Theoret. chim. Acta (Berl.) 7, 75—79 (1967)

Commentationes

Physical Properties of Many-Electron Atomic Systems Evaluated from Analytical Hartree-Fock Functions

V. Magnetic Hyperfine Structure Constants*

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Received September 28, 1966

Available Hartree-Fock functions have been used to evaluate the magnetic hyperfine structure constants for various neutral atoms and positive and negative ions with configurations involving equivalent *p*- and *d*-electrons. The necessary formulation is presented; in particular, the *J*-dependence of the hyperfine structure constant is tabulated for the mentioned configurations.

Mittels vorhandener Hartree-Fock-Funktionen werden die magnetischen Hyperfeinstrukturkonstanten für neutrale Atome sowie positive und negative Ionen mit Konfigurationen von äquivalenten *p*- und *d*-Elektronen berechnet; der dazu notwendige Formelapparat wird zusammengestellt. Die für die erwähnten Konfigurationen berechneten Werte und ihre *J*-Abhängigkeit werden in Tabellenform angegeben.

On a employé des fonctions de Hartree-Fock pour le calcul des constantes de structure hyperfine magnétique pour quelques atomes neutres et ions positifs et négatifs, qui possèdent des configurations électroniques avec des électrons *p* ou *d* équivalents. Les formules nécessaires sont présentées. On donne la dépendance de *J* de la constante de structure hyperfine.

Introduction

In previous papers of this series [*5*—*8*] the values of various physical properties (nuclear magnetic shielding constants, diamagnetic susceptibilities, field gradients and quadrupole coupling constants, and Fermi contact interaction terms) for many-electron atoms, evaluated from analytical Hartree-Fock (HF) functions, have been reported. In this paper the magnetic hyperfine structure (hfs) constants, also evaluated from analytical Hartree-Fock functions, are presented for a large number of atomic systems.

Magnetic Hyperfine Structure

The magnetic hyperfine structure** arises from the interaction of the nuclear magnetic moment $\boldsymbol{\mu}_I$ with the magnetic field produced at the nucleus by an electron of spin angular momentum $\boldsymbol{s}$ and orbital angular momentum $\boldsymbol{l}$.

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* This work has been supported in part by the National Research Council of Canada.

** Only the magnetic dipole interaction, following the general treatment of TREES [*13*], will be considered in this paper.

The so-called dipole-dipole hyperfine structure Hamiltonian operator is defined by

$$H_d = (2\mu_B \mu_N \mu_I / I) \sum_i (\boldsymbol{N}_i \cdot \boldsymbol{I} / r_i^3) \,, \tag{1}$$

where μ_B is the Bohr magneton, μ_N is the nuclear magneton, and μ_I is the nuclear magnetic moment, measured in units of nuclear magnetons. $\boldsymbol{N}_i$ is defined by

$$\boldsymbol{N}_i = \boldsymbol{l}_i - \boldsymbol{s}_i + 3(\boldsymbol{r}_i \cdot \boldsymbol{s}_i)\,(\boldsymbol{r}_i / r_i^2) \,, \tag{2}$$

$\boldsymbol{r}_i$ being the position vector for the i-th electron, and $\boldsymbol{l}_i$ and $\boldsymbol{s}_i$ being the corresponding orbital and spin angular momentum vector operators. Similarly, $\boldsymbol{I}$ denotes the nuclear spin angular momentum vector operator, I being the corresponding quantum number.

The interaction represented by Eq. (1) is the scalar product of two vectors, and therefore the matrix elements of H_d can be evaluated using the tensor algebra of RACAH [*10*, *11*]. These matrix elements, independent of the total angular momentum projection quantum number* M_F can be represented by

$$(\alpha J, I, F \mid H_d \mid \alpha J, I, F) = 2\mu_B \mu_N (\mu_I / I)\,(\alpha J, I, F \mid \sum_i (\boldsymbol{N}_i \cdot \boldsymbol{I} / r_i^3) \mid \alpha J, I, F) \,, \tag{3}$$

where α is an additional quantum number required to complete the description of the state under consideration. But according to the Wigner-Eckart theorem [*14*, *2*], the matrix elements of $\sum_i (\boldsymbol{N}_i \cdot \boldsymbol{I} / r_i^3)$ for any of the $(2J+1)$ substates corresponding to a given level are proportional to those of $\boldsymbol{J} \cdot \boldsymbol{I}$ and therefore one can write

$$(\alpha J, I, F \mid \sum_i (\boldsymbol{N}_i \cdot \boldsymbol{I} / r_i^3) \mid \alpha J, I, F) = A'(J)\,(\alpha J, I, F \mid \boldsymbol{J} \cdot \boldsymbol{I} \mid \alpha J, I, F)\,\langle r^{-3} \rangle \,, \tag{4}$$

leading, according to RACAH [*10*], to

$$(\alpha J, I, F \mid H_d \mid \alpha J, I, F) = 2\mu_B \mu_N (\mu_I / I)\, A'(J)\,(K/2)\,\langle r^{-3} \rangle \,, \tag{5}$$

$A'(J)$ being the constant of proportionality and K being defined by

$$K = F(F+1) - I(I+1) - J(J+1) \,. \tag{6}$$

Eq. (5) can be rewritten also as

$$(\alpha J, I, F \mid H_d \mid \alpha J, I, F) = A(J)\,(K/2) \,, \tag{7a}$$

where $A(J)$ and $A'(J)$ are related by the expression

$$A(J) = 2\mu_B \mu_N (\mu_I / I)\,\langle r^{-3} \rangle\, A'(J) \,. \tag{7b}$$

For an atom showing $L-S$ coupling GOUDSMIT [*3*] has given** for $A'(J)$ the expression

$$A'(J) = \lambda(2-g) - \sigma[6\Gamma(2-g) - 2(g-1)\,L(L+1)]/(2L-1)\,(2L+3) \tag{8}$$

(for $L \neq 0$, $J \neq 0$), with (as proved by TREES [*13*])

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* The total angular momentum projection quantum number M_F has values $-F \leq M_F \leq F$, where F is the total angular momentum quantum number of the atom, defined by the possible values

$$F = (J+I), (J+I-1), \ldots, |J-I| \,,$$

where J is the total electronic angular momentum quantum number and I is the nuclear spin angular momentum quantum number.

** This expression has also been derived by TREES [*13*].

$$\lambda = [L(L+1)\,(2L+1)]^{-1/2}\,(\alpha S\,L\,||\,\sum_i \boldsymbol{l}_i\,||\,\alpha S\,L)\,, \tag{9a}$$

$$\sigma = -\,[(2L-1)\,(2L+3)]^{1/2}\,[S(S+1)\,(2S+1)\,L(L+1)\,(2L+1)]^{-1/2} \\ (\alpha S\,L\,||\,\sum_i \boldsymbol{s}_i\cdot\boldsymbol{C}_i^{(2)}\,||\,\alpha S\,L)\,, \tag{9b}$$

$$\Gamma = (1/2)\,[J(J+1) - L(L+1) - S(S+1)]\,, \tag{9c}$$

$$g = 1 + [J(J+1) + S(S+1) - L(L+1)]/(2J+1)\,, \tag{9d}$$

where the double barred matrices are given by Racah [*10, 11*]; $\boldsymbol{C}_i^{(2)}$ is a tensor operator*. Hubbs, Marrus, Nierenberg, and Worcester [*4*] have also derived an expression for $A'(J)$ for the groundstate ($J = L + S$) of a configuration of n equivalent electrons (or of n missing electrons)

$$A'(J) = \{[J(J+1) + L(L+1) - S(S+1)]/2J(J+1)\} + \\ + 2[(2L - n^2)/n^2(2L-1)\,(2l-1)\,(2l+3)]\,\{L(L+1)\,(g-1) - \\ - (3/2)\,\Gamma[J(J+1) + L(L+1) - S(S+1)]/[2J(J+1)]\}\,, \tag{10}$$

where l is the angular momentum quantum number for the shell under consideration, and Γ and g are given by Eqs. (9c) and (9d), respectively.

Values of $A'(J)$, calculated independently from Eqs. (8) and (10), were found to be identical. These values are collected in Tab. 1 for various configurations of equivalent p- and d-electrons.

Table 1. *Values of $A'(J)$ for various atomic configurations*[a]

Configuration	State	$A'(J)$
p^1, p^5	^2P	8/15
p^2, p^4	^3P	3/5
d^1, d^9	^2D	24/35
d^2, d^8	^3F	5/7
d^3, d^7	^4F	44/63
d^4, d^6	^5D	4/7

[a] In this table the results are presented for the case $J = L + S$.

It is common to define also the so-called hyperfine structure constant a_d, corresponding to the magnetic dipole interactions considered in this section. This constant is given by

$$a_d = 2\mu_B\mu_N(\mu_I/I)\,A'(J)\,\langle r^{-3}\rangle\,,$$

and can therefore be calculated if the expectation value $\langle r^{-3}\rangle$ is known.

Results and Discussion

The expectation values $\langle r^{-3}\rangle$ were calculated from the analytical Hartree-Fock functions of Clementi [*1*] and Malli [*9*]. The corresponding values of a_d, for a number of neutral atoms, positive ions, and negative ions are presented in Tab. 2 and 3, which include also experimental values wherever available**.

Comparison of the theoretical and experimental values of the magnetic dipole hyperfine structure constants a_d for atomic systems with p^n configurations shows an excellent agreement. In general the theoretical values agree with the experimental values within 5%; the only exceptions are Al^{27} and Cl^{37}, for which the discrepancy is 15% and 7%, respectively.

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* For more details see the original work of Trees [*13*].

** The experimental values of a_d, as well as the values of the nuclear magnetic moments μ_I, have been taken from Ramsey [*12*].

Table 2. *Magnetic hyperfine structure constants a_d for some states*[a] *of various neutral atoms and negative and positive ions with configurations p^n*
(in Mc/sec)

Z	M	Positive Ions		Neutral Atoms		Negative Ions	
		State	a_d	State	a_d	State	a_d
5	10			^2P	23.7	^3P	16.0
	11			^2P	70.8	^3P	47.9
6	13	^2P	158.9	^3P	136.2		
7	14	^3P	88.7			^3P	54.8
	15	^3P	− 124.3			^3P	− 76.8
8	17			^3P	− 215.9	^2P	−156.5
9	18	^3P	406.2	^2P	307.6		
	19	^3P	2669.5	^2P	2021.1		
10	21	^2P	− 212.1				
13	26			^2P	31.0	^3P	21.4
	27			^2P	80.6	^3P	55.6
14	29	^2P	− 150.1	^3P	− 130.6		
15	30	^3P	139.2			^3P	89.4
	31	^3P	525.0			^3P	337.1
16	33			^3P	118.9	^2P	88.0
	35			^3P	186.6	^2P	136.8
17	34	^3P	209.4	^2P	160.8		
	35	^3P	244.8	^2P	188.8		
	36	^3P	287.1	^2P	221.5		
	37	^3P	203.8	^2P	157.2		
31	67			^2P	180.7	^3P	122.1
	69			^2P	198.0	^3P	133.8
	71			^2P	251.5	^3P	170.0
32	71	^2P	339.4	^3P	300.2		
	73	^2P	− 60.7	^3P	− 53.7		
33	75	^3P	461.4			^3P	300.4
34	77			^3P	567.7	^2P	420.9
	79			^3P	154.6	^2P	114.6
35	79	^3P	1104.6	^2P	856.6		
	81	^3P	1190.7	^2P	923.3		

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[a] The calculated values have been obtained using the Hartree-Fock functions of CLEMENTI [*1*] and MALLI [*9*]. The experimental values of a_d for $B^{11}(Z = 5)$, $Al^{27}(Z = 13)$, $Cl^{35}(Z = 17)$, $Cl^{37}(Z = 17)$, $Ga^{69}(Z = 31)$, $Ga^{71}(Z = 31)$, $Br^{79}(Z = 35)$ and $Br^{81}(Z = 35)$, as given by RAMSEY [*12*], are 73.347, 94.25, 205.050, 170.681, 190.794, 242.434, 884.810, and 953.770 Mc/sec, respectively.

One must conclude that, in general, Hartree-Fock functions are adequate for the evaluation of magnetic dipole hyperfine structure constants. The discrepancy mentioned above must be due, most probably, to an error in the experimental values, either of a_d or of the corresponding nuclear moment, and this suggestion is based on the following argument.

The accuracy of the calculated value of a_d seems to be independent of Z; for B^{11} the error is 4% and for Br^{79} and Br^{81}, the heaviest atoms considered in this work, the discrepancy with the experimental value is 5%. On the other hand, the Hartree-Fock functions used seem to be satisfactory, because the calculated value for the isotope Cl^{35} has only an error of 4%. Therefore the only possibility that remains is the one mentioned above.

Table 3. *Magnetic hyperfine structure constants a_d for some states*[a] *of various neutral atoms and negative and positive ions with configurations d^n*
(in Mc/sec)

Z	M	Positive Ions		Neutral Atoms		Negative Ions	
		State	a_d	State	a_d	State	a_d
21	45	^3F	110.3	^2D	127.1	^3F	98.1
22	47	^4F	361.1	^3F	43.3	^4F	34.0
	49	^4F	361.2	^3F	43.4	^4F	34.0
23	50	^5D	70.0	^4F	98.4	^5D	67.7
	51	^5D	184.4	^4F	259.5	^5D	178.6
24	53			^5D	57.8		
25	55	^5D	278.5			^5D	273.6
26	57	^4F	10.0	^5D	9.1	^4F	9.8
27	57	^3F	489.4	^4F	525.3	^3F	484.5
	58	^3F	644.6	^4F	691.9	^3F	638.1
	59	^3F	489.2	^4F	525.1	^3F	484.3
	60	^3F	257.8	^4F	276.7	^3F	255.3
28	61			^3F	31.8		

[a] Values calculated using the Hartree-Fock functions of CLEMENTI [*1*].

One feels, therefore, confident that the values reported for a_d for atomic systems with d^n configurations should present similar accuracy.

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