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Relativistic self-consistent-field calculations of the hyperfine structure in the 3*d*-shell atoms

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Nonrelativistic and relativistic self-consistent-field wave functions of the Hartree-Fock type and with statistical exchange have been used for the calculation of radial hyperfine integrals for the 3*d*-shell atoms within the $3d^{N+1}4s$ and $3d^{N+2}$ configurations. The mean value of r^{-3} for the 3*d* electron and the electron density at the nucleus for the 4*s* electron have been evaluated with the nonrelativistic wave functions. The relativistic wave functions have been used for the calculation of radial integrals appearing in an effective hyperfine Hamiltonian for the magnetic dipole and electric quadrupole interaction. For the magnetic dipole interaction the relativistic wave functions calculated with a statistical exchange potential are found to describe the hyperfine interaction for the 4*s* electron in a better way than what is achieved with the HF potential. The experimental orbital, spin-dipole, and contact radial parameters for the 3*d* electrons of some of the elements seem to be strongly influenced by configuration-interaction effects, which are not included in our theoretical values. The magnitude of configuration-interaction effects has been estimated for the orbital and spin-dipole parts by comparing existing experimental radial integrals with the corresponding relativistic ones. The pure relativistic parameters in the effective Hamiltonian for the quadrupole interaction are found to be in good agreement with the experimental values for manganese and cobalt, while the experimental uncertainty for the parameters of the other elements is still too large for a critical comparison to be done. Quadrupole moments have been evaluated with the use of published experimental hyperfine parameters and theoretical radial integrals calculated in this work. A comparison between ratios of experimental quadrupole parameters and relativistic ones gave an estimate of the quadrupole shielding, known as the Sternheimer effect.

I. INTRODUCTION

The knowledge of the hyperfine structure (hfs) for the 3*d*-shell atoms in the two lowest configurations $3d^N4s^2$ and $3d^{N+1}4s$ has increased considerably during the last few years. This is particularly due to high-precision measurements with radiofrequency (rf) methods as the conventional atomic-beam magnetic-resonance (ABMR) technique[1,2] and laser-induced hyperfine pumping combined with radiofrequency spectroscopy[3,4]

The new experimental data have usually been analyzed by means of the technique of effective operators.[5] With such a procedure, effects of configuration interaction as well as relativity are included in a convenient way. Of particular interest for this work are the pure relativistic quadrupole parameters in the effective Hamiltonian for which experimental values are now available for a number of elements. The influence of configuration-interaction effects on these parameters have been discussed by Armstrong and Feneuille.[6,7] They made a perturbation expansion of the relativistic interactions in nonrelativistic terms using the Foldy-Wouthuysen transformation. Using the transformed Hamiltonian it was found that the configuration-interaction contribution on these pure relativistic parameters is mainly due to spin-orbit and Breit interactions. These effects are often neglected in hyperfine structure analysis and zero-order relativistic self-consistent-field (SCF) calculations for the investigated configurations or states should then be able to describe these pure relativistic parameters.

Results from SCF calculations were presented earlier[8,9] for these elements within the $3d^N4s^2$ configuration and for V, Co, and Ni within the $3d^{N+1}4s$ configuration.[8] Therefore Dembczynski *et al.*[10] used the values for V, Co, and Ni, and obtained by interpolation the hyperfine integrals for Mn. The renewed interest in the hfs for the $3d$-shell atoms has motivated us to extend the earlier calculations. We present in this article nonrelativistic and relativistic hyperfine integrals of the magnetic dipole and electric quadrupole interaction for the $3d$-shell atoms within the configurations $3d^{N+1}4s$ and $3d^{N+2}$. These integrals have been calculated using nonrelativistic and relativistic (SCF) wave functions of Hartree-Fock (HF) type and with a statistical exchange known as optimized Hartree-Fock-Slater (OHFS).[8,11,12]

A short description of the hyperfine theory and the SCF methods used are presented in Sec. II. A detailed description of the calculation procedure is given in another article,[13] treating the $4d$- and $5d$-shell atoms. The result and comparison with experimental data are given in Sec. III.

II. THEORETICAL APPROACH

For the analysis of the magnetic dipole interaction within a $nl^N n's$ configuration the effective Hamiltonian is normally taken as[14]

$$H_{\text{hfs}}(M1)=\sum_{i=1}^{N}[\underline{l}_i a_{nl}^{01}-(10)^{1/2}(\underline{s}\,\underline{C}^2)_i^1 a_{nl}^{12}+\underline{s}_i a_{nl}^{10}]\cdot\underline{I}+a_{n's}^{10}\underline{s}_{n'}\cdot\underline{I}\ , \tag{1}$$

where $\underline{I}$ is the nuclear spin. $\underline{l}_i$, $(\underline{s}\,\underline{C}^2)_i^1$, and $\underline{s}_i$ are the orbital, spin dipole, and spin operators for the electrons with orbital angular momentum l. $\underline{s}_{n'}$ is the spin operator for the unpaired s electron. The effective Hamiltonian for the quadrupole interaction of a nl^N or $nl^N n's$ configuration is usually given as[5,15]

$$H_{\text{hfs}}(E2)=\sum_{i=1}^{N}[-\underline{C}_i^2 b_{nl}^{02}+(\tfrac{3}{10})^{1/2}\underline{U}_i^{(13)2}b_{nl}^{13}+(\tfrac{3}{10})^{1/2}\underline{U}_i^{(11)2}b_{nl}^{11}]\cdot\frac{\underline{T}^2(n)}{eQ}\ , \tag{2}$$

where Q is the quadrupole moment and $\underline{T}^2(n)$ the nuclear quadrupole operator. $\underline{C}_i^2$ is a second-rank tensor operator and $\underline{U}^{(\kappa\lambda)k}$ are double tensor operators of rank κ in spin space, rank λ in orbital space, and of rank k in the combined spin-orbital space as discussed by Judd and Sandars.[16,5] The quantities a_{nl}^{ij}, $a_{n's}^{10}$, in Eq. (1) and b_{nl}^{ij} in Eq. (2) are related to the nuclear moments μ_I, Q, and the radial hyperfine integrals in the following way:

$$a_{nl}^{ij}=\frac{\mu_0}{4\pi}2\mu_B\frac{\mu_I}{I}\langle r^{-3}\rangle_{nl}^{ij}\ , \tag{3}$$

$$b_{nl}^{ij}=\frac{e^2}{4\pi\epsilon_0}Q\langle r^{-3}\rangle_{nl}^{ij}\ . \tag{4}$$

In the analysis of experimental hfs using these Hamiltonians, the a_{nl}^{ij} and b_{nl}^{ij} quantities are normally treated as free parameters. It is necessary here to use hfs constants corrected for perturbations due to neighboring J states. The origin of these perturbations is that the hfs operators are not diagonal in J. Breakdown of LS coupling in the considered states also have to be taken into account in the analysis by the use of adequate wave functions intermediate between the LS- and jj-coupling limits. It is shown in earlier works[8] that the values of the experimental parameters are sensitive to the intermediate-coupling coefficients, which put great demands on the quality of the intermediate wave functions used. The $3d$-shell elements are characterized by the three even configurations $3d^N4s^2$, $3d^{N+1}4s$, and $3d^{N+2}$, which are very close in energy and are therefore strongly mixed. This strong configuration mixing has to be taken into account by the use of angular wave functions expanded in all three configurations. Extensive analysis of this type has for example been done by Dembczynski for Mn[10] and Fe.[17]

Generally a magnetic dipole interaction constant for a certain $|SLJ\rangle$ state of these elements will be expressed in 12 different radial parameters; three for the d electrons from each configuration; one from the unpaired s electron, and two cross-configuration parameters. For the quadrupole interaction 11 parameters are needed, i.e., three for the d electrons from each configuration and two cross-configuration parameters. These cross-configuration parameters are proportional to the integral $\langle 3d\,|\,r^{-3}\,|\,4s\rangle$ and are normally neglected in the analysis. We have estimated these integrals nonrelativistically as well as relativistically to be of the order of $\sim 10^{-3}$ a.u. and the neglection of them is therefore justified in comparison with the diagonal integrals (Tables II and III). Although a reduction of the number of parameters is obtained in this way, it is in most cases not possible to get a complete determination of them due to lack of experimental data. Further approximations as, for example, fixing the ratios between some of the parameters, are therefore usually done in the analyses.

The experimentally determined radial integrals include, besides the zero-order nonrelativistic HF values, relativistic and configuration-interaction effects as discussed by Judd,[18,19] Sandars,[20] and Armstrong, and Feneuille.[6,7] For the analysis of these effects it is convenient to rewrite the experimentally determined integrals in the following way:

$$\langle r^{-3}\rangle^{01}_{nl,E}=\langle r^{-3}\rangle^{01}_{nl,R}(1+\Delta^{01}_{nl})\ , \tag{5a}$$

$$\langle r^{-3}\rangle^{12}_{nl,E}=\langle r^{-3}\rangle^{12}_{nl,R}(1+\Delta^{12}_{nl})\ , \tag{5b}$$

$$\langle r^{-3}\rangle^{10}_{nl,E}=\langle r^{-3}\rangle^{10}_{nl,R}+\langle r^{-3}\rangle^{10}_{nl,C}\ , \tag{5c}$$

$$\langle r^{-3}\rangle^{10}_{n's,E}=\langle r^{-3}\rangle^{10}_{n's,R}(1+\Delta^{10}_{n's})\ , \tag{5d}$$

$$\langle r^{-3}\rangle^{02}_{nl,E}=\langle r^{-3}\rangle^{02}_{nl,R}(1+\Delta^{02}_{nl})\ , \tag{5e}$$

$$\langle r^{-3}\rangle^{13}_{nl,E}=\langle r^{-3}\rangle^{13}_{nl,R}\ , \tag{5f}$$

$$\langle r^{-3}\rangle^{11}_{nl,E}=\langle r^{-3}\rangle^{11}_{nl,R}\ . \tag{5g}$$

The indices E, R, and C refer here to experimental, relativistic Hartree-Fock, and core-polarization values, respectively. $\langle r^{-3}\rangle^{ij}_{nl,R}$ represents the relativistic effective hyperfine integrals as introduced by Sandars and Beck[5] and also defined in other works.[8,14,15] The contribution of configuration interaction is taken into account by introducing the parameters Δ^{ij}_{nl}. The relativistic $\langle r^{-3}\rangle^{01}_{nl,R}$, $\langle r^{-3}\rangle^{12}_{nl,R}$, and $\langle r^{-3}\rangle^{02}_{nl,R}$ integrals will, in the nonrelativistic limit, be equal to the nonrelativistic mean value of r^{-3}, while the integrals $\langle r^{-3}\rangle^{10}_{nl,R}$, $\langle r^{-3}\rangle^{13}_{nl,R}$, and $\langle r^{-3}\rangle^{11}_{nl,R}$ are of purely relativistic nature and approach zero in the nonrelativistic limit. The $\langle r^{-3}\rangle^{13}_{nl,E}$ and $\langle r^{-3}\rangle^{11}_{nl,E}$ integrals are influenced by configuration mixing mainly due to the spin-orbit and Breit interactions as mentioned before.[6,7] These effects are here assumed to be small compared to the zero-order SCF values $\langle r^{-3}\rangle^{11}_{nl,R}$ and $\langle r^{-3}\rangle^{13}_{nl,R}$. The Δ^{ij}_{nl} parameters are therefore omitted in Eqs. (5f) and (5g). The further analysis will show the validity of this assumption. For the $\langle r^{-3}\rangle^{10}_{nl,E}$ parameter, however, the most dominant contribution is from configuration interaction. The valence electrons polarize the core and this gives a net spin density at the nucleus resulting in an induced contact parameter for the nl shell. This effect is also denoted as spin polarization. The $\langle r^{-3}\rangle^{10}_{nl,E}$ parameter has therefore been expressed in a different way compared to the others.

In this work we have calculated nonrelativistic and relativistic SCF wave functions for the $3d$ elements within the configuration $3d^{N+1}4s$ and $3d^{N+2}$. The calculations have been done within the Hartree-Fock (HF) and optimized Hartree-Fock-Slater[8,11,12] (OHFS) schemes nonrelativistically as well as relativistically. All these wave functions have been evaluated for the average energy of the considered configuration[21] and not for a particular LS term. Applying this scheme in the relativistic case leads to the average energy of a certain jj configuration, i.e., a configuration where the occupation numbers are given for each nlj shell. Such a treatment is, however, only meaningful when jj coupling dominates. The $3d$ elements are closer to LS coupling than to jj coupling and it is in such a case that only the occupation numbers of the different nl shells are relevant. The relativistic wave functions are, with such an approach, calculated for the entire LS configuration and denoted as LS average. More detailed descriptions of the SCF calculations are given in the earlier review article[8] or in the article for the $4d$ and $5d$ elements.[13]

III. RESULTS AND DISCUSSION

A compilation of stable isotopes for which accurate hfs measurements are known for the $3d$-shell atoms in the $3d^N4s^2$ and $3d^{N+1}4s$ configurations is presented in Table I. No measurements have up to now been done for states within the $3d^{N+2}$ configuration. The hfs is known for many elements in more than three or four states for the $3d^N4s^2$ and $3d^{N+1}4s$ configurations, which means that an extensive analysis can be performed. It is also of particular interest to observe that for some elements the hfs has been measured in two different LS terms for one of the configurations. It may therefore be possible to check the importance of LS-dependent configuration-interaction contributions as discussed by Bauche-Arnoult[23,24] and Armstrong.[6] For the further analysis, nuclear magnetic dipole moments and nuclear spins[22] are included in this table.

Radial hyperfine integrals for the magnetic dipole and electric quadrupole interaction are presented in Tables II and III for the $3d^{N+1}4s$ and $3d^{N+2}$ configurations, respectively. The mean value of r^{-3} for the valence d electrons and the electron density at the nucleus for the $4s$ electron

TABLE I. Nuclear spins and nuclear magnetic dipole moments for stable isotopes of the $3d$ elements for which accurate hfs measurements have been performed in different states of the $3d^N4s^2$ and $3d^{N+1}4s$ configurations.

Isotope	I	μ_I (nm)	N	States in which hfs has been measured $3d^N4s^2$ configuration	Ref.	$3d^{N+1}4s$ configuration	Ref.
^{45}Sc	$\frac{7}{2}$	4.749	1	$^2D_{3/2,5/2}$	28	$^4F_{3/2-9/2}$	29,30
^{47}Ti	$\frac{5}{2}$	-0.787	2	$^3F_{2-4}$	31,32	$^5F_{2-5}$	32
^{49}Ti	$\frac{7}{2}$	-1.102	2				
^{51}V	$\frac{7}{2}$	5.142	3	$^4F_{3/2-9/2}$	33,34	$^6D_{1/2-9/2}$ $^4D_{1/2-7/2}$	33,35
^{50}V	6	3.341	3	$^4F_{3/2}$	47		
^{53}Cr	$\frac{3}{2}$	-0.470	4			$^7S_3$	36
^{55}Mn	$\frac{5}{2}$	3.446	5	$^6S_{5/2}$	37	$^6D_{1/2-9/2}$	10
^{57}Fe	$\frac{1}{2}$	0.0903	6	$^5D_{1-4}$	38,39	$^5F_{2-5}$ $^3F_{2-4}$	17,39
^{59}Co	$\frac{7}{2}$	4.61	7	$^4F_{3/2-9/2}$	31,40, 41	$^4F_{5/2-9/2}$	40
^{61}Ni	$\frac{3}{2}$	-0.748	8	$^3F_{2-4}$	42,43	$^3D_{2,3}$	42,43
^{63}Cu	$\frac{3}{2}$	2.218	9	$^2D_{3/2,5/2}$	44,45	$^2S_{1/2}$	46
^{65}Cu	$\frac{3}{2}$	2.376	9				

have been evaluated with the nonrelativistic wave functions. The relativistic effective radial integrals for the d electrons, given as linear combinations of relativistic one-electron integrals for the j states $j=\frac{3}{2}$, $\frac{5}{2}$ are presented. We have for the $4s$ electrons in Table II given the relativistic correspondence of $(dP/dr)^2_{r=0}$ so that the relativistic correction factor (RCF) can be evaluated directly.[8,13] It should be noted that the $\langle r^{-3}\rangle^{10}_{4s}$ parameter in Eq. (5d) is related to $\langle r^{-3}\rangle^{M}_{4s}$ and $(dP/dr)^2_{r=0}$ through

$$\langle r^{-3}\rangle^{10}_{4s}=\tfrac{2}{3}\langle r^{-3}\rangle^{M}_{4s}=\tfrac{2}{3}F^{10}_{4s}\left[\frac{dP}{dr}\right]^2_{r=0}, \tag{6}$$

where F^{10}_{4s} is the RCF. Earlier, when *ab initio* relativistic radial integrals were not available, RCF evaluated from hydrogenic wave functions[25] were almost exclusively used in hfs analysis. Using Tables II and III, the RCF for the different hyperfine parameters for the $3d$ electrons can also be calculated as the ratio between the relativistic and nonrelativistic integrals.

A. Magnetic dipole interaction

Figure 1 shows a graph of the experimental values of $(dP/dr)^2_{r=0}$ within the $3d^{N+1}4s$ configuration. For comparison, the theoretical nonrelativistic value $(dP/dr)^2_{r=0}$ and the corresponding relativistic quantity $\langle r^{-3}\rangle^{M}_{4s}$, calculated with orbitals of HF and OHFS type, are given in the same figure. The RCF for the contact parameter of the $4s$ electron, i.e., F^{10}_{4s} is almost the same for both methods and varies from 1.075 for Sc to 1.149 for Cu. Hence the relativistic contribution to this parameter is a factor of 2 greater for the slightly heavier element Cu than for Sc. A better agreement is achieved between experiment and theory if the OHFS or ROHFS wave functions are used instead of HF or RHF wave functions for calculation of this parameter. This is a general trend which has been found in many cases.[8] By the use of formula (5d) the configuration-interaction contribution Δ^{10}_{4s} can be deduced from a comparison of the experimental and the RHF values. Δ^{10}_{4s} varies from -0.05 to $+0.45$.

A detailed discussion of the effective $\langle r^{-3}\rangle^{ij}_{3d}$ values for the $3d$ elements within the $3d^N4s^2$ configurations was presented in the earlier analysis.[8,9] The result for the $3d^{N+1}4s$ and the $3d^{N+2}$ configurations for these elements presented in Tables II and III, shows the same general trends as obtained within the $3d^N4s^2$ configuration. Within all three configurations the electrons are more bound with increasing N, which give an increase in the

TABLE II. Nonrelativistic and relativistic hyperfine integrals for the magnetic dipole and electric quadrupole interaction for the $3d$ elements in the $3d^{N+1}4s$ configuration. Experimental integrals are given for the magnetic dipole interaction.

				Nonrelativistic		Relativistic							
						Magnetic dipole					Electric quadrupole		
Z	Element	Config.	Method	$\langle r^{-3}\rangle_{3d}$	$\left[\frac{dP}{dr}\right]^2_{r=0}$ $4s$	$\langle r^{-3}\rangle^{01}_{3d}$	$\langle r^{-3}\rangle^{12}_{3d}$	$\langle r^{-3}\rangle^{10}_{3d}$	$\frac{\langle r^{-3}\rangle^{01}_{3d}}{\langle r^{-3}\rangle^{12}_{3d}}$	$\langle r^{-3}\rangle^{M}_{4s}$	$\langle r^{-3}\rangle^{02}_{3d}$	$\langle r^{-3}\rangle^{13}_{3d}$	$\langle r^{-3}\rangle^{11}_{3d}$
21	Sc	$3d^2 4s$	OHFS	1.155	21.936	1.134	1.159	−0.0115	0.978	23.414	1.134	0.0387	−0.0184
			HF	1.056	16.123	1.034	1.048	−0.0067	0.987	17.325	1.034	0.0251	−0.0109
			Expt			0.911	2.395		0.38	22.6			
22	Ti	$3d^3 4s$	OHFS	1.707	25.440	1.683	1.718	−0.0166	0.980	27.357	1.683	0.0590	−0.0269
			HF	1.592	18.738	1.566	1.591	−0.0115	0.984	20.152	1.567	0.0440	−0.0189
			Expt			1.506(1)	1.162(12)	−0.12(6)	1.295	23.8(3)			
23	V	$3d^4 4s$	OHFS	2.314	28.905	2.286	2.337	−0.0235	0.978	31.317	2.287	0.0862	−0.0383
			HF	2.177	20.983	2.150	2.189	−0.0182	0.982	22.590	2.151	0.0698	−0.0299
			Expt			2.204(36)	1.93(14)	−1.36(4)	1.142	33.23(33)			
24	Cr	$3d^5 4s$	OHFS	2.994	32.459	2.962	3.031	−0.0325	0.977	35.453	2.964	0.122	−0.0533
			HF	2.839	23.585	2.807	2.865	−0.0268	0.980	25.802	2.809	0.103	−0.0441
			Expt							24.9			
25	Mn	$3d^6 4s$	OHFS	3.757	36.036	3.721	3.815	−0.0440	0.975	39.700	3.723	0.168	−0.0725
			HF	3.580	26.030	3.545	3.627	−0.0383	0.977	28.558	3.548	0.148	−0.0630
			Expt			2.959(3)	3.256(19)	−1.33(32)	0.909	39.9(1.9)			
26	Fe	$3d^7 4s$	OHFS	4.610	39.774	4.569	4.695	−0.0587	0.973	44.207	4.572	0.226	−0.0968
			HF	4.413	28.836	4.373	4.487	−0.0530	0.975	31.995	4.377	0.205	−0.0872
			Expt			3.913	3.982	−1.448	0.947	37.0			
27	Co	$3d^8 4s$	OHFS	5.558	43.635	5.513	5.678	−0.0769	0.971	48.958	5.518	0.299	−0.127
			HF	5.350	31.512	5.301	5.457	−0.0730	0.971	35.379	5.305	0.281	−0.120
			Expt			5.1	5.1	−1.39(14)		50 (1)			
28	Ni	$3d^9 4s$	OHFS	6.610	47.568	6.559	6.774	−0.0993	0.968	53.899	6.567	0.389	−0.165
			HF	6.369	34.492	6.321	6.526	−0.0958	0.968	39.239	6.327	0.370	−0.157
			Expt	5.92						56			
29	Cu	$3d^{10} 4s$	OHFS		51.68					59.16			
			HF		37.48					43.07			
			Expt							62.39			

TABLE III. Nonrelativistic and relativistic hyperfine integrals for the magnetic dipole and electric quadrupole interaction for the $3d$ elements in the $3d^{N+2}$ configuration.

					Relativistic						
				Nonrelativistic	Magnetic dipole				Electric quadrupole		
Z	Element	Config.	Method	$\langle r^{-3}\rangle_{3d}$	$\langle r^{-3}\rangle_{3d}^{01}$	$\langle r^{-3}\rangle_{3d}^{12}$	$\langle r^{-3}\rangle_{3d}^{10}$	$\frac{\langle r^{-3}\rangle_{3d}^{01}}{\langle r^{-3}\rangle_{3d}^{12}}$	$\langle r^{-3}\rangle_{3d}^{02}$	$\langle r^{-3}\rangle_{3d}^{13}$	$\langle r^{-3}\rangle_{3d}^{11}$
21	Sc	$3d^3$	OHFS	0.952	0.884	0.911	−0.0129	0.970	0.884	0.0398	−0.0202
			HF	0.750	0.736	0.750	−0.0066	0.981	0.736	0.0222	−0.0105
22	Ti	$3d^4$	OHFS	1.439	1.375	1.417	−0.0201	0.970	1.374	0.0642	−0.0318
			HF	1.244	1.226	1.253	−0.0132	0.978	1.226	0.0446	−0.0211
23	V	$3d^5$	OHFS	1.994	1.931	1.991	−0.0290	0.970	1.930	0.0953	−0.0461
			HF	1.794	1.773	1.820	−0.0222	0.974	1.773	0.0750	−0.0354
24	Cr	$3d^6$	OHFS	2.627	2.564	2.648	−0.0404	0.968	2.564	0.135	−0.0644
			HF	2.419	2.394	2.464	−0.0336	0.972	2.394	0.114	−0.0536
25	Mn	$3d^7$	OHFS	3.344	3.279	3.394	−0.0545	0.966	3.279	0.186	−0.0874
			HF	3.122	3.093	3.196	−0.0489	0.968	3.093	0.167	−0.0781
26	Fe	$3d^8$	OHFS	4.151	4.084	4.237	−0.0723	0.964	4.085	0.251	−0.116
			HF	3.914	3.882	4.025	−0.0682	0.964	3.882	0.234	−0.109
27	Co	$3d^9$	OHFS	5.054	4.984	5.183	−0.0942	0.962	4.986	0.331	−0.152
			HF	4.803	4.765	4.962	−0.0940	0.960	4.765	0.322	−0.150

$\langle r^{-3}\rangle_{3d}$ and $\langle r^{-3}\rangle_{3d}^{ij}$ values. A comparison of the $\langle r^{-3}\rangle_{3d}^{ij}$ values, with a nonrelativistic counterpart, evaluated for the different configurations of a certain element, shows that the $3d$ orbitals are more contracted when the $4s$ electrons are present. This is due to the fact that the $4s$ orbital is mainly located outside the $3d$ shell. The RCF for the orbital part is smaller than unity, while the RCF for the spin-dipole term varies from 0.99 to 1.02. The relativistic effective radial integral $\langle r^{-3}\rangle_{3d}^{10}$ for the contact term is very small for both configurations, i.e., of the order of −0.01 to −0.10. The experimental values are, as seen from Table II, about $-1.5a_0^{-3}$ for most of the elements. The main contribution to the experimental contact parameters for the d electrons is therefore configuration interaction. More detailed many-body calculations are necessary to describe these configuration interactions as, for example, those made by Kelly and Ron for iron.[26] An estimation of the spin-polarization effects can be obtained by use of spin polarized wave functions as was done for the $^7S_3$ state in chromium.[27]

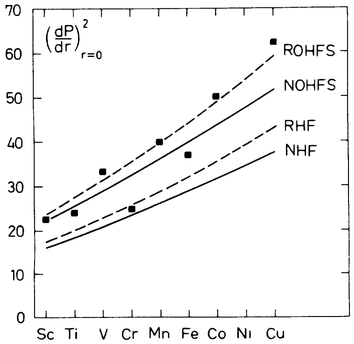

FIG. 1. A comparison between the experimental and theoretical radial hyperfine integrals (in units of a_0^{-3}) for the $4s$ electron of the $3d$ elements in the $3d^{N+1}4s$ configuration.

As seen from Table II the $\langle r^{-3}\rangle_{3d}^{01}$ integrals describe the general trend of the experimental values for the orbital part in the $3d^{N+1}4s$ configuration. This is not so pronounced for the spin-dipole integrals, where the difference between the theoretical and experimental values vary somewhat more compared with the orbital case. This is probably caused by the higher rank of the spin-dipole operator which is 2 in the orbital space and 1 in the spin space, compared to 1 and 0, respectively,

TABLE IV. Values of experimental configuration-interaction contributions as evaluated by use of Eq. (5).

Element	Configuration $3d^N4s^2$ $1+\Delta^{01}$	$1+\Delta^{12}$	Configuration $3d^{N+1}4s$ $1+\Delta^{01}$	$1+\Delta^{12}$
Sc	0.92	0.81	0.88	2.29
Ti	0.96	0.93	0.96	0.73
V	0.98	0.87	1.03	0.88
Mn			0.84	0.90
Fe[a]	0.92	0.92	0.90	0.89
Co	0.94	0.99	0.96	0.94
Ni	0.97	0.92		

[a]Corrected for two-body effects (see Ref. 17).

for the orbital operator. The spin-dipole operator therefore mixes more configurations than the orbital one.

The different contributions of configuration interaction to these terms are usually analyzed by evaluating the ratio $\langle r^{-3}\rangle_{nl}^{01}/\langle r^{-3}\rangle_{nl}^{12}$, which, in the absence of relativistic and configuration-interaction effects, is equal to unity. This was done in the analysis of the $3d^N4s^2$ configuration and is given in Fig. 7 of Ref. 8. It is observed that the pure relativistic contributions have no significant influence on this ratio. Absolute values of the configuration interaction to the orbital and spin-dipole values can also be evaluated by using Eq. (5) and the experimental and theoretical values in Table II. The $1+\Delta^{01}$ and $1+\Delta^{12}$ factors calculated in this way and presented in Table IV are for most elements in the range of 0.8 – 1.0, which means that the Δ^{01} and Δ^{12} contributions are negative. We present the values with two decimals although the uncertainties in the experimental parameters vary significantly for different elements. The different uncertainties are due to lack of experimental hyperfine structure data and the assumptions made in the analysis. The original papers should therefore be checked in each case. The Δ^{01} values vary almost linearly for the elements Sc, Ti, V, and Mn, Fe, Co, Ni in both configurations, while the spin-dipole part Δ^{12} has a more irregular behavior. More definite conclusions of the variation of Δ^{ij} parameters seem to be not possible at present.

B. Electric quadrupole interaction

From the hyperfine structure measurements in the different states as presented in Table I experimental quadrupole parameters b_{3d}^{ij} have been extracted. A compilation of published values are given in Table V.

Of particular interest for the calculations presented in this work are the pure relativistic operators $\underline{U}^{(11)2}$ and $\underline{U}^{(13)2}$ in the electric quadrupole Hamiltonian. If we assume that Eqs. (5f) and (5g) are valid, the ratio between the experimental parameters b_{3d}^{11} and b_{3d}^{13} should be equal to the ratio between the corresponding relativistic integrals in Tables II and III. A comparison of theoretical and experimental values for this ratio is given in Fig. 2. The theoretical ratios are nearly the same

TABLE V. Experimental quadrupole hyperfine parameters and quadrupole moments evaluated using relativistic Hartree-Fock integrals. The notation Q^{ij} for the quadrupole moments means that they have been evaluated from the experimental b_{3d}^{ij} parameters by use of the theoretical integrals $\langle r^{-3}\rangle_{3d}^{ij}$.

Isotope	I	Configuration	Ref.	b_{3d}^{02} (MHz)	b_{3d}^{13} (MHz)	b_{3d}^{11} (MHz)	Q^{02} (b)	Q^{13} (b)	Q^{11} (b)
^{45}Sc	$\frac{7}{2}$	$3d^24s$	30	−48(2)	5(5)	1.5(6)	−0.20(1)	0.9(9)	−0.6(2)
^{47}Ti	$\frac{5}{2}$	$3d^34s$	32	99.8(1.6)	1.85(1.4)	−1.25(2.0)	0.271(4)	0.18(14)	0.28(45)
^{49}Ti	$\frac{7}{2}$	$3d^34s$	32	81.8(1.3)	1.5(1.2)	−1.0(1.6)	0.222(4)	0.15(12)	0.23(36)
^{51}V	$\frac{7}{2}$	$3d^34s^2$	35	−29.0(2)	1.3(4)	−0.4(2)	−0.0482(3)	0.08(2)	0.06(3)
		$3d^44s$	35	−24.6(2)	0.6(9)	0.1(7)	−0.0487(4)	0.036(54)	−0.01(10)
^{55}Mn	$\frac{5}{2}$	$3d^64s$	10	229.883(28)	9.877(200)	−4.375(100)	0.2757(1)	0.284(6)	0.296(7)
^{59}Co	$\frac{7}{2}$	$3d^74s^2$	40	487.7(5.6)	24.6(1.2)	−7.2(9)	0.354(4)	0.382(19)	0.281(35)
		$3d^84s$	40	406.7(8.1)	12.9(5.0)	9.9(11.1)	0.326(7)	0.20(8)	−0.35(40)
^{61}Ni	$\frac{3}{2}$	$3d^84s^2$	43	200.9	11.8	−5.4	0.123	0.140	0.158

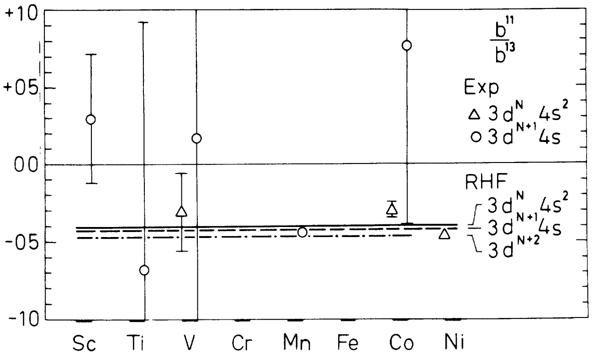

FIG. 2. Experimental and theoretical (RHF) ratios of the pure relativistic integrals $\langle r^{-3}\rangle^{11}$ and $\langle r^{-3}\rangle^{13}$ for the $3d^N4s^2$, $3d^{N+1}4s$, and $3d^{N+2}$ configurations.

for all the elements in the three different configurations and is about -0.4. The agreement between the theoretical and experimental values for Mn is surprisingly good. This indicates that the configuration-interaction effects on these two parameters are very small or that these effects are of the same relative sign and magnitude in both parameters. A comparatively good agreement is also achieved for V, Co, and Ni within the $3d^N4s^2$ configuration.

The uncertainty in the experimental data for the other elements is too great for a critical test to be done. However, it should be noted that these two parameters are very hard to extract due to their magnitude compared with the nonrelativistic one. Further, the coefficients for these parameters in the parametrized expression for the quadrupole-interaction constants are small and very sensitive to the type of intermediate wave functions used. More experimental data and refined analysis for most of these elements seem therefore necessary to test the importance of relativistic configuration-interaction effects on these parameters.

The experimental b_{3d}^{ij} parameters can, by neglecting configuration-interaction effects, be used directly for the evaluation of the quadrupole moments by use of the corresponding theoretical radial integrals in Table II in this work and Table 29 of Ref. 8. The result is given in the columns to the right in Table V. The notation Q^{ij} for the quadrupole moments means that they have been evaluated from the experimental b_{3d}^{ij} parameters by use of the theoretical integrals $\langle r^{-3}\rangle_{3d}^{ij}$. We notice how the quadrupole moments Q^{13} and Q^{11} are generally associated with large uncertainties. However, for Co in the $3d^N4s^2$ configuration and for Mn in the $3d^{N+1}4s$ configuration the experimental b_{3d}^{13} and b_{3d}^{11} parameters are given with small uncertainties and for these cases the values Q^{13} and Q^{11} are consistent. The experimental ratios b_{3d}^{11}/b_{3d}^{13} are here also well described by the corresponding theoretical values as seen from Fig. 2. The experimental uncertainty of the b_{nl}^{02} parameter is generally much smaller than that of the b_{nl}^{13} and b_{nl}^{11} parameters. The evaluated quadrupole moments Q^{02} are therefore determined with higher accuracy. However, this high precision is in many cases deceptive due to the influence of configuration interaction as given by the Δ_{3d}^{02} parameter in Eq. (5e). The estimation of this parameter has been the source for a great deal of work by, for example, Sternheimer.[48] A semiempirical way of estimating the Δ^{02} corrections would be to use the experimental Δ^{01} and Δ^{12} corrections for the magnetic dipole interaction as evaluated in Table IV. We notice that the Δ^{01} and Δ^{12} corrections are, for most of the elements, of the order of -0.1 and one would therefore expect the Δ^{02} to be of the same order. However, one must be very careful in such a semiempirical way of estimating Δ^{02} since the Δ^{ij} factors include a number of contributions originating from different types of configuration mixing. These contributions can in some cases even be of a different sign, which is illustrated for the two-particle effects to second order for some of the $3d$ elements by Bauche-Arnoult.[24] *Ab initio* calculations should therefore be done for each element and *LS* multiplet which is beyond the scope of the present work.

Experimental values of the Δ_{3d}^{02} parameter can be

TABLE VI. Values of experimental configuration-interaction contribution as evaluated by the use of Eq. (7).

Element	Configuration	$\frac{b_{3d,E}^{02}}{b_{3d,E}^{11}}$	$\frac{b_{3d,E}^{02}}{b_{3d,E}^{13}}$	$\frac{\langle r^{-3}\rangle_{3d,R}^{02}}{\langle r^{-3}\rangle_{3d,R}^{11}}$	$\frac{\langle r^{-3}\rangle_{3d,R}^{02}}{\langle r^{-3}\rangle_{3d,R}^{13}}$	$1+\Delta^{02}(11)$	$1+\Delta^{02}(13)$
Mn	$3d^6 4s$	$-52.5(1.2)$	23.3(5)	-56.3	24.0	0.93(2)	0.97(2)
Co	$3d^7 4s^2$	$-68(10)$	19.8(1.2)	-53.8	21.4	1.26(20)	0.93(6)
Ni	$3d^8 4s^2$	-37.2	17.0	-47.8	19.2	0.78	0.89

estimated by comparing the quadrupole moments evaluated from the b^{02}_{3d} parameter with those evaluated from the b^{13}_{3d} and b^{11}_{3d} parameters. If we assume that Eqs. (5) hold, we get

$$1+\Delta^{02}(11)=\frac{Q^{02}}{Q^{11}}=\frac{b^{02}_{3d,E}\langle r^{-3}\rangle^{11}_{3d,R}}{b^{11}_{3d,E}\langle r^{-3}\rangle^{02}_{3d,R}}\ . \tag{7}$$

A similar relation holds also for the b^{13} parameter. The result from this type of analysis is presented for Mn, Co, and Ni in Table VI. No uncertainties are given for Ni since there was no uncertainty given in the original paper for the b^{ij}_{3d} parameters. We notice that $\Delta^{02}(11)$ and $\Delta^{02}(13)$ do not overlap. The reason is probably that the uncertainties in the experimental b^{ij} parameter are underestimated. An estimation of Δ^{02} at this stage is to take the average of $\Delta^{02}(13)$, $\Delta^{02}(11)$, which gives $(1+\Delta^{02})$ as 0.95(4), 1.0(2), and 0.83(6) for Mn, Co, and Ni, respectively. These values are consistent with those obtained for the Δ^{01} and Δ^{12} parameters.

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