Approaching Experimental Ionization Energies of Atoms. An Extension to 3d Electrons

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A three parameter equation derived for atoms with electrons $1s^2$ to $3p^6$ was applied to calculate the screening constants for atoms with 3d electrons. Further, these shielding constants were used to estimate effective nuclear charges. Ionization energies involving 3d electron removal, calculated using this method, resulted in errors below 0.5% for more than 88% of the results, compared to the experimental values.

INTRODUCTION

In a previous work (1) an empirical equation for the screening effect was established, starting from experimental ionization energies (IE) for atoms with electrons s and p

$$S = A + BX^{-1/2} + CX^{-1/4} \tag{1}$$

where *A*, *B*, and *C* are empirical constants and *X* represents the IE order (i.e., first, second, and third, etc). This equation can be used to obtain shielding constants for electrons $1s^2$ to $3p^6$ in order to calculate ionization energies according to (2):

$$\mathrm{IE} = 13.577\left(\frac{Z^*}{n}\right)^2 \tag{2}$$

Equation 1 agrees with the fact that orbital penetration must increase with increasing nuclear charge, for electrons with the same set of quantum numbers.

The present work is intended to demonstrate the applicability of this method to calculate ionization energies for 3d electrons. Unfortunately, for elements with atomic numbers between 21 and 39 there are only two series of data complete, $3d^1$ and $3d^{10}$. The rest of them, $3d^2$ to $3d^9$, present an increasing number of missing data (2). Thus, from a total of ten data for each series, there is one IE missing in series $3d^2$, two IEs are missing in series $3d^3$, three in $3d^4$, and so on.

EXPERIMENTAL

In order to overcome this lack of experimental data, all available IEs (2) for 3d electrons of elements with atomic number from 21 through 39 were tabulated, grouping together IEs for electrons with the same quantum numbers. Then each group of experimental IEs were plotted versus atomic number (See Figure 1). Each plot shows a notoriously regular increasing trend, and therefore missing data can be estimated along the dashed lines in Figure 1. Estimated experimental IEs appear in Table 1 with an asterisk and from now they will be referred to as experimental IEs.

By substituting experimental IEs in (2) we get the values for effective nuclear charge, Z^*, and substracting these from their respective atomic numbers, actual shielding constants (*S*) are obtained. Next each set of actual values of *S* were plotted against IE order and the resulting curves are very similar to those for s and p electrons (see Figure 2).

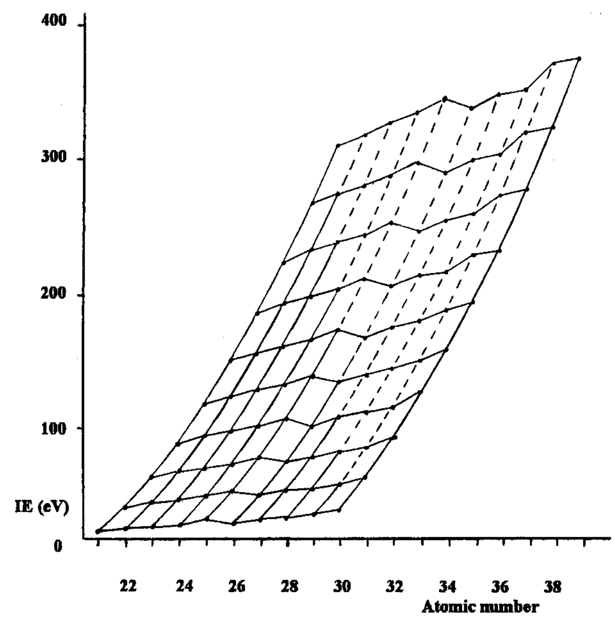

Figure 1. Ionization energies vs atomic numbers for series $3d^1$ to $3d^{10}$.

Assuming that these curves fit (1) the empirical constants *A*, *B*, and *C* were calculated for each electron configuration (see Table 2) and then replaced in(1) in order to obtain the calculated values of *S* in a straightforward manner and from them finally calculate ionization energies, which are shown in Table 3 along with the % of error.

RESULTS AND DISCUSSION

Calculated values of *S* obtained from (1) are listed in Table 3 for electron configuration $3d^3$, and if roughly compared they seem close enough to the actual values which were calculated from experimental IEs. Values of *S* and calculated IEs for the other nine configurations studied are available upon request.

Figure 2 shows plots of *S*, both actual and calculated, vs IE order. It can be observed that both curves are coincident for all configurations, except for $3d^{10}$, where the curve of actual values of *S* is not as smooth as the calculated curve. Yet, for this curve the poorest result obtained is only 5% from the experimental value.

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Table 1. Experimental and Estimated Ionization Energies of Atoms for 3d Electrons[a]

Z	elem	III	IV	V	VI	VII	VIII	IX	X	XI	XII
21	Sc	24.76									
22	Ti	27.49	43.27								
23	V	29.32	46.71	65.23							
24	Cr	30.96	49.1	69.3	90.56						
25	Mn	33.67	51.2	72.4	95	119.27					
26	Fe	30.65	54.8	75.0	99	125	151.06				
27	Co	33.50	51.3	79.5	102	129	157	186.13			
28	Ni	35.17	54.9	75.5	108	133	162	193	224.5		
29	Cu	36.83	55.2	79.9	103	139	166	199	232	266	
30	Zn	39.72	59.4	82.6	108	134	174	203	238	274	310.8
31	Ga		64	86[a]	112[a]	140[a]	168[a]	212[a]	244[a]	281[a]	319[a]
32	Ge			93.5	116[a]	144[a]	175[a]	206[a]	253[a]	287[a]	327[a]
33	As				127.6	150[a]	179[a]	214[a]	246[a]	298[a]	334[a]
34	Se					155.4	188[a]	217[a]	255[a]	290[a]	345[a]
35	Br						192.8	228[a]	259[a]	300[a]	337[a]
36	Kr							230.9	273[a]	303[a]	348[a]
37	Rb								277.1	320[a]	351[a]
38	Sr									324.1	371[a]
39	Y										374

[a] IEs values estimated from Figure 1.

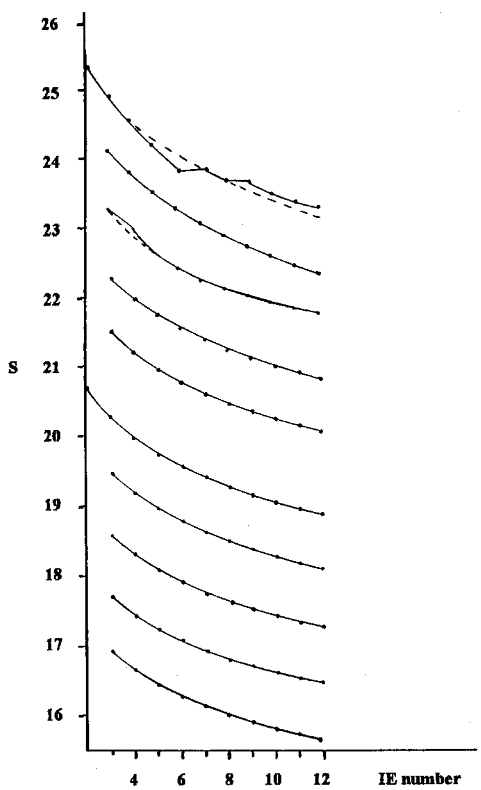

Figure 2. Plots of *S* versus IE number for electron configurations $3d^1$ to $3d^{10}$.

Table 2. Empirical Constants for (1) for Electron Configurations $3d^1$ to $3d^{10}$

electron	A	B	C
$3d^1$	12.166	−0.871	6.952
$3d^2$	12.714	−1.633	7.845
$3d^3$	13.323	−1.832	8.326
$3d^4$	13.807	−2.590	9.421
$3d^5$	14.228	−3.118	10.329
$3d^6$	15.691	−2.125	9.421
$3d^7$	15.998	−3.086	10.623
$3d^8$	18.673	0.879	5.249
$3d^9$	14.509	−8.792	19.250
$3d^{10}$	15.329	−8.792	19.250

The errors of calculated IEs—considering all configurations studied, with a total of 102 data—are summarized in Table 4.

Table 3. Ionization Energies and Shielding Constants for Species with $3d^3$ Electron Configuration

Z	IE order	IE exptl	*Z**	*S*[a] actual	*S*[b] calcd	IE[c] calcd	error (%)
23	3	29.310	4.408	18.592	18.591	29.325	0.052
24	4	49.1	5.705	18.295	18.294	49.116	0.033
25	5	72.4	6.928	18.072	18.071	72.427	0.038
26	6	99	8.101	17.899	17.895	99.1	0.101
27	7	129	9.247	17.753	17.749	129.1	0.080
28	8	162	10.363	17.637	17.626	162.35	0.216
29	9	199	11.485	17.515	17.519	198.85	0.076
30	10	238	12.561	17.439	17.426	238.5	0.210
31	11	281*	13.648	17.352	17.342	281.4	0.142
32	12	327*	14.723	17.277	17.268	327.4	0.122

[a] Calculated values of *S* starting from experimental IEs. [b] Calculated values of *S* using (1). [c] Calculated IEs using the proposed method for estimating *S*.

Table 4

no. of data	% data	% error
55	53.9	<0.1
35	34.3	0.1−0.5
8	7.8	0.5−2.0
4	3.9	>2.0

From the results above we can see that more than 88% of calculated IEs are below 0.5% of error, so we can conclude that this method is applicable to 3d electrons.

The most important application of this method is that it is a very accurate and simple method for calculating ionization energies of atoms with 3d electrons, and, secondly, it provides a new method for estimating screening constants, which could be used to calculate related topics, such as ionic radii, electronegativity, etc.

REFERENCES AND NOTES

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