Theoret. chim. Acta (Berl.) 6, 54—63 (1966)

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

III. Electric Field Gradients and Quadrupole Coupling Constants*

GULZARI MALLI and SERAFIN FRAGA

Division of Theoretical Chemistry, Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada

Received April 28, 1966

Numerical values are presented for the electric field gradients (q) and nuclear quadrupole coupling constants (eq Q) for a series of neutral atoms and their positive and negative ions. The angular dependence of the field gradient integrals is tabulated for configurations involving equivalent *p* and *d* electrons, for LS-coupling and central-force-field functions (e.g., Hartree-Fock functions).

Für eine Reihe neutraler Atome und ihre positiven und negativen Ionen werden Zahlenwerte für die elektrischen Feldgradienten (q) und die Kernquadrupolkopplungskonstanten (eq Q) berechnet. Für Konfigurationen, die gleichwertige *p*- und *d*-Elektronen enthalten, wird für LS-Kopplung und Zentralkraftfeldfunktionen (z. B. Hartree-Fock-Funktionen) die Winkelabhängigkeit der Feldgradientenintegrale in Tabellenform angegeben.

On présente les valeurs numériques pour les gradients de champ (q) et les constantes de couplage quadrupolaire (eq Q) pour des atomes neutres et leurs ions positives et négatives. On a calculé les valeurs des intégrales qui donnent la dépendence angulaire du gradient de champ pour des configurations avec des électrons *p* et *d* équivalents, pour le couplage LS et fonctions de champ central (par exemple, fonctions de Hartree-Fock).

Introduction

The availability of exact analytical Hartree-Fock functions provides the opportunity of determining a series of interesting physical properties. On the other hand, a comparison of the predicted with the experimental values lays down a basis for a critical judgement of the goodness of the wave functions.

In the first two papers of this series, hereafter designated as I and II, respectively, the values of the nuclear magnetic shielding constants [*12*] and the magnetic susceptibilities [*13*], evaluated to first order from analytical Hartree-Fock functions, have been reported. The purpose of this paper is to present the results obtained for the field gradients and the related quantities, the quadrupole coupling constants.

Associated with the electronic density distribution in an atom there are three quantities — electric potential, electric field, and electric field gradient — which are of theoretical interest. Experimentally, though, it is the electric field gradient that merits most attention, being related to the fine and hyperfine structure

---

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

splittings*. Microwave and radiofrequency spectroscopy yield data about the interaction energy eqQ, which is the product of a nuclear property, the electrostatic nuclear quadrupole moment eQ of a nucleus, and an atomic (or molecular) property, the electrostatic field gradient q, existing at the same nucleus, due to the electrons in the system. Knowing two of the three related quantities it is possible to determine the third one: in the present work the quadrupole coupling constants have been evaluated from the theoretical values of q and the experimental data** on eQ.

The determination of field gradients has been attempted previously from semiempirical data and on a theoretical basis. From the observed fine-structure splittings, TOWNES and DAILEY [*21*] evaluated q for Cs, I, F, and Na in various electronic states, and BARNES and SMITH [*1*] reported q for a large number of atomic systems, in different states of excitation and ionization. BERSOHN [*2*] has determined the field gradients of some ions in ionic crystals and discussed the situation in these systems in comparison with the one existing in molecular crystals.

PLATAS [*14*] has calculated q for several ions of the five-electron isoelectronic series (^2P), using analytical open-shell functions determined by BRIGMAN [*4*]. The effect of the atomic core polarization has been studied by STERNHEIMER [*18, 19, 20*], and the existence of an induced quadrupole moment has been confirmed, in polar molecules, by FOLEY, STERNHEIMER, and TYCKO [*7*], who estimate the order of magnitude of this effect.

These corrections should be included in the a priori calculation of field gradients, but they will be omitted in the present work.

Outline of the Calculations

When considering the interaction between the electrons and the nucleus in an atomic system, it is customary to proceed in a stepwise manner, with successive inclusion of terms of increasing complexity.

Within the framework of the basic approximation (as used in the electronic Hamiltonian of the system under consideration), the nucleus (as well as the electrons) is regarded as a point charge, its charge being Ze. The interaction between the electrons and the nucleus arises then from the simple Coulomb term*** $-\sum_i Ze^2/r_i$, where r_i represents the distance of the i-th electron from the nucleus, and the summation extends over all the electrons in the atom.

This simple description neglects, in the first place, the existence of the electron spin. When one takes it into account, it is found that the coupling of the electron spin angular momentum $\boldsymbol{S}$ and the electron orbital angular momentum $\boldsymbol{L}$ (through their spin-orbit interaction, due to the magnetic dipole moment associated with

---

* Calculated values of fine-structure and hyperfine-structure splittings will be presented in a following paper of this series.

** Nuclear quadrupole moments have been recently measured with great precision by microwave spectroscopy and by the atomic and molecular beam resonance techniques of KUSH, MILLMAN, and RABI [*10*].

*** If the nucleus is thought of as having a spatial extension (i.e., if it is not considered any more as a point charge), then the Coulomb interaction should be replaced by a more general expression.

the electron spin and the magnetic field due to the orbital motion of the electron) determines the so-called fine-structure (*fs*) splitting of the electronic energy levels.

Furthermore, the nuclear spin angular momentum $\boldsymbol{I}$ interacts with the total electronic angular momentum $\boldsymbol{J}$ of the atomic system and leads to the magnetic dipole-dipole interaction. In addition the electric quadrupole moment (Q) interacts with the field gradient (q) produced at the nucleus by the electrons. These two interaction terms constitute together the so-called hyperfine-structure (*hfs*) splitting of the fine-structure levels.

In this paper only the last term of the *hfs* splitting will be considered. The corresponding formulation has been presented in detail by Kopfermann [*9*], Townes and Schawlow [*22*], and Casimir [*5*]. For this reason only those equations used for the numerical calculations are presented.

The hyperfine interaction between the electrons and the nucleus in an atomic system is given by

$$W_F = W_J + \tfrac{1}{2} AK + BK(K+1)\,, \tag{1}$$

where

$$K = F(F+1) - I(I+1) - J(J+1)\,, \tag{2}$$

$$F = I+J,\, I+J-1\,, \ldots \, |\, I-J\, |\,; \tag{3}$$

in Eqs. (2) and (3) J, I, and F are the total electronic angular momentum, nuclear spin angular momentum, and the total angular momentum quantum numbers, respectively.

The term $AK/2$ arises from the magnetic dipole interaction between the electrons and the nucleus, and the term $BK(K+1)$ corresponds to the interaction of the electric nuclear quadrupole moment (Q) with the field gradient (q) produced at the nucleus by the electrons.

The electric field gradient q at the nucleus in an atom is defined [*9*] by

$$q = \frac{\partial^2 V}{\partial z^2} = e \langle \Phi \,|\, \sum_i [(3\cos^2\theta_i - 1)\, r_i^{-3}] \,|\, \Phi \rangle\,, \tag{4}$$

which can be rewritten as

$$q = e \langle \sum_i (3\cos^2\theta_i - 1) \rangle \langle r^{-3} \rangle\,, \tag{5}$$

when the total function can be factored into the product of a radial function and an angular function. The summations in Eqs. (4) and (5) extend, in principle, over all the electrons in the system, but closed shells and half-filled shells do not contribute (because of the spherical symmetry) to the field gradient at the nucleus; therefore the summation should extend only over the open-shell electrons (with the exception of half-filled shells).

Casimir [*5*] has shown that $B(J)$ is related to the field gradient (q) and the quadrupole moment (Q) by the relation

$$B(J) = -\tfrac{3}{8} e^2 Q \langle \{ \sum_i [(3\cos^2\theta_i - 1)\, r_i^{-3}] \}_{M_J=J} \rangle \, [I(2I-1)\, J(2J-1)]^{-1}\,. \tag{6}$$

On the other hand, Trees [*23*] has derived for $B(J)$, using Racah [*15, 16*] tensor algebra, the expression

$$\begin{aligned} B(J) = 8\gamma\, \{ & 3(2-g)\, [J(J+1)\,(2-g) - \tfrac{1}{2}] - L(L+1) \} \\ & [(2J-1)\,(2J+3)\,(2L-1)\,(2L+3)]^{-1}\,, \end{aligned} \tag{7}$$

Table 1. *Values for the angular factors* $\langle \sum_i (3 \cos^2\theta_i - 1)\rangle_{JJ}$ *for atomic configurations*[a]

Configuration	State		Configuration	State	
p^1	^2P	$-2/5$	d^2	^3F	$-2/7$
p^2	^3P	$2/5$	d^3	^4F	$2/7$
	^1D	$-4/5$	d^4	^5D	$4/7$
p^4	^3P	$-2/5$	d^6	^5D	$-4/7$
	^1D	$4/5$	d^7	^4F	$-2/7$
p^5	^2P	$2/5$	d^8	^3F	$2/7$
d^1	^2D	$-4/7$	d^9	^2D	$4/7$

---

[a] In all the tables of this work the results are presented for the largest value of J, i.e., $J = L + S$.

where

$$g = 1 + [J(J+1) + S(S+1) - L(L+1)]\,[2J(J+1)]^{-1}\,, \tag{8}$$

$$\gamma = -\,b_l(l\,||\mathscr{C}^{(2)}||\,l)\,[(2L-1)(2L+3)]^{1/2}\,(l^n\alpha SL\,||\,\mathscr{U}^{(2)}\,||\,l^n\alpha SL)\,[L(L+1)(2L+1)]^{-1/2}\,, \tag{9}$$

with

$$b_l = (3/16)\,e^2Q\,\langle r^{-3}\rangle\,[I(2I-1)]^{-1}\,. \tag{10}$$

The double-barred submatrices of the double-tensor operator $\mathscr{U}^{(2)}$ are given by Racah [*16*] for configurations of equivalent p and d electrons and the double-barred matrix of $\mathscr{C}^{(2)}$ is given by the expression

$$(l\,||\mathscr{C}^{(2)}||\,l) = -\,[l(l+1)(2l+1)]^{1/2}\,[(2l-1)(2l+3)]^{-1/2}\,. \tag{11}$$

It was mentioned above that the term $[BK(K+1)]$ corresponds to the nuclear quadrupole interaction, as it can be seen now by inspection of Eq. (6). The quadrupole coupling constant, eqQ, which appears within $B(J)$, can be calculated if one knows the values of $\langle r^{-3}\rangle$ and $\langle \sum_i (3\cos^2\theta_i - 1)\rangle$.

The values of $\langle r^{-3}\rangle$ can be calculated if the corresponding electronic state functions are known (see next section). For the determination of $\langle \sum_i (3\cos^2\theta_i - 1)\rangle$ one can proceed in the following manner. The value of $B(J)$ can be determined by using Eqs. (7) — (11); equating this result with Eq. (6) one can determine then the value of $\langle \sum_i (3\cos^2\theta_i - 1)\rangle$. The values obtained for various terms arising from equivalent p and d electrons are given in Tab. 1.

Results and Discussion

The values of $\langle r^{-3}\rangle$ have been calculated in this work from the analytical Hartree-Fock functions of Clementi [*6*] and Malli [*11*]. Tab. 2 collects*, for comparison purposes, some of these values for neutral atoms with configurations p^n. These values are compared with the values obtained by Barnes and Smith [*1*] from experimental data; the values of these authors have been corrected by dividing by the appropriate relativistic correction, as given by Kopfermann [*9*]. The

---

* In this table, as well as in all the other tables presented in this work, the results are presented with five decimal figures. Though in most cases they do not have much significance, they are given for computer program checking purposes.

Table 2. *Values of $\langle r^{-3} \rangle$ for the groundstates of some neutral atoms with configurations p^n (in a.u.)*

Atom	Configuration	State	$\langle r^{-3} \rangle$ This work[a]	$\langle r^{-3} \rangle$ Experimental[b]	Correction factor[c]
B[d, e]	$2p^1$	^2P	0.77523	0.608	0.78428
C	$2p^2$	^3P	1.69116	1.23	0.72731
O[f]	$2p^4$	^3P	4.97416	4.29	0.86246
F[e]	$2p^5$	^2P	7.54676	6.55	0.86792
Al	$3p^1$	^2P	1.08657	1.28	1.17802
Si	$3p^2$	^3P	2.05260	2.30	1.12053
S	$3p^4$	^3P	4.83638	4.99	1.03176
Cl[e]	$3p^5$	^2P	6.76565	7.11	1.05090
Ga	$4p^1$	^2P	2.89116	3.42	1.18292
Ge	$4p^2$	^3P	4.79693	5.61	1.16950
Se	$4p^4$	^3P	9.27312	9.36	1.00937
Br	$4p^5$	^2P	11.97844	13.16	1.09864

---

[a] Values per electron calculated from the Hartree-Fock functions of CLEMENTI [*6*] and MALLI [*11*].

[b] Values reported by BARNES and SMITH [*1*]. These values have been corrected by dividing by the appropriate relativistic correction H_r, as given by KOPFERMANN [*9*].

[c] These values represent the ratio of the experimental to the theoretical value.

[d] PLATAS [*14*] reports for B a value of 0.7821.

[e] GOODINGS [*8*] has reported the values 0.7756, 7.544, and 6.679 for B, F, and Cl, respectively.

[f] BESSIS, LEFEBVRE-BRION, and MOSER [*3*] have reported a value of 4.98 for O.

Table 3. *Field gradients for groundstates of positive ions, neutral atoms, and negative ions with configurations*[a] *p^n (in a.u.)*

Configuration	State	Positive ion	q	Neutral atom	q	Negative ion	q
$2p^1$	^2P	C^+	0.88836	B	0.31009		
$2p^2$	^3P	N^+	1.53264	C	0.67646	B^-	0.18643
$2p^4$	^3P	F^+	3.54416	O	1.98966	N^-	0.94699
$2p^5$	^2P	Ne^+	4.99729	F	3.01871	O^-	1.62204
$3p^1$	^2P	Si^+	1.06097	Al	0.43463		
$3p^2$	^3P	P^+	1.61902	Si	0.82104	Al^-	0.26632
$3p^4$	^3P	Cl^+	3.11835	S	1.93455	P^-	1.03969
$3p^5$	^2P	A^+	4.11448	Cl	2.70626	S^-	1.61086
$4p^1$	^2P	Ge^+	2.44020	Ga	1.15646		
$4p^2$	^3P	As^+	3.35681	Ge	1.91877	Ga^-	0.69468
$4p^4$	^3P	Br^+	5.49232	Se	3.70925	As^-	2.18578
$4p^5$	^2P	Kr^+	6.77161	Br	4.79137	Se^-	3.09438

---

[a] Absolute values calculated from the Hartree-Fock functions of CLEMENTI [*6*] and MALLI [*11*].

agreement can be considered quite satisfactory, especially considering the reasons for the existence of discrepancies. The theoretical values have been calculated from Hartree-Fock functions that cannot predict an accurate value (as pointed out before, when discussing the atomic core polarization); on the other hand, the evaluation of the experimental values implies an estimate of other quantities (namely, the effective atomic numbers). Comparison has also been made with the

Table 4. *Field gradients for some states of positive ions, neutral atoms, and negative ions with configurations*[a] d^n *(in a.u.)*

Configuration	State	Positive ion		Neutral atom		Negative ion	
			q		q		q
$3d^1$	^2D			Sc	0.81590		
$3d^2$	^3F	Sc$^+$	0.33975	Ti	0.57564	Sc$^-$	0.30245
$3d^3$	^4F	Ti$^+$	0.49053	V	0.75578	Ti$^-$	0.46388
$3d^4$	^5D	V$^+$	1.31306			V$^-$	1.27140
$3d^6$	^5D	Mn$^+$	2.10187	Fe	2.84453	Mn$^-$	2.06524
$3d^7$	^4F	Fe$^+$	1.28276	Co	1.69326	Fe$^-$	1.26507
$3d^8$	^3F	Co$^+$	1.54244	Ni	1.99499	Co$^-$	1.52700
$3d^9$	^2D	Ni$^+$	3.66946				

[a] Absolute values calculated from the Hartree-Fock functions of CLEMENTI [*6*].

Table 5. *Field gradients for some excited states of positive ions, neutral atoms, and negative ions with configurations*[a] p^n *(in a.u.)*

Configuration	State	Positive ion		Neutral atom		Negative ion	
			q		q		q
$2p^2$	^1D	N$^+$	2.99478	C	1.30524	B$^-$	0.33628
$2p^4$	^1D	F$^+$	7.03216	O	3.93956	N$^-$	1.86546
$3p^2$	^1D	P$^+$	3.18968	Si	1.59940	Al$^-$	0.48266
$3p^4$	^1D	Cl$^+$	6.24194	S	3.86342	P$^-$	2.06330
$4p^2$	^1D	As$^+$	6.61492	Ge	3.72602	Ga$^-$	1.25384
$4p^4$	^1D	Br$^+$	10.99658	Se	7.39978	As$^-$	4.33436

[a] Absolute values calculated using the Hartree-Fock functions of CLEMENTI [*6*] and MALLI [*11*].

Table 6. *Field gradients for some systems of the isoelectronic series*
$(1s)^2(2s)^2(2p)^1$, ^2P
(in a.u.)

System	This work[a]	PLATAS[b]
B	0.31009	0.2413
C^{1+}	0.88836	0.7464
N^{2+}	1.87052	1.637
O^{3+}	3.35777	3.014
F^{4+}	5.44992	4.968
Ne^{5+}	8.24738	7.615

[a] Absolute values calculated from the Hartree-Fock functions of CLEMENTI [*6*].

[b] Values reported by PLATAS [*14*].

few available theoretical results*; the agreement of the present results with those values is vary satisfactory.

The last column in Tab. 2 contains the correction factors by which it would be necessary to multiply the Hartree-Fock results in order to obtain the experimental

---

* See footnotes of Tab. 2.

Table 7. *Quadrupole coupling constants eqQ for the groundstates of some neutral atoms*[a] (*in* Mc)

Atom	*M*	*I*	*Q*[b]	*eqQ*	
				Evaluated	Experimental[c]
B	10	3	+0.06(4)	4.37171	
	11	3/2	+0.0355(2)	2.58659	2.695
			0.00036[d]	2.62303	
O	17	5/2	−0.005(2)	2.33755	
			0.00075	0.35063	
Al	27	5/2	+0.155(3)	15.82938	18.76 ± 0.25
			+0.149	15.21661	
S	33	3/2	−0.050	22.72806	
			−0.064	29.09192	
	35	3/2	+0.035	15.90964	
			+0.038	17.27333	
Cl	35	3/2	−0.0782(2)	49.72659	54.873 ± 0.005
			−0.0789	50.17171	
	36	2	0.0172(4)	10.93731	
	37	3/2	−0.0616(2)	39.17082	43.255 ± 0.010
			−0.0621	39.48876	
V	51	7/2	0.2	35.51713	
Co	59	7/2	+0.5	198.93265	
Ga	69	3/2	+0.189(3)	51.35761	62.522490 ± 0.000100
			+0.178	48.36855	
	71	3/2	+0.1461(15)	39.70025	39.399030 ± 0.000100
Ge	73	9/2	−0.21(10)	94.67921	
Se	75	5/2	+1.1	958.71872	
	79	7/2	0.7	610.09373	
Br	79	3/2	+0.33(2)	371.52331	384.878 ± 0.008
			+0.335	377.15245	
	81	3/2	+0.28(2)	315.23190	321.516 ± 0.008
			+0.280	315.23190	

---

[a] Absolute values calculated from the Hartree-Fock functions of Clementi [*6*] and Malli [*11*].

[b] The values of the nuclear quadrupole moments *Q* have been taken from Kopfermann [*9*] and Ramsey [*17*]. These values are in 10^{-24} cm^2; the values in parentheses represent the error in the last figure of the number given.

[c] Values reported by Ramsey [*17*].

[d] It would seem that this value is probably in error. The corresponding factor (10^{-2}) has been omitted in the coupling constant.

values. Because of the uncertainty in the experimental values, too much importance should not be attached to these correction factors.

Tabs. 3 and 4 contain the calculated values of q for the groundstates of various atomic systems involving p^n and d^n configurations, respectively, while Tab. 5 collects the values for some excited states with configurations p^n. Tab. 6 provides a comparison with the results obtained by Platas [*14*] for the five-electron isoelectronic series $(1s)^2(2s)^2(2p)$, ^2P, occurring in the first row of the periodic table.

Tabs. 7—9 present the quadrupole coupling constants, evaluated from the field gradients obtained in this calculation and using the nuclear quadrupole moments given by Kopfermann [*9*] and Ramsey [*17*]. In Tab. 7 comparison is

Table 8. *Quadrupole coupling constants eqQ for groundstates of some positive and negative ions*[a] *(in* Mc*)*

Atom	*M*	*I*	*Q*[b]	Positive ion	Negative ion
B	10	3	+0.06(4)		2.62833
	11	3/2	+0.0355(2)		1.55509
			0.00036[c]		1.57700
N	14	1	+0.02	7.20249	
O	17	5/2	−0.005(2)		1.90565
			0.00075		0.28585
Al	27	5/2	+0.155(3)		9.69947
			+0.149		9.32400
S	33	3/2	−0.050		18.92519
			−0.064		24.22424
	35	3/2	+0.035		13.24763
			+0.038		14.38314
Cl	35	3/2	−0.0782(2)	57.29860	
			−0.0789	57.81151	
	36	2	0.0172(4)	12.60276	
	37	3/2	−0.0616(2)	45.13547	
			−0.0621	45.50183	
V[d]	51	7/2	0.2		59.74817
Co[d]	59	7/2	+0.5		179.39960
Ga	69	3/2	+0.189(3)		30.85027
			+0.178		29.05475
	71	3/2	+0.1461(15)		23.84775
Ge	73	9/2	−0.21(10)	120.40850	
As	75	3/2	+0.3(2)	236.62489	154.07782
Se	75	5/2	+1.1		799.79512
	79	7/2	0.7		508.96053
Br	79	3/2	+0.33(2)	425.87504	
			+0.335	432.32769	
	81	3/2	+0.28(2)	361.34852	
			+0.280	361.34852	
Kr	83	9/2	+0.15	238.66878	

---

[a] Absolute values calculated from the Hartree-Fock functions of CLEMENTI [*6*] and MALLI [*11*].

[b] The values of the nuclear quadrupole moments *Q* have been taken from KOPFERMANN [*9*] and RAMSEY [*17*]. These values are in 10^{-24} cm^2. The values in parentheses represent the error in the last figure of the number given.

[c] It would seem that this value is probably in error. The corresponding factor (10^{-2}) has been ommitted in the coupling constant.

[d] The quadrupole coupling constants for V$^+$ (^5D) and Co$^+$ (^3F) are 61.70594 and 181.21356 Mc, respectively.

made with the available experimental values; the agreement can be considered extremely satisfactory.

Because no attempt has been made at judging the accuracy of the existing values for the quadrupole moments, Tabs. 7—9 contain both the values of KOPFERMANN [*9*] and RAMSEY [*17*]. The reason for presenting both sets of values is to show the possible deviations which can affect the theoretically predicted quadrupole coupling constants.

Finally, Tab. 10 includes the results for the excited states ^5D and ^2D of Cr and Cu, respectively.

Table 9. *Quadrupole coupling constants eqQ for some excited states* ^1D *of positive ions, neutral atoms, and negative ions*[a] *(in* Mc*)*

Atom	M	I	Q[b]	Positive ion	Neutral atom	Negative ion
B	10	3	+0.06(4)			4.74094
	11	3/2	+0.0355(2)			2.80506
			0.00036[c]			2.84457
N	14	1	+0.02	14.07368		8.76654
O	17	5/2	−0.005(2)		4.62840	
			0.00075		0.69426	
Al	27	5/2	+0.155(3)			17.57864
			+0.149			16.89818
S	33	3/2	−0.050		45.38940	
			−0.064		58.09842	
	35	3/2	+0.035		31.77258	
			+0.038		34.49594	
Cl	35	3/2	−0.0782(2)	114.69348		
			−0.0789	115.72016		
	36	2	0.0172(4)	25.22670		
	37	3/2	−0.0616(2)	90.34680		
			−0.0621	91.08012		
Ga	69	3/2	+0.189(3)			55.68220
			+0.178			52.44144
	71	3/2	+0.1461(15)			43.04322
Ge	73	9/2	−0.21(10)		183.85562	
As	75	3/2	+0.3(2)	466.29232		305.53338
Se	75	5/2	+1.1		1912.59894	
	79	7/2	0.7		1217.10842	
Br	79	3/2	+0.33(2)	852.67592		
			+0.335	865.59524		
	81	3/2	+0.28(2)	723.48260		
			+0.280	723.48260		

---

[a] Absolute values calculated from the Hartree-Fock functions of Clementi [*6*] and Malli [*11*].

[b] The values of the nuclear quadrupole moments Q have been taken from Kopfermann [*9*] and Ramsey [*17*]. These values are in 10^{-24} cm². The values in parentheses represent the error in the last figure of the value given for Q.

[c] It would seem that this value is in error. The corresponding factor (10^{-2}) has been omitted in the coupling constant.

Table 10. *Summary of results for excited states*[a] *of* Cr(^5D) *and* Cu(^2D)

	Cr	Cu
Field gradient (a.u.)	1.91236	4.65774
Quadrupole coupling constant (Mc)		171.82538[b] 158.69223[c]

---

[a] Absolute values calculated from the Hartree-Fock functions of Clementi [*6*].

[b] Using $Q = -0.157 \cdot 10^{-24}$ cm², for $M = 63$, $I = 3/2$, as given by Ramsey [*17*].

[c] Using $Q = -0.145 \cdot 10^{-24}$ cm², for $M = 65$, $I = 3.2$, as given by Ramsey [*17*].

As a summary, it can be said that Hartree-Fock functions constitute an adequate basis for the evaluation of field gradients and quadrupole coupling constants.

References

[*1*] Barnes, R. G., and W. V. Smith: Physic. Rev. **93**, 95 (1954).
[*2*] Bersohn, R.: J. chem. Physics **29**, 326 (1958).
[*3*] Bessis, N., H. Lefebvre-Brion, and C. M. Moser: Physic. Rev. **128**, 213 (1962).
[*4*] Brigman, G. H.: Unpublished results (1957).
[*5*] Casimir, H. B. G.: On the interaction between atomic nuclei and electrons. San Francisco: W. H. Freeman & Co. 1963.
[*6*] Clementi, E.: Tables of atomic functions. International Business Machines Corporation 1965.
[*7*] Foley, H. M., R. M. Sternheimer, and D. H. Tycko: Physic. Rev. **93**, 734 (1954).
[*8*] Goodings, D. A.: Physic. Rev. **123**, 1706 (1961).
[*9*] Kopfermann, H.: Nuclear moments. New York: Academic Press 1958.
[*10*] Kush, P., S. Millman, and I. I. Rabi: Physic. Rev. **55**, 1176 (1939).
[*11*] Malli, G.: submitted for publication.
[*12*] —, and S. Fraga: Theoret. chim. Acta (Berlin) **5**, 275 (1966).
[*13*] — — Theoret. chim. Acta (Berlin) **5**, 284 (1966).
[*14*] Platas, O.: J. chem. Physics **37**, 2755 (1962).
[*15*] Racah, G.: Physic. Rev. **62**, 438 (1942).
[*16*] — Physic. Rev. **63**, 367 (1963).
[*17*] Ramsey, N. F.: Molecular beams. Oxford: Oxford University Press 1956.
[*18*] Sternheimer, R. M.: Physic. Rev. **84**, 244 (1951).
[*19*] —, and H. M. Foley: Physic. Rev. **92**, 1460 (1953).
[*20*] — Physic. Rev. **95**, 736 (1954).
[*21*] Townes, C. H., and B. P. Dailey: J. chem. Physics **17**, 782 (1949).
[*22*] —, and A. L. Schawlow: Microwave spectroscopy. New York: McGraw-Hill Book Company, Inc. 1955.
[*23*] Trees, R. E.: Physic. Rev. **92**, 308 (1953).

Prof. Serafin Fraga
Division of Theoretical Chemistry,
Department of Chemistry
University of Alberta
Edmonton, Alberta, Canada