total relativistic wave function is obtained from the nonrelativistic one, in j-j coupling, by replacing the nonrelativistic spin orbitals $(nljm)$ by the four-component spinor as defined in (3). Although the nonrelativistic wave functions used as a starting point are simultaneous eigenfunctions of the total electronic angular momentum operators L^2, S^2, J^2, and J_z, the relativistic wave functions thus obtained are not eigenfunctions of L^2 and S^2, since the radial parts corresponding to $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$ are different. In present examples the overlaps are of the order of 0.998, and thus the lack of *LS* coupling is very small.

The radial functions $P(r)$ and $Q(r)$ are obtained from a minimization of the total energy corresponding to the Hamiltonian

$$\mathcal{H}=\sum_i\left(-ic\vec{\alpha}_i\cdot\vec{\nabla}_i+\beta_i' c-\frac{Z}{r_i}\right)+\sum_{i<j}\frac{1}{r_{ij}}\ , \qquad (4)$$

with the constraint that the wave functions form an orthonormal set, i.e.,

$$\int_0^\infty \left[P_{nk}(r)P_{n'k}(r)+Q_{nk}(r)Q_{n'k}(r)\right]dr=\delta_{nn'}\ ,$$

where $\delta_{nn'}$ is the Kronecker δ. For each electron i, the components of $\vec{\alpha}_i$ are the first three Dirac matrices and β_i' is given by

$$\beta'=\beta-\begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}.$$

The rest-mass energy of the electron (c^2 in a.u.) is substracted from the Dirac one-electron Hamiltonian. The first term of the Breit's operator (magnetic interaction)[4]

$$\mathcal{H}_B=\sum_{i<j}\frac{\vec{\alpha}_i\cdot\vec{\alpha}_j}{r_{ij}} \qquad (5)$$

is used as the relativistic interelectronic interaction term and is treated as a first-order perturbation. The second term (retardation) is neglected. It should be pointed out that for scandium and copper atoms, whose configurations are, respectively, $(3d)\,(4s)^2$ and $(3d)^9\,(4s)^2$, the symmetry $(l=2)$ of the open-shell orbitals $3d$ is different from those of the closed shells $(l=0,\ l=1)$, and the DHF equations, including the exchange terms, do not involve off-diagonal Lagrange multipliers. For gallium and bromine atoms whose configurations are, respectively, $(4p)$ and $(4p)^5$, the variational DHF equations do involve off-diagonal multipliers and have been solved rigorously.

The relativistic unrestricted Hartree-Fock (DUHF) wave functions are obtained in allowing all the spin orbitals φ_{nkm} to have different radial parts; one then obtains hyperfine-structure radial integrals which depend, in addition, on the value of the quantum number m. Programs, using a numerical solution of the variational equations have been written by one of us (J.P.D.)[5] to calculate the DHF and DUHF radial functions as well as the corresponding radial integrals.

For the sake of illustration, we have listed (Table I) for the ${}^2P_{3/2}$ state of gallium the values of the relativistic one-electron energies and of the radial integrals $\langle r\rangle$, $\langle r^2\rangle$, $\langle r^4\rangle$, where

$$\langle r^x\rangle=\int_0^\infty \left[P^2(r)+Q^2(r)\right]r^x\,dr\ ,$$

to compare with the nonrelativistic corresponding quantities. The total energies obtained with the different methods are given in Table II. From the comparison of the relativistic and the nonrelativistic results, it can be seen that the relativistic contributions are, respectively, for scandium, copper, gallium, and bromine atoms, of the order of 0.4%, 0.8%. 0.9%, and 1.1% of the total energies. Furthermore, the relativistic calculated fine-structure intervals (Table II, columns 6 and 7) are in very good agreement with the observed ones.

TABLE I. Comparison of nonrelativistic and relativistic restricted Hartree-Fock results for Ga$({}^2P_{3/2})$.

	$-\epsilon_{nl}$		$\langle r\rangle$		$\langle r^2\rangle$		$\langle r^4\rangle$	
nl	HF	DHF	HF	DHF	HF	DHF	HF	DHF
1*s*	378.8185	383.920 43	0.049 408	0.048 576	0.003 271	0.003 175	0.000 027	0.000 026
2*s*	48.1683	49.305 284	0.220 632	0.216 705	0.057 352	0.055 462	0.005 699	0.005 358
$\overline{2p}$	⋯	43.441 198	⋯	0.188 223	⋯	0.043 511	⋯	0.003 845
	42.4939	⋯	0.192 085	⋯	0.045 150	⋯	0.004 104	⋯
2*p*	⋯	42.413 133	⋯	0.191 660	⋯	0.044 987	⋯	0.004 085
3*s*	6.3945	6.582 942	0.660 471	0.650 264	0.502 651	0.487 551	0.407 076	0.383 472
$\overline{3p}$	⋯	4.620 028	⋯	0.672 974	⋯	0.533 352	⋯	0.497 158
	4.4823	⋯	0.684 091	⋯	0.550 705	⋯	0.529 328	⋯
3*p*	⋯	4.479 352	⋯	0.682 817	⋯	0.548 971	⋯	0.526 933
$\overline{3d}$	⋯	1.177 750	⋯	0.787 660	⋯	0.796 153	⋯	1.568 163
	1.1933	⋯	0.787 901	⋯	0.796 194	⋯	1.568 130	⋯
3*d*	⋯	1.158 332	⋯	0.794 875	⋯	0.812 248	⋯	1.647 793
4*s*	0.4246	0.435 011	2.488 908	2.447 484	7.207 083	6.973 845	90.391 276	84.831 064
4*p*	0.2085	0.205 890	3.424 098	3.438 590	13.899 550	14.032 609	357.640 111	365.766 88

TABLE II. Comparison of nonrelativistic and relativistic[a] total energies (in a.u.).

	J	E_{HF}	E_{DHF}	Breit's[b] contribution	Fine-structure interval E_J(calc)	Fine-structure interval E_j(expt)[c]
Sc(^2D)	$\frac{3}{2}$	−759.7355	−763.1327	0.246 20	0.0007	0.0007
	$\frac{5}{2}$		−763.1320	0.246 07		
Cu(^2D)	$\frac{3}{2}$	−1638.9491	−1652.7064	0.745 61	−0.0094	−0.00 93
	$\frac{5}{2}$		−1652.7158	0.746 29		
Ga(^2P)	$\frac{1}{2}$	−1923.2795	−1941.6363	0.938 90	0.0036	0.003 76
	$\frac{3}{2}$		−1941.6327	0.938 82		
Br(^2P)	$\frac{1}{2}$	−2572.4396	−2603.6001	1.430 54	−0.0169	−0.016 79
	$\frac{3}{2}$		−2603.6170	1.430 86		

[a] The magnetic Breit's contribution is included in the relativistic values.

[b] See Eqs. (5).

[c] *Atomic Energy Levels*, Natl. Bur. Std. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1949).

2. *Hyperfine-Structure Constants*

The relativistic values of the hyperfine-structure dipolar magnetic $a(J)$ and quadrupole electric $b(J)$ constants are obtained for single-determinant DHF and DUHF wave functions from the following relations[6]:

$$a(J) = -2\beta_e\left(\frac{\mu}{I}\right)\frac{1}{J}\sum_i \frac{k_i m_i}{j_i(j_i+1)}\langle r^{-2}\rangle_i ,$$

$$b(J) = e^2 Q \sum_i \frac{2[3m_i^2 - j_i(j_i+1)][\frac{3}{4} - j_i(j_i+1)]}{j_i(j_i+1)(2j_i+3)(2j_i-1)}\langle r^{-3}\rangle_i , \tag{6}$$

where

$$\langle r^{-2}\rangle_i = 2\int_0^\infty P_i(r)Q_i(r)(1/r^2)\,dr ,$$

$$\langle r^{-3}\rangle_i = \int_0^\infty [P_i^2(r) + Q_i^2(r)](1/r^3)\,dr . \tag{7}$$

It can be shown[6] that, for s orbitals ($l=0$), the nonrelativistic limit of the radial quantity $[r^{-2}]_{ns} = (2/3\alpha)\langle r^{-2}\rangle_{ns}$ is $\frac{1}{3}(ns)^2$, while for other orbitals ($l \neq 0$) the nonrelativistic radial integrals $\langle R_i(r) \times | r^{-3} | R_i(r)\rangle$, which come into the calculation of the magnetic dipole and electric quadrupole constants, are, respectively, the limits of the relativistic quantities

$$[r^{-2}]_i = -\frac{1}{\alpha}\frac{1}{(k_i+1)}\langle r^{-2}\rangle_i \quad \text{and} \quad \langle r^{-3}\rangle_i .$$

In these expressions, ns is the value at the nucleus of the radial part of the nonrelativistic orbital, α is the fine-structure constant, and k is the relativistic quantum number previously defined. We have listed (Table III), for the $^2P_{3/2}$ state of gallium, the values of the relativistic quantities $[r^{-2}]_{ns}$, $[r^{-2}]_i$, and $\langle r^{-3}\rangle_i$ in comparison with their nonrelativistic counterparts. Using restricted functions, the correspondence between the DHF and HF integrals is well defined, and it can be seen that the relativistic values are, for the inner shells, slightly larger than the nonrelativistic ones. Moreover, in the relativistic case, it should be pointed out that, within the same nl shell, there is a large dependence of the integrals on the value of the quantum number j ($j = l - \frac{1}{2}$, $j = l + \frac{1}{2}$.) For unrestricted functions, if the DUHF and UHF polarization effects can be compared easily for s shells, the comparison for the other shells is more tedious and will be discussed in Sec. IV.

III. RESULTS AND DISSCUSSION

Theoretical DUHF and UHF values for the dipolar magnetic constants $a(J)$ as well as the individual core-polarization contributions from each nl shell are reported in Table IV. Results indicate that core-polarization effects are, in that case, essentially unaltered by incorporating relativistic effects in the calculation. To better compare DUHF and UHF core-polarization contributions to the quadrupole electric constants $b(J)$, we give (Table V) the values which are obtained for the states $J = L + S$ if one uses the following quadrupole moments (in 10^{-24} cm^2): $Q(^{45}\mathrm{Sc}) = -0.22$, $Q(^{65}\mathrm{Cu}) = -0.19$, $Q(^{69}\mathrm{Ga}) = 0.19$, and $Q(^{79}\mathrm{Br}) = 0.33$. Although the relativistic total vlaues are seen to compare favorably with the nonrelativistic ones, there is some discrepancy between the relativistic and nonrelativistic individual "$2p$" and "$3p$" core polarization contributions. In order to explain this difference, it is necessary to point out that there is no one-to-one correspondence between the DUHF and UHF methods for non-s shells.

If the nonrelativistic UHF contributions to the

TABLE III. Hyperfine-structure radial integrals for the $^2P_{3/2}$ state of Ga.

			Nonrelativistic values			Relativistic values			
nl	*j*	*m*	Dipolar-quadrupolar	Dipolar magnetic	Quadrupolar electric	Dipolar magnetic		Quadrupolar electric	
			HF	UHF		DHF	DUHF	DHF	DUHF
1*s*	$\frac{1}{2}$	$\frac{1}{2}$	38459.57	38459.45	···	41602.51	41602.39	···	···
	$\frac{1}{2}$	$-\frac{1}{2}$		38459.64			41602.60		
2*s*	$\frac{1}{2}$	$\frac{1}{2}$	3693.959	3693.987	···	4125.237	4125.248	···	···
	$\frac{1}{2}$	$-\frac{1}{2}$		3693.938			4125.228		
3*s*	$\frac{1}{2}$	$\frac{1}{2}$	537.322	537.368	···	603.420	603.495	···	···
	$\frac{1}{2}$	$-\frac{1}{2}$		537.298			603.345		
4*s*	$\frac{1}{2}$	$\frac{1}{2}$	29.228	28.416	···	33.230	32.371	···	···
	$\frac{1}{2}$	$-\frac{1}{2}$		29.798			34.154		
2*p*	$\frac{1}{2}$	$\frac{1}{2}$	841.902	841.876	···	927.763	927.757	···	···
	$\frac{1}{2}$	$-\frac{1}{2}$		841.889	···		927.767	···	···
	$\frac{3}{2}$	$\frac{3}{2}$		842.030		848.775	848.887	858.282	858.392
	$\frac{3}{2}$	$\frac{1}{2}$		841.876	841.884		848.741		858.245
	$\frac{3}{2}$	$-\frac{1}{2}$		841.889	841.845		848.736		858.239
	$\frac{3}{2}$	$\frac{3}{2}$		841.873			848.736		858.239
3*p*	$\frac{1}{2}$	$\frac{1}{2}$	108.093	108.073	···	120.360	120.364	···	-
	$\frac{1}{2}$	$-\frac{1}{2}$		108.059	···		120.357	···	-
	$\frac{3}{2}$	$\frac{3}{2}$		108.314		109.593	109.800	111.080	111.290
	$\frac{3}{2}$	$\frac{1}{2}$		108.073	107.953		109.498		110.984
	$\frac{3}{2}$	$-\frac{1}{2}$		108.059	108.003		109.506		110.992
	$\frac{3}{2}$	$-\frac{3}{2}$		108.101			109.569		111.056
3*d*	$\frac{3}{2}$	$\frac{3}{2}$	11.6547	11.681	11.706	11.713	11.728	11.834	11.850
	$\frac{3}{2}$	$\frac{1}{2}$		11.661	11.649		11.705		11.826
	$\frac{3}{2}$	$-\frac{1}{2}$		11.652	11.657		11.704		11.825
	$\frac{3}{2}$	$-\frac{3}{2}$		11.669	11.663		11.716		11.837
	$\frac{5}{2}$	$\frac{5}{2}$		11.595		11.470	11.414	11.493	11.437
	$\frac{5}{2}$	$\frac{3}{2}$		11.637	11.535		11.452		11.474
	$\frac{5}{2}$	$\frac{1}{2}$		11.661	11.642		11.468		11.491
	$\frac{5}{2}$	$-\frac{1}{2}$		11.652	11.659		11.477		11.500
	$\frac{5}{2}$	$-\frac{3}{2}$		11.669	11.677		11.490		11.512
	$\frac{5}{2}$	$-\frac{5}{2}$		11.695			11.516		11.539
4*p*	$\frac{3}{2}$	$\frac{3}{2}$	2.8912	2.					
4*p*	$\frac{3}{2}$	$\frac{3}{2}$	2.8912	2.867		2.910	2.881	2.949	2.920

hyperfine constants $a(J)$ and $b(J)$ arising from each (nlj) shell are expressed, in j-j coupling, as a function of the UHF radial integrals $\langle R(r)|r^{-3}|R(r)\rangle = \langle r^{-3}\rangle_{nlm_lm_s}$, one then obtains the following expressions for the contribution of each "$\bar{p}$" ($j=\frac{1}{2}$) and "p" ($j=\frac{3}{2}$) shells to $b(J)$:

$$b(\bar{p}) = e^2Q\tfrac{4}{15}\,(\langle r^{-3}\rangle_{p0} - \langle r^{-3}\rangle_{\bar{p}+} - \langle r^{-3}\rangle_{p-} + \langle r^{-3}\rangle_{\bar{p}0})\,, \tag{8}$$

$$b(p) = e^2Q(-\tfrac{2}{5}\langle r^{-3}\rangle_{p+} + \tfrac{8}{15}\langle r^{-3}\rangle_{p0} - \tfrac{2}{15}\langle r^{-3}\rangle_{\bar{p}+} - \tfrac{2}{15}\langle r^{-3}\rangle_{p-} + \tfrac{8}{15}\langle r^{-3}\rangle_{\bar{p}0} - \tfrac{2}{5}\langle r^{-3}\rangle_{\bar{p}-})\,.$$

When the UHF values of the radial integrals $\langle r^{-3}\rangle_{nlm_lm_s}$ are used, it occurs that one gets (Table VI) a nonzero contribution to $b(J)$ from the "$2\bar{p}$" and "$3\bar{p}$" shells ($j=\frac{1}{2}$) while, as is well known, the relativistic ones are zero. Moreover, quite different nonrelativistic UHF and relativistic DUHF contributions from the "$2p$" and "$3p$" shells are found. If analogous expressions of the partial contributions $a(\bar{p})$ and $a(p)$ to $a(J)$ in jj coupling are used, one obtains, in that case, quite comparable calculated UHF and DUHF values $a(\bar{p})$ and $a(p)$ from the $2p$ and $3p$ shells. Of course, the relations (8) are obtained in assuming the validity of the usual correspondence between $(nljm)$ and (nlm_lm_s) spin orbitals although, within the unrestricted scheme, different radial parts are associated with different angular and spin quantum numbers. Nevertheless, it should be noted that, if $b(\bar{p})$ and $b(p)$ [or $a(\bar{p})$ and $a(p)$] are added, the usual expression of the UHF contribution from the total p shell is found again.

TABLE IV. Nonrelativistic and relativistic core-polarization contribution to a (*J*).

Atom	J	Method	$1s$	$2s$	$3s$	$4s$	$2p$	$3p$	$3d$	$4p$	$a(J)$
^{45}Sc (^2D)	$\frac{3}{2}$	UHF	−2	53	1	−47	−63	16	297	···	255
		DUHF	0	52	1	−50	−57	12	294		252
	$\frac{5}{2}$	UHF	2	−53	−1	47	−17	5	127	···	110
		DUHF	1	−53	−3	50	−20	5	125		105
^{65}Cu (^2D)	$\frac{3}{2}$	UHF	7	233	−164	−61	−270	185	1992	···	1922
		DUHF	4	228	−136	−82	−235	170	1996		1945
	$\frac{5}{2}$	UHF	−7	−233	164	61	−62	54	857	···	834
		DUHF	−6	−228	134	83	−78	60	850		815
^{69}Ga (^2P)	$\frac{1}{2}$	UHF	16	−4	−6	117	46	83	−44	973	1181
		DUHF	18	−5	−7	132	52	93	−49	1085	1319
	$\frac{3}{2}$	UHF	−16	4	6	−117	9	16	−13	195	84
		DUHF	−18	2	12	−151	9	16	−15	196	51
^{79}Br (^2P)	$\frac{1}{2}$	UHF	55	−2	−65	32	146	276	−34	4203	4611
		DUHF	58	−2	−74	38	175	321	−40	4879	5355
	$\frac{3}{2}$	UHF	−55	2	65	−32	28	53	−9	819	871
		DUHF	−58	3	74	−111	29	55	−12	840	820

The use of relations (8) provides a better understanding but not an explanation of the discrepancy between UHF and DUHF core-polarization effects on $b(J)$. We are led to believe that this discrepancy is one among the logical inconsistencies involved in the use of unrestricted wave functions, and it must be remembered that UHF and DUHF wave functions, indeed, are defined from different restricted wave functions; if a nonrelativistic UHF wave function were defined from a restricted HF wave function, in *jj* coupling, i.e., in allowing all the nonrelativistic Φ_{nljm} spin orbitals (instead of the $\Phi_{nlm_lm_s}$ ones) to have different radial parts, the nonrelativistic contributions to $b(J)$ which would be obtained from each *p* shell ($j=\frac{1}{2}$) would be zero as are the relativistic ones.

The quadrupole moments Q deduced from the experimental values of the constant $b(J)$ are given in Table VI: For scandium and copper, both values deduced from the two states $J=\frac{3}{2}$ and $J=\frac{5}{2}$ are reported when they are different. In Table VII, the theoretical values of the constants $a(J)$ and $b(J)$ obtained from the different methods are recapitulated. Since the UHF wave function is only defined for $J=L+S$, to calculate the UHF core-polarization effects for the other J states, one may assume that either the validity of relations (8) and same core-polarization contributions are obtained for all J states arising from the same (L, S) term, or the validity of the expression (2). The more usual latter method has been used to calculate the UHF values reported (Table VI and VII). This difficulty does not arise within the relativistic framework, since the DUHF wave functions are defined for all J states studied.

Finally, the relativistic contributions to the hyper-

TABLE V. Nonrelativistic and relativistic core-polarization contribution to $b(J)$.[a]

Atom	J	Method	$2\bar{p}$	$2p$	$3\bar{p}$	$3p$	$3\bar{d}$	$3d$	$4\bar{p}$	$4p$	$b(J)$
^{45}Sc (^2D)	$\frac{5}{2}$	UHF	−6	−1	2	1		−42			−46
		DUHF	0	4	0	−1		−41			−38
^{65}Cu (^2D)	$\frac{5}{2}$	UHF	13	−2	−8	7	−6	198			202
		DUHF	0	−15	0	13	−4	198			192
^{69}Ga (^2P)	$\frac{3}{2}$	UHF	0	3	2	8	1	0		51	65
		DUHF	0	3	0	7	1	0		52	63
^{79}Br (^2P)	$\frac{3}{2}$	UHF	−2	−16	−6	−36	−2	−2	4	−355	−415
		DUHF	0	−15	0	−31	−2	−1	0	−369	−418

[a] The notation is $\bar{\varphi}$ for $j=l-\frac{1}{2}$ and φ for $j=l+\frac{1}{2}$.

TABLE VI. Quadrupole moments $Q(10^{-24}\,\mathrm{cm}^2)$ deduced from observed $b(J)$ constants.[a]

Atom	HF	UHF	DHF	DUHF	Other values
^{45}Sc	−0.193; −0.195	−0.176; −0.178	−0.200	−0.182; −0.216	−0.22(1)[b,c]
^{65}Cu	−0.166; −0.159	−0.171; −0.164	−0.164; −0.162	−0.171; −0.162	−0.224[b]; −0.19[d] [−0.16(1); −0.224(5)][e]
^{69}Ga	0.232	0.182	0.225	0.192	0.19(1)[b] 0.178[f]
^{79}Br	0.345	0.308	0.332	0.306	0.33(2)[b] 0.335[e]

[a] Both values deduced from the two states $J=\frac{3}{2}$ and $J=\frac{5}{2}$ are reported when they are different.

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fine-structure constants as well as to the energies are, indeed, more significant as Z increases. However, although relativistic calculations give very good results for the values of the fine-structure intervals, they do not lead to a systematic improvement of the theoretical values of the hyperfine-structure constants. The explanation of the remaining discrepancy between theory and experiment would require explicit consideration of correlation effects.

ACKNOWLEDGMENTS

We are indebted to P.S. Bagus for communicating to us his computational program to calculate the UHF wave functions. We wish to thank Dr. H. Lefebvre-Brion and Dr. C. M. Moser for their critical reading of the manuscript and many stimulating discussions.

TABLE VII. Hyperfine-structure constants a(J) and $b(J)$ (in MHz).

		HF	UHF	DHF	DUHF	Experiment
^{45}Sc (^2D)	$a(\frac{3}{2})$	297	255	294	252	269.56 ±0.02
	$a(\frac{5}{2})$	127	110	125	105	109.034±0.01
	$b(\frac{3}{2})$	− 30	− 33	− 29	− 32	−26.37 ±0.1
	$b(\frac{5}{2})$	− 42	− 46	− 41	− 38	−37.31 ±0.1
^{65}Cu (^2D)	$a(\frac{3}{2})$	1978	1922	1980	1945	1983.9
	$a(\frac{5}{2})$	848	834	833	815	800.37
	$b(\frac{3}{2})$	146	142	147	141	127.5
	$b(\frac{5}{2})$	208	202	204	192	174.3
^{69}Ga (^2P)	$a(\frac{1}{2})$	973	1181	1090	1319	1338.78±0.5
	$a(\frac{3}{2})$	195	84	197	51	190.79428±0.00015
	$b(\frac{3}{2})$	52	65	53	63	62.52247±0.00030
^{79}Br (^2P)	$a(\frac{1}{2})$	4227	4611	4987	5355	···
	$a(\frac{3}{2})$	845	871	863	820	884.810±0.003
	$b(\frac{3}{2})$	− 370	− 415	− 385	− 418	−384.878±0.008

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