Electric Field Gradients of Atomic p Electrons*

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Calculations from optical spectrums data of the electrostatic field gradient existing at the position of the nucleus in atoms depend on the effective atomic number Z_i. The present article presents a survey of Z_i values obtained for various elements in varying degrees of ionization. One may conclude from this survey that the relation $Z_i = Z - n$ is a good approximation for calculations dealing with p electrons. On the basis of this relation the average $\langle 1/r^3 \rangle$ has been evaluated for low-lying states of interest in chemical bonding for atoms having p valence electrons. The results are presented in a graphical form from which the values for the more complicated cases of N, P, As, and Sb are obtained by interpolation. Atomic field gradients obtained in this article are compared with previous estimates in a number of cases of interest.

INTRODUCTION

ONE of the important types of data obtained by the techniques of microwave and radiofrequency spectroscopy is the interaction energy eqQ between the electrostatic quadrupole moment eQ of a nucleus and the electrostatic field gradient $q = \partial^2 V/\partial z^2$ existing at the nucleus. For cylindrical symmetry about the z axis (usually the bond axis), the scalar eQq adequately describes the interaction; lower symmetries require a tensor representation. In any case, the measured interaction is the product of a nuclear property eQ and a molecular property q which arises primarily from the electrostatic fields of the electrons. An accurate knowledge of the electronic wave functions affords a means of calculating nuclear quadrupole moments from observed interaction energies whereas comparison of quadrupole couplings of a particular nucleus in different molecules reveals information about molecular bonding. Among the nuclei whose quadrupole moments have been determined in the above fashion are boron,[1] nitrogen,[2] oxygen,[3] and sulfur,[2,4] to mention but a few. Since these nuclear interactions are measured in molecules, the problem of estimating the electron distribution in these molecules can be divided into two parts: first, that of determining the best combination of atomic orbitals into which the molecular orbitals can be decomposed; and second, that of estimating the contribution to the field gradient made by each atomic orbital. Townes and Dailey's paper[2] contributes much to both parts of this problem and shows, among other things, that for most molecules the predominant contributions to the molecular field gradients arise from p atomic orbitals in the valence shell. It is the purpose of this paper to present a systematic compilation of p atomic field gradients as derived from the fine structure of atomic spectra. This compilation suggests that in a number of cases the atomic field gradients previously

chosen have been too high. It is hoped that the atomic field gradients listed here will provide a useful starting point in arriving at improved estimates of nuclear quadrupole moments.

BACKGROUND

Casimir[5] has shown that for the case of a single electron outside of closed shells the fine-structure splitting δ resulting from the interaction between the magnetic field of the circulating electron and the magnetic moment μ_0 associated with the electron spin can be expressed as

$$hc\delta = -2(l+\tfrac{1}{2})(\mu_0^2/e)\langle(1/r)(\partial V/\partial r)\rangle\mathcal{H}, \qquad (1)$$

or as

$$\delta = \mathcal{H}(dn^*/dn)[Z_0^2 Z_i^2/n^{*3}l(l+1)]R\alpha^2. \qquad (2)$$

Here V is the potential in which the electron moves outside the closed shells, and $\mathcal{H}$ is a small relativistic correction given by Casimir,[5] important mainly for heavy atoms $(Z>50)$. The effective quantum number n^* is determined from the term energies measured in Rydbergs by

$$E_n = -(Z_0/n^*)^2, \qquad (3)$$

where $Z_0 = 1$ for neutral atoms, 2 for singly ionized atoms, etc. The effective atomic number Z_i can be defined by the relation[6]

$$\langle(1/r)(\partial V/\partial r)\rangle = -Z_i e\langle 1/r^3\rangle. \qquad (4)$$

We are interested in the atomic field gradient q in a z direction fixed in space for the state $m = l$:

$$q = \partial^2 V/\partial z^2 = -e\langle 1/r^3\rangle\langle 3\cos^2\theta - 1\rangle = -e(2l/2l+3)\langle 1/r^3\rangle$$

$$= -\left[\frac{4l}{(2l+3)(2l+1)}\right]\left[\frac{e}{R\alpha^2 a_0^3\mathcal{H}}\right]\left(\frac{\delta}{Z_i}\right). \qquad (5)$$

CALCULATION OF Z_i

The calculation by these equations of the atomic field gradient consists essentially of two steps: (1) the

[1] H. G. Dehmelt, Z. Physik **133**, 528 (1952); **134**, 642 (1953).
[2] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).
[3] Geschwind, Gunther-Mohr, and Townes, Phys. Rev. **83**, 209 (1951).
[4] H. G. Dehmelt (private communication).
[5] H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Teylers Tweede Genootschap, Haarlem, 1936).
[6] G. F. Koster, Phys. Rev. **86**, 148 (1952).

TABLE I. Values of δ, n^*, and Z_i for various elements and degrees of ionization. Z_i values followed by an asterisk have been corrected by dn^*/dn.

Atom		Configuration	δ cm^{-1}	n^*	Z_i
Li	I	$2p$	0.3372	1.97	0.94
Be	I	$2s2p$	3.03	1.44	1.77
	II	$2p$	6.6	1.95	2.06
B	I	$2p$	16.0	1.28	3.40
	II	$2s2p$	22.8	1.63	2.91
	III	$3p$	10.2	2.96	3.17
C	II	$3p$	11.03	2.60	4.11
	III	$2s3p$	18.3	2.80	3.92
	IV	$4p$	13.3	3.96	4.21
N	III	$3p$	36	2.69	5.06*
	IV	$2s3p$	51.2	2.83	4.98
	V	$3p$	74.2	2.96	5.14
O	IV	$3p$	87.1	2.80	6.30*
	VI	$4p$	63.9	3.97	6.19
F	V	$3p$	177	2.78	7.12*
	VII	$3p$	282	2.97	7.20
Na	I	$6p$	1.25	5.14	7.62
Mg	I	$3s3p$	60.8	1.66	9.80
	II	$6p$	7.6	5.30	9.85
Al	I	$6p$	2.82	4.71	10.05
	II	$3s6p$	9.9	5.10	10.63
	III	$6p$	20.59	5.40	11.12
Si	II	$5p$	24.31	3.96	11.40
	III	$3s4p$	106.2	3.22	11.70
	IV	$6p$	43	5.48	12.30
P	III	$4p$	137.1	3.12	12.20*
	IV	$3s3p$	695	2.25	13.05
	V	$5p$	140.7	4.55	13.45
S	VI	$5p$	218	4.58	14.14
Cl	V	$3p$	1492	2.24	14.80*
	VII	$4p$	688	3.62	15.10
A	VI	$3p$	2210	2.32	15.70*
	VIII	$5p$	446	4.65	15.50
K	I	$7p$	4.48	5.29	15.10
Ca	I	$4s6p$	11.74	4.02	16.20
	II	$6p$	35.9	4.55	17.00
Cu	I	$4p$	248.4	1.86	23.4
Zn	I	$4s6p$	30.9	3.78	24.0
	II	$5p$	245.1	3.18	26.0
Ga	I	$7p$	20.9	4.71	27.4
	II	$4s5p$	299	3.06	27.2
	III	$5p$	539	3.38	27.6*
Ge	II	$5p$	359.6	2.98	28.2*
	III	$4s5p$	627	3.23	28.4*
	IV	$5p$	938	3.52	29.0*
As	III	$5p$	723	3.20	30.2*
	IV	$4s5p$	1073	3.39	30.0*
	V	$4p$	4110	2.60	30.5*
Se	IV	$5p$	1198	3.36	30.8*
	VI	$4p$	5700	2.70	31.8*
Rb	I	$7p$	35	4.33	31.3
Sr	I	$5s7p$	45.9	4.11	33.2
	II	$6p$	288.2	3.64	34.5
Ag	I	$8p$	42.1	4.97	42.2
Cd	I	$5s6p$	244.8	2.79	42.7
	II	$6p$	675	3.26	45.0
In	I	$8p$	54.3	4.78	45.2
	II	$5s7p$	321	4.18	45.0
Sn	II	$8p$	191	5.10	46.6
	III	$5s5p$	5681	2.28	48.0*
Sb	III	$6p$	1668	3.42	49.4*
	IV	$5s5p$	8125	2.47	48.6*
	V	$5p$	8987	2.75	49.4*
Te	IV	$6p$	2619	3.50	48.3*
	V	$5s5p$	10888	2.59	48.3*
	VI	$5p$	11814	2.86	49.8*
Cs	I	$7p$	181.1	3.40	49.2
Ba	I	$6s8p$	1097.8	4.09	50.6
	II	$8p$	300.9	4.80	53.6

determination of the effective atomic number Z_i, and (2) the calculation of the average $\langle 1/r^3 \rangle$. By considering the term energies and splittings of doublet and triplet states belonging to the configurations np, $nsmp$, and ns^2mp $(m \geqslant n)$, values of n^*, dn^*/dn, and Z_i have been determined from Eqs. (2) and (3). In general, the correction factor dn^*/dn tends toward unity with increasing n with the result that wherever possible an excited state is used to make this correction small. For the isoelectronic sequences Li I, Na I, etc., there is never any appreciable deviation of dn^*/dn from unity. The sequences beginning with B I, Al I, etc., are very similar to one another with dn^*/dn tending to unity within a few excited states and generally decreasing as one goes to more ionized stoms. Similar effects are noted for the Be I, Mg I, etc., sequences. In those cases where data are available only for the lowest state of a series, the dn^*/dn correction has been estimated from its behavior in a similar element or in a sequence of elements. Beyond Cs and Ba, the Z_i values determined from different excited states or different degrees of ionization of the same element exhibit so much scattering that there appears to be no way to deduce a single representative value. No data for these other elements of the $6p$ shell have been included here.

Table I lists δ and n^* values for 33 elements in various degrees of ionization together with the Z_i values obtained from these data. The data for elements through Nb have been obtained from the first two volumes of Charlotte Moore's compilation of atomic energy levels,[7] and for heavier elements from the Landolt-Börnstein tables.[8] Only one state is listed for each element and ionization, that state being generally the most excited one for which an accurate δ is available. The relativistic correction $\mathcal{K}$ has not been taken into account; its effect is to reduce the Z_i values of the heavier elements by a small amount.

All of the Z_i values listed in Table I (except Cs and Ba) are plotted in Figs. 1, 2, and 3. In each of these figures the line $(Z-n)$ is also drawn. Note that of the thirteen examples for which two ionized states are
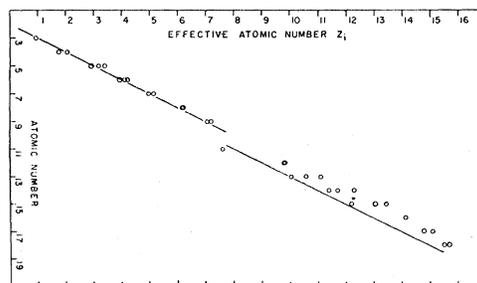

Fig. 1. Z_i values from Table I of elements with $2p$- and $3p$-valence electrons (Li through Cl).

[7] Charlotte E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D. C., 1949, 1952), Vols. I, II.
[8] Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer Verlag, Berlin, 1950), sixth edition, Vol. 1, Part I.

available, ten show a definitely greater Z_i for the greater ionization. Similarly, of the eleven examples for which three ionized states are available, three show this trend strongly and four others less strongly; therefore one may conclude that in general the Z_i value of a neutral atom is smaller than that of the same atom highly ionized. The $(Z-n)$ line is seen to pass through or very close to those neutral atoms whose Z_i should be most reliably determined (Na, K, Al, Ga, etc.). Furthermore, it passes somewhat below the Z_i values belonging to the more ionized cases, where one would expect the neutral atom Z_i to be lower. Accordingly, we suggest that $(Z-n)$ be used as an approximation to Z_i in calculations of the present type. This is not a very different conclusion from that reached by Landé in a similar survey[9] ($Z_i=Z-2$ for the first period, and $Z_i=Z-4$ for all others) and which has been followed by most other investigators, but it is a simple rule and it does represent fairly well the data available today.

Checks on our Z_i values for light elements are obtained by comparison with Koster's values[6] of $Z_i=10$ for Al and 13.7 for Cl. For these elements accurate field gradients can be obtained from atomic beam data using the magnetic coupling constant and known nuclear magnetic moments. While this method has also been applied to heavier elements, Koster has shown that configuration interactions involving S states invalidates its use there. Our Z_i values for Al and Cl, 10 and 14, respectively, are in good agreement with Koster's results.
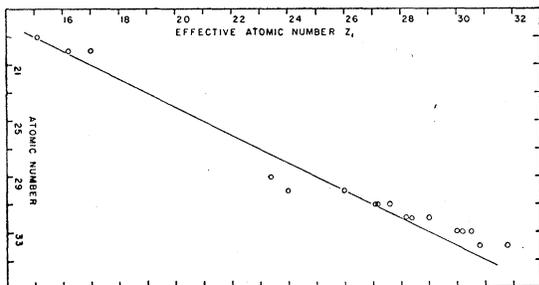

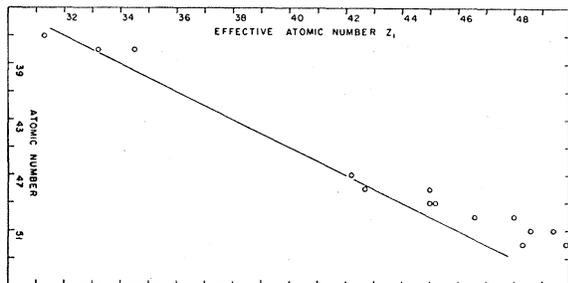FIG. 2. Z_i values from Table I of elements with $4p$-valence electrons (K through Br).

FIG. 3. Z_i values from Table I of elements with $5p$-valence electrons (Rb through I).

[9] A. Landé, Z. Physik 25, 46 (1924).

TABLE II. Values of δ and $\langle(a_0/r)^3\rangle\mathfrak{K}$ for bonding states of the neutral atoms of Table I. The effective atomic number Z_i is taken equal to $(Z-n)$ as discussed in the text. Values of δ and $\langle(a_0/r)^3\rangle\mathfrak{K}$ in parentheses have been interpolated from Fig. 4.

Atom	Configuration	State	δ cm^{-1}	Z_i	$\langle(a_0/r)^3\rangle\mathfrak{K}$
Li	$2p$	^2P	0.3372	1	0.0387
Be	$2s2p$	^3P	3.03	2	0.173
B	$2p$	^2P	16.0	3	0.608
C	$2p^2$	^3P	43.5	4	1.23
N	$2p^3$		(108)	5	(2.46)
O	$2p^4$	^3P	226.5	6	4.30
F	$2p^5$	^2P	404	7	6.56
Na	$3p$	^2P	17.2	8	0.244
Mg	$3s3p$	^3P	60.8	9	0.77
Al	$3p$	^2P	112.0	10	1.28
Si	$3p^2$	^3P	223.3	11	2.31
P	$3p^3$		(367)	12	(3.48)
S	$3p^4$	^3P	573.6	13	5.02
Cl	$3p^5$	^2P	881.0	14	7.16
K	$4p$	^2P	57.72	15	0.438
Ca	$4s4p$	^3P	158.04	16	1.13
Ga	$4p$	^2P	826	27	3.50
Ge	$4p^2$	^3P	1409	28	5.75
As	$4p^3$		(1910)	29	(7.51)
Se	$4p^4$	^3P	2534	30	9.62
Br	$4p^5$	^2P	3685	31	13.55
Rb	$5p$	^2P	237.6	32	0.845
Sr	$5s5p$	^3P	581	33	2.00
In	$5p$	^2P	2213	44	5.72
Sn	$5p^2$	^3P	4428	45	11.2
Sb	$5p^3$		(5250)	46	(13.0)
Te	$5p^4$	^3P	6204	47	15.0
I	$5p^5$	^2P	7603	48	18.0
Cs	$6p$	^2P	554.1	49	1.29
Ba	$6s6p$	^3P	1249	50	2.85
Tl	$6p$	^2P	7792	75	11.8
Pb	$6p^2$	^3P	10648	76	16.0
Bi	$6p^3$		16583	77	24.6

CALCULATION OF $1/r^3$

By use of the fine-structure splittings of low-lying states of elements with p valence electrons and the approximation $Z_i=Z-n$ discussed in the previous section, the values of $\langle1/r^3\rangle$ have been calculated according to Eq. (1). In cases involving several electrons, the determination of the splitting equivalent to that of one p electron has been made in accordance with well-established relations of atomic spectrums theory.[10-12] Only in the p^3 configuration is the splitting affected by the coupling scheme to such an extent that there is no clear way to infer the splitting equivalent to that of one p electron,[11] and the elements N, P, As, Sb are accordingly omitted. In the p^2 configuration, the coupling scheme has no effect; and in the p^4 configuration the effect is only just noticeable with Te.[12] Assuming that the rule $Z_i=Z-n$ applies also to the entire $6p$ shell (as well as to Cs and Ba), one can evaluate $\langle1/r^3\rangle$ for Tl, Pb, and Bi. In Bi the coupling of the $6p^3$ configuration is so nearly pure jj that a good

[10] H. E. White, Introduction to Atomic Spectra (McGraw-Hill Book Company, Inc., New York, 1934), Chap. XIV.
[11] D. R. Inglis, Phys. Rev. 38, 862 (1931).
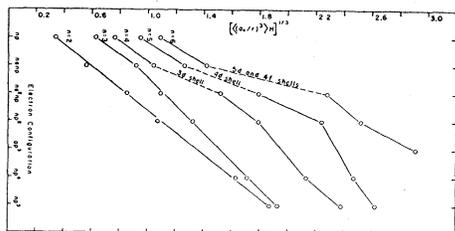[12] S. Goudsmit, Phys. Rev. 35, 1325 (1930).

FIG. 4. Values of $[\langle(a_0/r)^3\rangle\mathcal{K}]^{\frac{1}{3}}$ for elements having p-valence electrons.

estimate of the equivalent one-electron splitting can be made.

The values of δ, Z_i, and the $\langle 1/r^3\rangle$ calculated therefrom are listed in Table II. Again the relativistic correction $\mathcal{K}$ has been neglected; therefore the quantity calculated is $\langle 1/r^3\rangle\mathcal{K}$. For numerical convenience, the values are tabulated as $\langle(a_0/r)^3\rangle\mathcal{K}$. Figure 4 shows the cube root of this last quantity, $[\langle(a_0/r)^3\rangle\mathcal{K}]^{\frac{1}{3}}$, for all of the entries in Table II.

CONCLUSIONS

In terms of the tabulated values of $\langle(a_0/r)^3\rangle\mathcal{K}$, the atomic field gradients are given by Eq. (5), which becomes

$$q = \partial^2 V/\partial z^2 = -1.298\langle(a_0/r)^3\rangle\mathcal{K}\times10^{15} \text{ esu.} \quad (6)$$

In the molecular case,[2] $m=0$, and these values must be multiplied by $-2l/(2l-1)$ or -2.

One use of Fig. 2 is to infer the values of $\langle 1/r^3\rangle$ for N, P, As, and Sb by interpolation. This appears to be quite reasonable in the cases of N and P, and perhaps less so in the cases of As and Sb. The values of q obtained in this manner for the molecular case are 6.37, 9.05, 19.5, and 33.8×10^{15} esu, respectively.

Generally, the factor most subject to individual adjustment in these calculations is Z_i. For instance, Townes and Dailey[2] calculated $\partial^2 V/\partial z^2$ for N, $m=0$, as 9.9×10^{15} esu, larger by a factor of 1.55 than our value. About half of this discrepancy arises from their choice of $Z_i=4$, whereas we use $Z_i=5$. The remaining disagreement apparently results from our different methods of extrapolating from optical data. Similarly, for S, the above authors quote $q=14.7\times10^{15}$ esu for $m=0$, a factor of 1.13 greater than our value of 13.0 $\times10^{15}$ esu. Their choice of $Z_i=12.5$ as against our value $Z_i=13$ accounts for a third of this rather small discrepancy. Our agreement with Dehmelt's value[4] of 13.8 $\times10^{15}$ esu is even closer. Here the discrepancy is entirely due to the difference in assumed Z_i values.

Our calculated field gradients neglect the polarization effects calculated by Sternheimer.[13] These corrections have the effect of further lowering the calculated field gradients. Consequently, many published values of nuclear quadrupole moments are considerably too small. We have not attempted to revise the quadrupole moments, however, since a revision should include a careful study of the best choice of atomic orbitals for constructing the molecular orbitals. We have not considered this important problem in the present paper.

[13] R. Sternheimer, Phys. Rev. 84, 244 (1951); 80, 102 (1950).