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X-ray energy levels: Deviations between experimental and theoretical values

AMAR NATH NIGAM and OM PRAKASH RAJPUT
Physics Department, H. B. Technological Institute, Kanpur 208 002, India

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Abstract. Energy values of K, L_{II} and L_{III} levels calculated by the relativistic self consistent field method have been used to compute the energies of $K\alpha_{1,2}$ lines. These values deviate considerably from the experimental values due to Bearden and Burr. The deviations are discussed and given an empirical fit.

Keywords. Relativistic self consistent field; field theoretical effects; solid state effects.

1. Introduction

The theoretical information on x-ray energy levels is now accurate upto 10^{-3} eV. These values have been obtained by relativistic self-consistent field calculations. Huang *et al* (1976) compiled this data and also added a few field theoretical corrections, thus making their compilation superior to that of Rosen and Lindgren (1968). We can thus calculate theoretical energies of $K\alpha_{1,2}$ lines. The experimental measurements on $K\alpha_{1,2}$ lines have been published by Bearden (1967) and Bearden and Burr (1967) and are mostly correct upto 10^{-1} eV. A comparison of the experimental and theoretical data shows systematic deviation (2–12 eV) which lie well outside the range of experimental errors and therefore merit attention. An empirical fit of these deviations leads us to the law: $\Delta E = aZ^{2 \cdot 7}$.

2. Choice of data

Borchert (1976) reported $K\alpha_{1,2}$ lines emitted by radioactive elements (Tm, Th, U, and Pu). His value for uranium alone differs from that of Bearden and Burr (1967). The mode of excitation used by the two groups is different and one need not worry much about this single disagreement. Sevier (1979) has published the results of measurement on x-ray absorption edges for elements $Z = 83$ to 106. However accurate these measurements may be, the absorption edges are greatly affected by the chemical binding and solid state effects and in principle should not be used for an accurate estimate of x-ray $K\alpha_{1,2}$ line energies. To maintain a consistency we have confined ourselves to the results of Bearden and Burr (1967) where all the values have been obtained by electron-beam-excitation of solid targets in an x-ray tube. The so emitted $K\alpha_{1,2}$ lines will be least affected by the solid state and chemical binding. Only for low atomic members ($Z < 26$) $K\alpha_{1,2}$ lines show perceptible chemical binding effects (Sandström 1957).

2.1 $K\alpha_{1,2}$ *energy values*

Table 1 collects the theoretical K and L_{III} energies in eV taken from Huang *et al* (1976). These have been used for evaluating $(K\alpha_1)_{\text{theor.}}$ energies. Table 2 contains the corresponding values for K and L_{II} level and $(K\alpha_2)_{\text{theor.}}$ energies. The experi-

Table 1. ΔE for $K\alpha_1$ line (all values in eV.)

Z	K	L_{III}	$(K\alpha_1)_{\text{theor.}}$	$(K\alpha_1)_{\text{exp.}}$	ΔE (exp-theor.) (eV)
50	29206·493	3937·1955	25269·297	25271·3	2·003
51	30497·934	4141·3551	26356·578	26359·1	2·552
52	31820·839	4350·9955	27469·843	27472·3	2·457
53	33175·631	4566·0106	28609·620	28612·0	2·38
54	34562·508	4786·534	29775·974	29779·0	3·026
55	35987·784	5018·3355	30969·448	30972·8	3·352
56	37446·448	5255·7578	32190·69	32193·6	2·91
57	38935·032	5496·1712	33438·86	33441·8	2·94
58	40441·765	5724·6074	34717·157	34719·7	2·543
59	41989·158	5965·9726	36023·185	36026·3	3·115
60	43569·959	6211·9285	37358·03	37361·0	2·97
61	45184·788	6462·6262	38722·161	38724·7	2·539
62	46833·911	6718·2175	40115·693	40118·1	2·407
63	48518·571	6979·1098	41540·461	41542·2	1·739
64	50245·705	7252·9692	42992·735	42996·2	3·465
65	51993·859	7515·2158	44478·643	44481·6	2·957
66	53785·564	7790·6674	45994·896	45998·4	3.504
67	55614·278	8071·1053	47543·172	47546·7	3·528
68	57480·246	8356·4423	49123·803	49127·7	3·897
69	59383·822	8646·6418	50737·173	50741·6	4·427
70	61325·675	8941·8452	52383·829	52388·9	5·071
71	63314·990	9251·0008	54063·989	54069·8	5·811
73	67414·088	9886·0741	57528·013	57532·0	3·987
74	69525·093	10211·923	59313·17	59318·24	5·07
75	71678·802	10544·11	61134·692	61140·3	5·608
76	73874·878	10881·885	62992·993	63000.5	7·507
77	76108·145	11218·868	64889·277	64895·6	6·323
78	78394·592	11570·991	66823·801	66832·0	8·199
79	80722·939	11925·379	68797·56	68803·7	6·14
80	83100·982	12289·835	70811·147	70819·0	7·853
81	85526·954	12661·835	72865·119	72871·5	6·381
82	88000·820	13040·111	74960·709	74969·4	8·691
83	90524·443	13424·998	77099·445	71107·9	8·455
84	93097·838	13816·000	79281·838	79290·0	8·162
89	106754·19	15876·547	90877·643	90884·0	6·357
90	109649·13	16307·491	93341·639	93350·0	8·361
91	112593·58	16734·107	95869·473	95868·0	8·527
92	115597·91	17171·095	98426·815	98439·0	12·185

Table 2. ΔE for $K\alpha_2$ line (all values in eV)

Z	K	L_{II}	$(K\alpha_2)_{\text{theor.}}$	$(K\alpha_2)_{\text{exp.}}$	Δ (Exp−Theor.) (eV)
50	29206·493	4164·6466	25041·846	25044·0	2·154
51	30497·934	4389·7102	26108·223	26110·8	2·577
52	31820·839	4621·7239	27199·115	27201·7	2·585
53	33175·631	4860·6584	28314·972	28317·2	2·228
54	34562·508	5106·7299	29455·778	29458·0	2·222
55	35987·784	5365·8341	30621·949	30625·1	3·151
56	37446·448	5632·3669	31814·081	31817·1	3·091
57	38935·032	5903·8396	33031·192	33034·1	2·908
58	40441·765	6165·4054	34276·359	34278·9	2·541
59	41989·158	6441·9735	35547·211	35550·2	2·989
60	43569·959	6725·3387	36844·62	36847·4	2·78
61	45184·788	7015·7605	38169·027	38171·2	2·173
62	46833·911	7313·4957	39520·415	39522·4	1·985
63	48518·571	7619·0547	40899·516	40901·9	2·384
64	50245·705	7940·2142	42305·49	42308·9	3·41
65	51993·859	8252·5898	43741·269	43744·1	2·831
66	53785·564	8581·0556	45204·508	45207·8	3·292
67	55614·278	8917·5531	46696·724	46699·7	2·976
68	57480·246	9262·1374	48218·108	48221·6	3·492
69	59383·822	9614·9222	49768·899	49772·6	3·701
70	61325·675	9976·1929	51349·482	51534·0	4·518
71	63314·990	10355·024	52959·966	52965·0	5·034
73	67414·088	11141·049	56273·039	56277·0	3·961
74	69525·093	11548·526	57976·567	57981·7	5·133
75	71678·802	11966·589	59712·213	59717·9	5·687
76	73874·878	12394·77	61480·108	61486·7	6·592
77	76108·145	12826·808	63281·337	63286·7	5·363
78	78394·592	13278·863	65115·729	65122·0	6·271
79	80722·939	13738·717	66984·222	66989·5	5·278
80	83100·982	14213·897	68887·085	68895·0	7·915
81	85526·954	14702·294	70824·66	70831·9	7·24
82	88000·82	15202·905	72797·915	72804·2	6·285
83	90524·443	15716·30	74808·143	74814·8	6·657
84	93097·838	16242·291	76855·547	76862·0	6·453
91	112593·58	20314·367	92279·213	92287·0	7·787
92	115597·91	20950·555	94647·355	94665·0	17·645

mental values in both these tables are due to Bearden and Burr (1967). The last column in both the tables contains Δ E (Expt.—Theory).

The theoretical results of Huang *et al* (1976) have been reported upto 6 places of decimal in atomic units (a.u.) which were converted into eV using the relation 1 a.u. = 27·2116 eV. The theoretical values can be assumed to be correct upto at least the first decimal place.

In the tables of Bearden and Burr (1967): some values are given upto the 1st digit. From these the error range appears to be 0·1 to 1 eV.* For elements $Z = 85$ to 89 the

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*Error is ± 1 eV for Z = 54, 73, 78, 80, 84, 89, 90, 91, 92 (For the rest it is ± 0·1 eV). This is indicated by vertical lines in figures 1 and 2.

values are not precise and are omitted. Thus ΔE (Expt.—Theory) is precise upto 1 eV.

2.2 *Discussion of the deviations*

The theoretical energies given by Huang *et al* (1976) have been corrected by them for the following effects: (a) magnetic interaction energy correction, (b) retardation energy contribution, (c) vacuum polarisation, (d) higher order vacuum polarisation, and (e) screened self-energy shift.

On the other hand Novick *et al* (1955) list the following field theoretical corrections for $2S_{1/2} - 2P_{1/2}$ separations: (a) The Lamb shift, (b) second order vacuum polarisation, (c) second order magnetic moment, (d) second order relativistic shift, (e) fourth order radiative shift, (f) fourth order vacuum polarisation, (g) fourth order magnetic moment, (h) finite mass effect, and (i) finite size effect.

Huang *et al* (1976) have estimated the finite nuclear size effect on the x-ray levels (Table I of their compilation on p. 245) but have not included the same in the final estimate of the energies of levels (Table 3 makes no mention of this effect). Further magnetic corrections resulting from spin have been included but field theory corrections to magnetic moment have been overlooked.

The deviations are therefore no surprise. Figures 1 and 2 show the variation of these deviations with Z and $K\alpha_1$ and $K\alpha_2$ lines respectively. The deviations have been given the following empirical fit by computer programming for a polynomial by the least squares method:

$$E(K\alpha_1) = 71{\cdot}6906 - 3{\cdot}1119\,Z + 0{\cdot}0444\,Z^2 - 0{\cdot}000195\,Z^3,$$

$$E(K\alpha_2) = -33{\cdot}7502 + 1{\cdot}8213\,Z + 0{\cdot}03126\,Z^2 - 0{\cdot}000185\,Z^3. \tag{3}$$

The curves drawn in figures 1 and 2 represent these equations.

A plot of log (ΔE) against log (Z) was given a straight line fit by the computer. This yielded the following relations.

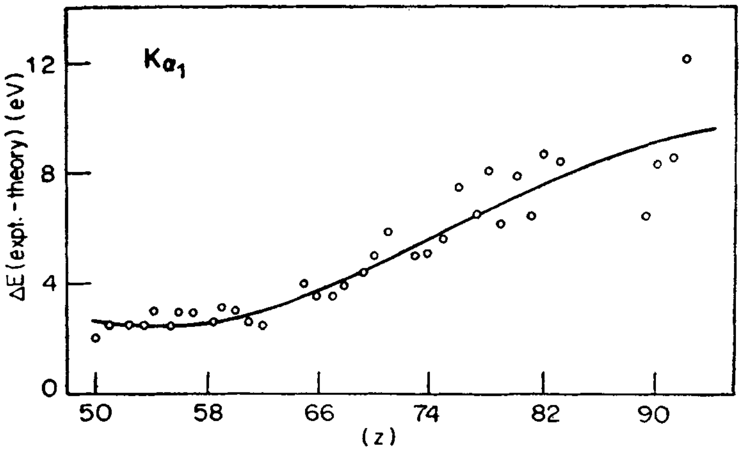

Figure 1. Variation of ΔE with Z for $K\alpha_1$ line.

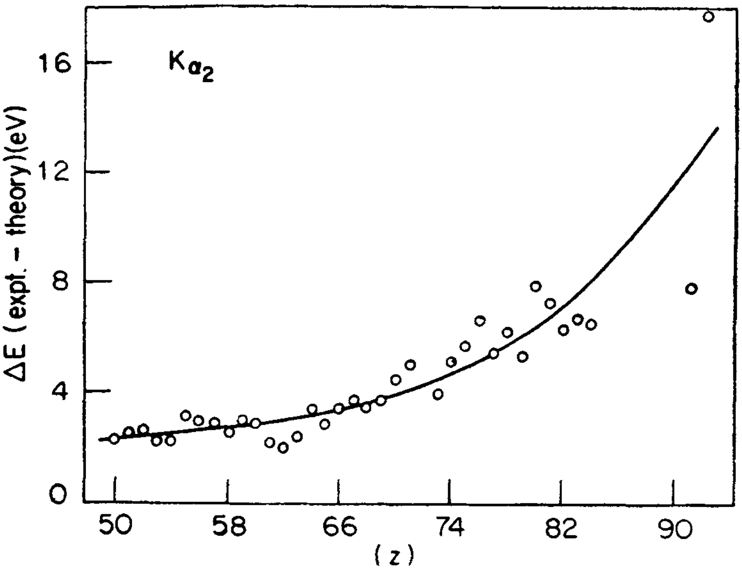

Figure 2. Variation of ΔE with Z for $K\alpha_2$ line.

$$\Delta E\,(K\alpha_1) = 5{\cdot}1 \times 10^{-5}\, Z^{2.71}\,\mathrm{eV},$$

$$\Delta E\,(K\alpha_2) = 4{\cdot}6 \times 10^{-5}\, Z^{2.72}\,\mathrm{eV}. \tag{4}$$

Most of the field theoretical corrections vary as Z^4 or Z^5 (Novick *et al* 1955). The above empirical fit does not match with any of the known correction and necessitates a fresh theoretical probe.

The theoretical values of Huang *et al* (1976) correspond to the isolated and free atoms, while the $K\alpha_{1,2}$ line measurements due to Bearden (1967) and Bearden and Burr (1967) were made using solid targets. Thus in principle the experimental values are not completely free from the solid state effects. Hedin and Johansson (1969) have estimated the solid state effect for low Z elements Na^+ and K^+. Equations (4) are meant for high Z elements. However they give a correct *order of magnitude* for the solid state effect. This is illustrated in table 3.

The agreement is far from quantitative but leads us to suspect that equation (4) are representatives of the solid state effect.

Table 3.

Element	Hedin and Johansson (1969)			Present estimate in Ryd. unit using equation (4)
	Level	Energy Ryd. units	Expected effect on $K\alpha$ lines	
Na^+	1s	0·088	0·088	0·002
	2p	0·000		
K^+	1s	−0·100	−0·005	0·010
	2p	−0·095		

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