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Hyperfine-Structure Calculations for Atoms with the $(4p)^N$ Ground-State Configuration

N. Bessis* and J. Picart
Centre de Mêcanique Ondulatoire Appliqueê, 23, *Rue Du Maroc-Paris* 19*ème-France*

J. P. Desclaux
Commissariat à l'Energie Atomique, 29, *rue de la Fêdêration-Paris* 15*ème-France*

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The magnetic dipole and electric quadrupole hyperfine constants have been calculated for the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ states of gallium and bromine and the ${}^3P_2$ and ${}^3P_1$ states of germanium and selenium, using unrestricted and projected unrestricted Hartree-Fock wave functions to include the polarization of closed-shell effects, and relativistic Hartree-Fock-Slater wave functions to evaluate relativistic effects. The results indicate that both kinds of effects are important. The Landé factors g_J have also been calculated (Breit-Margenau effect).

I. INTRODUCTION

It is well known by now that the calculated values of hyperfine constants of atoms obtained from "restricted" Hartree-Fock (HF) functions are not very satisfactory as a number of important effects have been neglected, viz., polarization of closed shells[1] and other correlation effects[2] and relativistic effects.[3] In this paper, we will calculate the hyperfine constants of atoms with $(4p)^N$ ground-state configuration and study the importance of these effects.

The polarization of the closed shells has been obtained from unrestricted Hartree-Fock (UHF) wave functions which include both "orbital" and "spin" polarization.[1,4] The relativistic effects have been found using relativistic Hartree-Fock (RHF) wave functions[3]; This method consists in substituting in the expression of the nonrelativistic wave function in *jj* coupling four-component relativistic spin orbitals.

II. METHODS

A. Polarization of Closed Shells

In nonrelativistic theory, the hyperfine magnetic dipole and electric quadrupole interactions can be written in the form[5]

$$\mathcal{H}_D = 2\beta_e\left(\frac{\mu}{I}\right)\vec{\mathrm{I}}\cdot[\textstyle\sum_i\langle r_l^{-3}\rangle_i\vec{\mathrm{l}}_i$$

$$+\langle r_d^{-3}\rangle_i\,10^{1/2}\,(sC^{(2)})^{(1)}+\langle r_c^{-3}\rangle_i\vec{\mathrm{s}}_i]\,,$$

$$\mathcal{H}_Q=\frac{eQ}{2I\,(I-1)}\textstyle\sum_i\langle r_q^{-3}\rangle_i[I^{(2)}\cdot C_i^{(2)}],$$

where $\beta_e = e\hbar/2mc$ is the Bohr magneton, and μ and Q are the magnetic dipole and electric quadrupole moments of the nucleus of spin I. In the restricted Hartree-Fock framework, the contribution of the closed shells to all $\langle r^{-3}\rangle$ parameters are zero and the values of $\langle r_l^{-3}\rangle$, $\langle r_d^{-3}\rangle$, and $\langle r_q^{-3}\rangle$ are equal for the open shells.

The unrestricted Hartree-Fock functions which are 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 total angular momentum $M_L=L$ maximum in allowing all the spin orbitals to have different radial parts. Although the UHF functions are not strictly eigenfunctions of L^2, S^2, and J^2 operators, we have assumed that the usual relations hold 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 parameters $\langle r_l^{-3}\rangle$, $\langle r_d^{-3}\rangle$, $\langle r_c^{-3}\rangle$, and $\langle r_q^{-3}\rangle$ calculated for the state $J=L+S$. The relations for the states which we have studied are given in the Appendix. Our intention is not to decide here of the relative merits of the UHF and projected unrestricted Hartree-Fock (PUHF) methods[6]; we mention only that the latter is obtained from the former by the correct projection spin. The hyperfine constants obtained from PUHF functions have been calculated using the approximation of multiplying the parameter $\langle r_c^{-3}\rangle_{\mathrm{UHF}}$ by the factor $S/(S+1)$.[7]

B. Relativistic Effects

1. *Calculation of the Wave Function*

In order to take into account relativistic effects, a possible first step would be to use the RHF method. Instead of using, as Sandars and Beck[3] do, effective operators to calculate the hfs constants, an explicit form for the wave function is obtained which could be used to calculate other physical quantities than the hyperfine constants (e.g., the g_J factors) or, in the future, for a variational calculation.

The nonrelativistic functions used as a starting point are, in jj coupling, simultaneously eigenfunctions of L^2, S^2, J^2, and J_z, built on the ensemble of jj configurations which are derived from each $(nl)^x$ configuration. To consider the lack of (L,S) coupling, we have carried out calculations using nonrelativistic jj wave functions determined for intermediate coupling. These functions are then eigenfunctions of total angular moment J^2 of the electrons for all pairs of compatible values L and S, such that $|L-S| \leqslant J \leqslant L+S$, generally $\Psi(JM_J)=\sum_i C_i\, \Psi(L_iS_iJM_J)$. The values of the C's are obtained by diagonalization of the matrix of the total Breit Hamiltonian.[8] The relativistic function RHF is obtained from the nonrelativistic wave function $\Psi(JM_J)$ by substituting the nonrelativistic spin orbitals $(nljm)$ with the four-component relativistic spin orbitals which are of the form

$$\varphi_{nljm}=\begin{pmatrix} [P_{nk}(r)/r]X_{ljm} \\ \\ \\ i[Q_{nk}(r)/r]X_{\bar{l}jm} \end{pmatrix}=\begin{pmatrix} [P_{nk}(r)/r]X_{km} \\ \\ \\ i[Q_{nk}(r)/r]X_{\bar{k}m} \end{pmatrix}=\varphi_{nkm}\ .$$

The spin angular functions X_{jm} are two-component eigenfunctions of the single-particle operators l^2, j^2, j_z, and $k=\beta(\vec{\sigma}'\circ\vec{1}+1)$, with corresponding eigenvalues $l(l+1)$, $j(j+1)$, m, and k such that $j=|k|-\frac{1}{2}, l=|k+\frac{1}{2}|-\frac{1}{2}, \bar{l}=|-k+\frac{1}{2}|-\frac{1}{2}$.

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 σx, σy, σz, and I are, respectively, the three Pauli matrices and the unit matrix of second order.

The RHF functions thus obtained are farther away from being rigorously simultaneous eigenfunctions of the angular operators L^2, S^2, and J^2, moreover, the relativistic radial parts are different for $\varphi(j=l+\frac{1}{2})$ and $\bar{\varphi}\,(j=l-\frac{1}{2})$. In fact, the overlap $\langle\bar{\varphi}|\varphi\rangle$ is of the order of 0.998.

2. *Calculation of hfs Constants*

The dipole magnetic $a\,(J)$ and electric quadrupole $b\,(J)$ hyperfine constants can be written[9]

$$a(J)=2\beta_e\left(\frac{\mu}{I}\right)\frac{1}{J}\langle JJ\,|\textstyle\sum_i[T_e^{(1)}]_i\,|JJ\rangle\ ,$$

$$b(J)=-eQ\langle JJ\,|\textstyle\sum_i[T_e^{(2)}]_i\,|JJ\rangle\ .$$

They are calculated for each J state as a function of single-electron matrix elements whose expressions are

$$\langle jm\,|T_e^{(1)}\,|j'm\rangle=(-1)^{-m-1/2}[(2j+1)(2j'+1)]^{1/2}\times\begin{pmatrix} j & 1 & j' \\ -m & 0 & m \end{pmatrix}\begin{pmatrix} j & 1' & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}(k+k')\langle r^{-2}\rangle_{jj'},$$

$$\langle jm\,|T^{(2)}\,|j'm\rangle=(-1)^{-m-1/2}[(2j+1)(2j'+1)]^{1/2}\times\begin{pmatrix} j & 2 & j' \\ -m & 0 & m \end{pmatrix}\begin{pmatrix} j & 2 & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}2\langle r^{-3}\rangle_{jj'},$$

where $\langle r^{-2}\rangle_{jj'}=\int_0^\infty[P(r)Q'(r)+Q(r)P'(r)]\frac{1}{r^2}\,dr$,

$$\langle r^{-3}\rangle_{jj'}=\int_0^\infty[P(r)P'(r)+Q(r)Q'(r)]\frac{1}{r^3}\,dr.$$

The quantities in parenthesis are the well-known Wigner $3j$ symbols.

It can be shown[9] that the nonrelativistic radial integrals $\langle r^{-3}\rangle$ which come into the calculation of the hyperfine magnetic dipole and electric quadrupole constants are, respectively, the nonrelativistic limits of the quantities

$$[r^{-2}]_{jj}=-\frac{1}{\alpha}\,\frac{2}{k+k'+2}\,\langle r^{-2}\rangle_{jj'}\ \text{and}\quad \langle r^{-3}\rangle_{jj'}$$

where α is the fine-structure constant, and k and k' are relativistic quantum numbers previously defined.

3. *Calculation of Landé Factors* g_J

In the presence of an external magnetic field $\vec{\mathrm{H}}_m$, there corresponds in the theory of Dirac an interaction term for each electron of the form

$$\mathcal{H}_{\mathrm{mag}}=e\vec{\alpha}\cdot\vec{\mathrm{A}},\quad \text{where}\quad \vec{\mathrm{A}}=\vec{\mathrm{r}}\times\vec{\mathrm{H}}_m\ .$$

The Landé factor g_J is then obtained from the general formula relating reduced matrix elements

$$\langle J\,\|e\textstyle\sum_i\vec{\alpha}_i\cdot\vec{\mathrm{A}}_i\|J\rangle=\beta_e g_J\langle J\,\|\vec{\mathrm{J}}\circ\vec{\mathrm{H}}_m\,\|\,J\rangle\ .$$

The general expression for the single-electron matrix element is

$$\langle ljm\,|e\vec{\alpha}\circ\vec{\mathrm{A}}|\bar{l}'jm\rangle=(-1)^{j-m+l'}[(2j+1)(2j'+1)]^{1/2}\times\begin{pmatrix} j & 1 & j' \\ -m & 0 & m \end{pmatrix}\begin{pmatrix} j & 1 & j' \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix}eH_m\langle r\rangle_{jj'},$$

where $\langle r\rangle_{jj'} = \int_0^\infty [P(r)Q'(r)+Q(r)P'(r)]\,r\,dr.$

The calculation of the factor g_J introduces radial parts of RHF spin orbitals (Breit-Margenau effect).

III. CALCULATIONS

To calculate the UHF wave functions and all the radial integrals $\langle r^{-3}\rangle$, each of them depending on the four quantum-number values(n, l, m_l, m_s) of the spin orbitals, we have used a numerical program written by Froese-Fisher and Bagus. The functions simultaneously eigenfunctions of L^2, S^2, J^2, and J_z, in jj couplings, are obtained by diagonalizing the product of the three matrices $\|L^2\|$, $\|S^2\|$, and $\|J^2\|$ in the basis of determinants corresponding to each eigenvalue M_J of J_z.[10] An automatic program of calculation has been written by one of us (NB). The expressions of the wave functions $\Psi\,(LSJM_J)$ corresponding to $M_J=J$ for the atoms considered are given in the Appendix. The total Breit Hamiltonian we used to obtain the wave functions in intermediate coupling, contains in addition to the electrostatic interaction of the nucleus and the electrons, the interelectronic electromagnetic interactions (the direct spin-orbit term of Landé, spin other orbit and spin-spin interaction). A program has been written to calculate the two electrons spin-spin and spin-order-orbit integrals using expressions of Blume and Watson.[11] The wave functions obtained in intermediate coupling are

$$\text{for Ge,}\quad \Psi(J=2)=0.9952568 \times\Psi(^3P_2)-0.09728238\,\Psi(^1D_2),$$

$$\text{for Se,}\quad \Psi(J=2)=0.99296961 \times\Psi(^3P_2)-0.11836955\,\Psi(^1D_2).$$

The RHF radial functions $P_{nk}(r)$ and $Q_{nk}(r)$ are obtained, for each given jj configuration, from the variational principle. This procedure does not rigorously minimize the energy of a RHF wave function which are in general linear combinations of determinants built on several jj configurations. These radial functions are calculated by a numerical solution of the variational equations, using Slater's[12] approximation for the exchange terms (RHFS method).[13] Nonrelativistic Hartree-Fock-Slater (HFS) calculations are also carried out to see more clearly the role of this approximation. Programs have been written by one of us (JPD) to obtain the HFS and RHFS wave functions.[14] As is known, the HFS and HF values of the total energy are not in good agreement for atoms with low Z: A relativistic HF program without using the Slater approximation for exchange is in progress to carry out better relativistic calculations. For the $^2P_{3/2}$ and $^2P_{1/2}$ states of Ga and Br, the RHFS wave function is built from a single jj configuration and we obtain the total RHFS energies for these two states. For Ga, $E(J=\frac{3}{2})-E(J=\frac{1}{2})=0.0045$ a.u. and for Br $E(J=\frac{3}{2})-E(J=\frac{1}{2})=-0.0184$ a.u. These values are not far from the observed values which are, respectively, 0.0038 and -0.0168 a.u.[15] For the $^3P_2$ and $^3P_1$ states of Ge and Se, the energy values obtained from the two possible jj configurations are quite close, and for that reason, we give only the results which correspond to the configurations of lowest energy, i.e., $(\bar{4}p)\,(4p)$ for Ge and $(\bar{4}p)^2\times(4p)^2$ for Se, $\bar{p}$ corresponding to $j=\frac{1}{2}$ and p to $j=\frac{3}{2}$.

In Tables I and II, we give the values of the RHFS quantities $[r^{-2}]_{jj'}$ and $\langle r^{-3}\rangle_{jj'}$, previously defined, to compare to the nonrelativistic $\langle\varphi|r^{-3}|\varphi\rangle$ radial integrals obtained both from HF and HFS calculations.

IV. RESULTS AND DISCUSSION

Comparison between results obtained from HF and UHF functions indicates the importance of polarization of the filled shells. In Table III, we give the values obtained for the effective parameters $\langle r^{-3}\rangle$ compared with the values of the HF integral $\langle 4p|r^{-3}|4p\rangle$. As one has already seen, for atoms with configuration $(p)^N$ it is important[16] to introduce not only spin but also orbital polarization. The polarization of the $3d$ shell gives always a much smaller effect than total polarization of $2p$ and $3p$ shells and in the magnetic dipole constants the polarization of filled "s" shells is by far the most important effect. Therefore, we give for the magnetic dipole constants the results obtained from both UHF and PUHF wave functions (Tables IV and V). The effective quadrupole parameters $\langle r_q^{-3}\rangle$ calculated from UHF wave functions are larger than HF values: This would diminish the quadrupole moments Q (Table VI) deduced from the experimental constant b (antishielding effect). To better understand the relative importance of the different effects, we also give (Tables IV and V) the calculated values of electric quadrupole constants using the quadrupole moments Q given in the last column of Table VI.

To ascertain the effect of the use of the Slater approximation to determine the relativistic RHFS radial functions, we have carried out calculations using nonrelativistic HFS functions. The comparison of the nonrelativistic results HFS and HF in Table II shows that the Slater exchange approximation leads to an overestimate of the integrals $\langle\varphi|r^{-3}|\varphi\rangle$. But, as the relativistic contributions to the hyperfine constants are differences between the integrals $\langle r^{-2}\rangle_{jj'}$ or $\langle r^{-3}\rangle_{jj'}$ where j and j' equal $l-\frac{1}{2}$ or $l+\frac{1}{2}$, it is difficult to know *a priori* the effect of the approximation on the calculated

TABLE I. Values of the RHFS integrals $[r^{-2}]_{jj'}$ and $\langle r^{-3}\rangle_{jj'}$, in comparison with nonrelativistic integrals $\langle\varphi|r^{-3}|\varphi\rangle$.

			Ga (^2P)						Br (^2P)				
		$[r^{-2}]_{jj'}$		$\langle r^{-3}\rangle_{jj'}$		$\langle\varphi\|r^{-3}\|\varphi\rangle$		$[r^{-2}]_{jj'}$		$\langle r^{-3}\rangle_{jj'}$		$\langle\varphi\|r^{-3}\|\varphi\rangle$	
	j	j'	$J=\frac{1}{2}$	$J=\frac{3}{2}$	$J=\frac{1}{2}$	$J=\frac{3}{2}$	HFS	HF	$J=\frac{1}{2}$	$J=\frac{3}{2}$	$J=\frac{1}{2}$	$J=\frac{3}{2}$	HFS	HF
	$\frac{1}{2}$	$\frac{1}{2}$	938.9118	938.9146	...	...			1443.1308	1443.1233	...	...		
$2p$	$\frac{3}{2}$	$\frac{3}{2}$	871.5412	871.5441	877.9207	877.9237	864.2033	840.6658	1306.1632	1306.1566	1321.0591	1321.0523	1291.0023	1260.3450
	$\frac{1}{2}$	$\frac{3}{2}$	887.4144	887.4172	913.8480	913.8509			1336.1351	1336.1283	1388.1316	1388.1243		
	$\frac{1}{2}$	$\frac{1}{2}$	126.3078	126.3062	...	...			213.4905	213.4843	...	...		
$3p$	$\frac{1}{2}$	$\frac{3}{2}$	116.6464	116.6451	117.7294	117.7280	114.9863	108.4318	192.4486	192.4422	195.2022	195.1957	188.8750	181.1166
	$\frac{1}{2}$	$\frac{3}{2}$	118.9420	118.9405	122.8551	122.8537			196.9030	196.8969	205.4113	205.4049		
	$\frac{3}{2}$	$\frac{3}{2}$	112.9047	12.9059	13.0453	13.0465			25.0583	25.0557	25.4384	25.4358		
$3d$	$\frac{5}{2}$	$\frac{5}{2}$	12.6591	12.6604	12.6852	12.6866	12.8509	11.6481	24.5245	24.5219	24.5953	24.5927	24.8460	23.0850
	$\frac{3}{2}$	$\frac{5}{2}$	12.7390	12.7404	12.7844	12.7857			24.6772	24.6747	24.7988	24.7963		
	$\frac{1}{2}$	$\frac{1}{2}$	4.3395	...	...	...			17.3320	17.2584	...	...		
$4p$	$\frac{3}{2}$	$\frac{3}{2}$	...	3.9609		3.9982	3.9647	2.8667	15.3843	15.3151	15.6095	15.5393	15.2470	11.8710
	$\frac{1}{2}$	$\frac{3}{2}$	...						15.8597	15.7903	16.5518	16.4794		

TABLE II. Values of the (RHFS) integrals $[r^{-2}]_{jj'}$ and $\langle r^{-3}\rangle_{jj'}$ in comparison with the nonrelativistic integrals $\langle\varphi|r^{-3}|\varphi\rangle$.

			Ge (^3P)				Se (^3P)			
			RHFS		HFS	HF	RHFS		HFS	HF
φ	j	j'	$[r^{-2}]_{jj'}$	$\langle r^{-3}\rangle_{jj'}$	$\langle\varphi\|r^{-3}\|\varphi\rangle$		$[r^{-2}]_{jj'}$	$\langle r^{-3}\rangle_{jj'}$	$\langle\varphi r^{-3}\varphi\rangle$	
	$\frac{1}{2}$	$\frac{1}{2}$	1050.4652	...			1302.0193	...		
$2p$	$\frac{3}{2}$	$\frac{3}{2}$	969.2426	977.3093	960.3486	935.1082	1186.2719	1198.5651	1173.5009	1144.9132
	$\frac{1}{2}$	$\frac{3}{2}$	987.9881	1019.5445			1212.0220	1256.2640		
	$\frac{1}{2}$	$\frac{1}{2}$	144.8160				188.2952	...		
$3p$	$\frac{3}{2}$	$\frac{3}{2}$	132.9679	134.3653	130.9458	124.0846	170.8144	173.0382	167.8485	159.5904
	$\frac{1}{2}$	$\frac{3}{2}$	135.6967	140.4902			174.6148	181.6829		
	$\frac{3}{2}$	$\frac{3}{2}$	15.5134	15.6980			21.5724	21.8750		
$3d$	$\frac{5}{2}$	$\frac{5}{2}$	15.2134	15.2478	15.4335	14.0948	21.1294	21.1858	21.4165	19.8111
	$\frac{3}{2}$	$\frac{5}{2}$	15.3074	15.3669			21.2594	21.3567		
	$\frac{1}{2}$	$\frac{1}{2}$	7.1526	...			13.5033	...		
$4p$	$\frac{3}{2}$	$\frac{3}{2}$	6.4363	6.5052	6.4570	4.7842	12.0548	12.2151	12.0427	9.1720
	$\frac{1}{2}$	$\frac{3}{2}$	6.6347	6.8703			12.4206	12.9277		

TABLE III. Effective (UHF) parameters $\langle r^{-3}\rangle$.

		Ga (^2P)		Ge (^3P)		Se (^3P)		Br (^2P)	
			$\langle r^{-3}\rangle_{\mathrm{tot}}$		$\langle r^{-3}\rangle_{\mathrm{tot}}$		$\langle r^{-3}\rangle_{\mathrm{tot}}$		$\langle r^{-3}\rangle_{\mathrm{tot}}$
$\langle r_s^{-3}\rangle_\varphi$	1*s*	−0.3750	−2.8929	−0.5531	−2.2136	−0.9873	−1.0041	−1.2348	−0.4504
	2*s*	0.1053		0.1068		0.0755		0.0482	
	3*s*	0.1415		0.4683		1.1301		1.4516	
	4*s*	−2.7647		−2.2356		−1.2224		−0.7154	
$\langle r_l^{-3}\rangle_\varphi$	2*p*	0.1320	3.0694	0.1976	5.1969	0.3120	9.4435	0.3960	12.6374
	3*p*	0.2423		0.3834		0.6032		0.7573	
	3*d*	−0.1723		−0.1660		−0.1232		−0.1197	
	4*p*	2.8674		4.7819		8.6515		11.6038	
$\langle r_d^{-3}\rangle_\varphi$	2*p*	0.1382	3.1613	0.2030	5.2877	0.3364	9.8275	0.4222	13.1481
	3*p*	0.2439		0.3900		0.6285		0.7951	
	3*d*	−0.0882		−0.0830		−0.0761		−0.0732	
	4*p*	2.8674		4.7777		8.9387		12.0040	
$\langle r_q^{-3}\rangle_\varphi$	2*p*	0.1934	3.7004	0.2932	5.9634	0.4492	10.0391	0.5642	13.2908
	3*p*	0.5665		0.8002		1.1060		1.3417	
	3*d*	0.0731		0.0923		0.1196		0.1371	
	4*p*	2.8674		4.7777		8.3643		11.2478	
$\langle 4p\|r^{-3}\|4p\rangle_{\mathrm{HF}}$		2.8667		4.7842		9.1720		11.8710	

TABLE IV. hfs constants $a(J)$ and $b(J)$ (in Mc/sec) and total energies $E(J)$ (in a.u.).

Atom		HF	UHF	PUHF	RHFS	Experiment
^{69}Ga (^2P)	a ($\frac{1}{2}$)	973	1180	1098	1473	(1338.78 ± 0.5)[a]
	a ($\frac{3}{2}$)	195	84	166	269	(190.79428 ± 0.00015)[b]
$I=\frac{3}{2}$	b ($\frac{3}{2}$)	48	62		67	(62.52247 ± 0.00030)
	E ($\frac{1}{2}$)	−1923.2795	−1923.2822		−1938.1588	...
	E ($\frac{3}{2}$)				−1938.1543	
^{73}Ge (^3P)	a (2)	−57	−37	−48	−80	−64.4270(7)[c]
	a (1)	0	21	11	9	15.5480(18)
$I=\frac{9}{2}$	b (2)	87	112		128	111.825(13)
	b (1)	−45	−56		−61	−54.566(9)
	E	−2075.3613	−2075.3613		−2092.8511	...
^{77}Se (^3P)	a (2)	518	529	554	699	...
	a (1)	0	−70	−45	−98	...
$I=\frac{1}{2}$	E	−2399.8667	−2399.8699		−2423.5808	...
^{79}Br (^2P)	a ($\frac{1}{2}$)	4227	4611	4597	6171	...
	a ($\frac{3}{2}$)	845	871	884	1090	(884.810 ± 0.003)[d]
$I=\frac{3}{2}$	b ($\frac{3}{2}$)	−374	−418		−489	−(384.878 ± 0.008)
	E ($\frac{1}{2}$)	−2572.4396	−2572.4430		−2599.8045	...
	E ($\frac{3}{2}$)				−2599.8229	

[a] G. E. Becker and P. Kusch, Phys. Rev. 73, 584 (1948).

[b] R. T. Daly and J. H. Holloway, Phys. Rev. 96, 539 (1954).

[c] W. J. Childs and L. S. Goodman, Phys. Rev. 141, 15 (1966).

[d] J. G. King and V. Jaccarino, Phys. Rev. 94, 1610 (1954).

TABLE V. Polarization and relativistic effects contributions (in Mc/sec).

		Polarization effects		Relativistic effects	HF values	Total		Experiment
		UHF (a)	PUHF (b)			(a)	(b)	
^{69}Ga (^2P)	a ($\frac{1}{2}$)	207	125	127	973	1307	1225	1338.78
	a ($\frac{3}{2}$)	−110	−29	0	195	85	166	190.79
	b ($\frac{3}{2}$)	14		0	48	62		62.518
^{73}Ge (^3P)	a (2)	16	5	−8	−53	−45	−56	−64.4270
	a (1)	21	11	9	0	30	20	15.480
	b (2)	22		7	90	119		111.825
	b (1)	−11		0	−45	−56		−54.566
^{77}Se (^3P)	a (2)	−2	24	−34	559	523	549	...
	a (1)	−56	−30	−98	0	−154	−128	...
^{79}Br (^2P)	a ($\frac{1}{2}$)	408	394	742	4226	5376	5362	...
	a ($\frac{3}{2}$)	52	65	5	845	902	915	884.810
	a ($\frac{3}{2}$)	−64		−9	−374	−447		−384.878

RHFS values of the constants. The relativistic contributions given in Table V are obtained by comparing HFS and RHFS results. Preliminary RHF calculations, not using Slater approximation, have been carried out in some cases where RHF equations could be solved without off-diagonal Lagrangian multipliers. The RHF $\langle r^{-2}\rangle_{jj'}$, $\langle r^{-3}\rangle_{jj'}$ integrals are really much smaller than the RHFS ones, nevertheless, the results would seem to indicate, in these cases, that the relativistic contributions obtained by comparing HF and RHF results are not very much different from those obtained by comparing HFS and RHFS results.

One must be reminded that our results only partially take into account relativistic effects, as the RHF calculations only are concerned with contributions from the outer $4p$ shell, although it is well known that these effects should be most important on the wave function near the nucleus. Nevertheless, we observe (Table V) that relativistic effects can be as important as polarization effects: The two effects add together when the HF values are much smaller than the observed values and give both an explanation of the nonzero experimental value of the magnetic dipole constant for $^3P_1$ state of Ge.

Finally, the RHFS values, as well as nonrelativistic values of the Landé factor g_J are given in Table VII.

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APPENDIX

A. hfs Constants $a(J)$ and $b(J)$ as a Function of the Effective Parameters $\langle r^{-3}\rangle$

1. ^2P *States*

$$a(\tfrac{3}{2}) = 2\beta_e\left(\frac{\mu}{I}\right)[\tfrac{2}{3}\langle r_l^{-3}\rangle - \tfrac{2}{15}\langle r_d^{-3}\rangle + \tfrac{1}{3}\langle r_c^{-3}\rangle] ,$$

$$a(\tfrac{1}{2}) = 2\beta_e\left(\frac{\mu}{I}\right)[\tfrac{4}{3}\langle r_l^{-3}\rangle + \tfrac{4}{3}\langle r_d^{-3}\rangle - \tfrac{1}{3}\langle r_c^{-3}\rangle] ,$$

$$b(\tfrac{2}{3}) = \epsilon e Q \tfrac{2}{5}\langle r_9^{-3}\rangle .$$

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

Atom	HF	UHF	RHFS	Both effects	Other values[a, b]
^{69}Ga	0.232	0.180	0.166	0.178	0.191; 0.178
^{73}Ge	−0.248	−0.199	−0.177	−0.190	−0.285; −0.2
^{79}Br	0.345	0.308	0.263	0.301	0.335

[a] E. Matthias and D. A. Shirley, Hyperfine Structure and Nuclear Radiations (North-Holland Publishing Co., Amsterdam, 1968).

[b] H. Kopfermann, Nuclear Moments (Academic Press Inc., New York, 1958).

TABLE VII. Landé factors g_J.

				Nonrelativistic calculations		RHFS calculations		
State	j	Atom	Landé value	(L, S) coupling	Intermediate coupling ($g_s = 2.0023$)	(L, S) coupling	Intermediate coupling	Experiment
^2P	$\frac{1}{2}$	Ga	$\frac{2}{3}$	0.66589	...	0.666603		
		Br				0.666464		
	$\frac{3}{2}$	Ga	$\frac{4}{3}$	1.33411	...	1.333276		
		Br				1.333154		
^3P	2	Ge	$\frac{3}{2}$	1.50117	1.49642	1.499768	1.495038	1.49458(9)[a]
		Se			1.49412	1.499721	1.492720	
	1	Ge		1.50117		1.499857		1.50111(7)[a]
		Se				1.499859		
^1D	2	Ge	1	1	1.004743	1.000013	1.004743	1.00639(8)[a]
		Se			1.007022	0.999983	1.006985	1.00639(8)[a]

[a] W. J. Childs and L. S. Goodman, Phys. Rev. 134, A66 (1964).

2. ^3P *States*

$$a(2) = 2\beta_e\left(\frac{\mu}{I}\right)\left[\tfrac{1}{2}\langle r_l^{-3}\rangle + \tfrac{1}{10}\langle r_d^{-3}\rangle + \tfrac{1}{2}\langle r_c^{-3}\rangle\right],$$

$$a(1) = 2\beta_e\left(\frac{\mu}{I}\right)\left[\tfrac{1}{2}\langle r_l^{-3}\rangle - \tfrac{1}{2}\langle r_d^{-3}\rangle + \tfrac{1}{2}\langle r_c^{-3}\rangle\right],$$

$$b(2) = \epsilon eQ\tfrac{2}{5}\langle r_9^{-3}\rangle,$$

$$b(1) = \epsilon eQ\tfrac{1}{5}\langle r_9^{-3}\rangle,$$

where $\epsilon = \pm 1$ according as the $(p)^N$ shell is less or more than half-filled.

B. Expression of the $\Psi(LSJM_J = J)$ Wave Functions in *jj* Coupling

In these expressions, the dots stand for $1s_{-1/2}1s_{1/2}\ldots 3d_{5/2}4s_{-1/2}4s_{1/2}$ closed shells, and the notation is

$$\varphi(nljm) = \varphi_m, \quad \text{for } j = l + \tfrac{1}{2}$$

and $\varphi(nljm) = \bar{\varphi}_m$, for $j = l - \frac{1}{2}$.

1. *Gallium*

$$\Psi(^2P_{3/2}) = \det\left|\cdots 4\bar{p}_{3/2}\right|,$$

and $\Psi(^2P_{1/2}) = \det\left|\cdots 4\bar{p}_{3/2}\right|$.

2. *Germanium*

$$\Psi(^3P_2) = \sqrt{\tfrac{1}{3}}$$

$$\Psi(^3P_2) = \sqrt{\tfrac{1}{3}}\det\left|\cdots 4p_{1/2}4p_{3/2}\right| + \sqrt{\tfrac{2}{3}}\det\left|\cdots 4p_{1/2}4p_{3/2}\right|,$$

and $\Psi(^3P_1) = \frac{1}{2}\sqrt{\frac{1}{3}}\det\left|\cdots 4p_{-1/2}4p_{3/2}\right| + \frac{1}{2}\det\left|\cdots 4p_{1/2}4p_{1/2}\right|$.

3. *Selenium*

$$\Psi(^3P_2) = \sqrt{\tfrac{2}{3}}\det\left|\cdots 4p_{-1/2}4p_{1/2}4p_{1/2}4p_{3/2}\right| + \sqrt{\tfrac{1}{3}}\det\left|\cdots 4p_{1/2}4p_{-1/2}4p_{1/2}4p_{3/2}\right|,$$

and $\Psi(^3P_1) = \frac{1}{2}\sqrt{3}\det\left|\cdots 4p_{-1/2}4p_{-1/2}4p_{1/2}4p_{3/2}\right| - \frac{1}{2}\det\left|\cdots 4p_{1/2}4p_{-3/2}4p_{1/2}4p_{3/2}\right|$.

4. *Bromine*

$$\Psi(^2P_{3/2}) = \det\left|\cdots 4p_{-1/2}4p_{1/2}4p_{-1/2}4p_{1/2}4p_{3/2}\right|,$$

and $\Psi(^2P_{1/2}) = \det\left|\cdots 4p_{1/2}4p_{-3/2}4p_{-1/2}4p_{1/2}4p_{3/2}\right|$.

[*] Present address: Laboratoire de Spectroscopie et de Luminescence Faculté des Sciences de Lyon, 69-Lyon-France.

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