

Nature of dependence of spin-orbit splittings on atomic number*

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MS received 28 August 1980 ; revised 7 October 1980

Abstract. It has been shown that Dirac equation employing a constant value of the screening constant Z_0 does not explain the variation of spin-orbit splittings of $2p$ and $3p$ levels with atomic number Z . A model which takes into account the variation of Z_0 with Z is shown to satisfactorily predict the dependence of spin-orbit splittings on Z .

Keywords. Spin-orbit splittings; Dirac equation; screening constant.

1. Introduction

Spin-orbit coupling and the consequent lifting of the degeneracy of the two J -multiplets of a singly occupied atomic orbital are described by solutions of Dirac's relativistic wave equation (Dirac 1958). The resulting spin-orbit splitting, $\Delta E_{nl} (= E_{nl_{j_1}} - E_{nl_{j_2}})$, for the hydrogenic case is given by

$$\Delta E_{nl} = mc^2 \left[\frac{(k_1^2 - \gamma^2)^{1/2} + n_1}{\{k_1^2 + n_1^2 + 2n_1(k_1^2 - \gamma^2)^{1/2}\}^{1/2}} - \frac{(k_2^2 - \gamma^2)^{1/2} + n_2}{\{k_2^2 + n_2^2 + 2n_2(k_2^2 - \gamma^2)^{1/2}\}^{1/2}} \right]. \quad (1)$$

Here, $\gamma = aZ$, a being the fine structure constant, Z the atomic number; k and n are quantum numbers, the subscripts 1 and 2 denoting the two different J -valued spin-orbit levels. For systems containing more than one electron (non-hydrogenic case), the effect of other electrons can be accounted for by replacing the nuclear charge Z by an effective charge $(Z - Z_0)$, where Z_0 represents the screening due to other electrons. In the non-relativistic limit, the above equation can be approximated as,

$$\Delta E_{nl} = \frac{mc^2}{2n^3} \left\{ \frac{1}{|k_1|} - \frac{1}{|k_2|} \right\} a^4 (Z - Z_0)^4. \quad (2)$$

* Communication No. 98 from the Solid State and Structural Chemistry Unit.

This equation still uses the spherical coulombic potential with an effective $(Z - Z_0) e$ charge at the nucleus. Small deviations from the spherical nature of the potential can be accommodated by writing equation (2) as,

$$\Delta E_{nl} = a (Z - Z_0)^4, \quad (3)$$

where a is the parameter accounting for the non-sphericity of the potential. Thus (1) and (3) have been employed to understand the dependence of experimental ΔE_{nl} values (from x-ray photoelectron spectroscopy) on Z in related series of metal oxides (Sarma and Rao 1980). These equations (with a constant Z_0 value) could not, however, explain why ΔE_{2p} in transition metal oxides ($Z = 22-29$) vary linearly with the atomic number (Rao *et al* 1979), the difference between the experimental and the calculated values of ΔE_{2p} in these systems being much beyond the experimental error. Large deviations of experimental ΔE_{2p} from values calculated from (1) have also been found in transition metals (Barrie *et al* 1974). Such deviations are noticed (Sarma and Rao 1980) for other levels (e.g., $3d$ and $4d$) in the case of metal oxides over narrow ranges of Z . These deviations cannot be explained on the basis of (1) and (2) which employ a constant Z_0 value for all elements for a given level (nl). It, therefore, becomes necessary to find a functional relation between Z_0 and Z which leads to satisfactory results for ΔE_{nl} over the entire range of Z values. In this paper, we have shown how the screening constant Z_0 varies with Z due to various electron-electron interactions and then, compared the observed ΔE_{nl} values with those predicted by equation (1) incorporating a $Z_0(Z)$ term based on our model. The results are indeed most encouraging and provide an insight into the nature of screening.

5. Methodology

Using the experimental values of ΔE_{2p} and ΔE_{3p} from the literature (Bearden and Burr 1967), Z_0 values for the elements were calculated from equation (1), the error in Z_0 being estimated from the errors in the values of the spin-orbit splittings. The uncertainties in Z_0 values were rather large in the case of $2p$ levels for elements with $Z < 20$ and $Z > 75$; for the $3p$ level, it was large for elements with $Z < 38$ and $Z > 83$ and also for $Z = 57-70$. We, however, retained ΔE_{3p} of Ar ($Z = 18$) as this value is known with great accuracy from UV photoelectron spectroscopy. In the region of $Z = 11-19$, the Z_0 value is extremely sensitive to small changes in the ΔE_{2p} values; although the absolute error of ΔE_{2p} over this region is not large, it leads to large errors in Z_0 values and thus, this region was not included in the data set for the $2p$ level. The Z_0 values thus obtained are plotted against Z in figures 1 and 2 for the $2p$ and $3p$ levels respectively. The figures clearly illustrate how Z_0 varies markedly when we consider a wide range of elements; furthermore, the nature of variation of Z_0 varies from one level to another.

In order to provide a simple heuristic model, we propose that there are three types of interactions that should be taken into account to explain the variation of screening constant with Z . These contributions are: (i) screening due to electrons closer to the nucleus than the level in question, (ii) coulombic contribution of outer electrons to screening and (iii) spin-spin interaction of the core

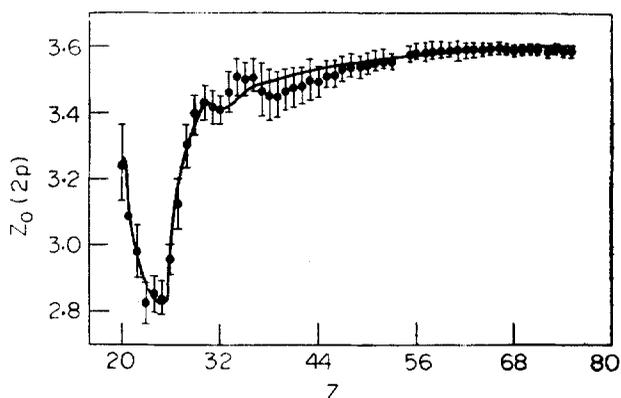


Figure 1. Plot of $Z_0(2p)$ against Z . The solid line is the least-square fit to the data points according to equation (4).

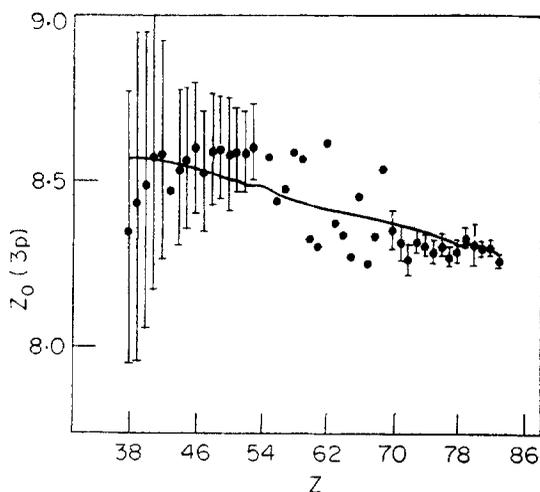


Figure 2. Plot of $Z_0(3p)$ against Z . The errors in Z_0 values are shown for the points which have been used for the least-square fit procedure; for other Z_0 values, the errors are very large. The solid line is the least-square fit according to equation (4) with only the first two terms.

hole with the outermost open shell. The largest contribution would be due to (i) and would vary from one level to another; we shall denote this by a constant Z_0^s , since this contribution essentially represents screening as is usually understood. Contribution from (ii) would involve electron-electron interaction including direct and exchange terms and would vary with the number of outer electrons. Since it is impossible to depict the functional relationship of these interactions on the outer electrons in a closed form, we have arbitrarily chosen

$$\sum_j n_j^i (E_{n_i}^i - E_j^i)$$

to represent the effect of the interactions, where j denotes an outer level, n_j^i , the occupancy of the level j in the i -th element, $E_{n_i}^i$ and E_j^i are the energies of the (nl) and j levels and X is a negative number. Similarly, we have chosen to represent the spin-spin interaction by

$$S_v^i \exp [(E_{n_i}^i - E_v^i)/y],$$

where S_v^i is the spin due to unpaired electrons in the outermost valence level, v , of the i -th element, E_s are the energies and y is a negative number. The weighting factors $(E_{n_i}^i - E_j^i)^x$ and $\exp [(E_{n_i}^i - E_j^i)/y]$ in these two interactions are chosen to be different because of the different spatial dependence of these two interactions. Both these factors approach a value of zero as the energy separation [between the levels (nl) and j or v] becomes larger representing the limiting behaviour of these interactions correctly. The factor $(E_{n_i}^i - E_j^i)^x$ diverges as E_j^i approaches the value of $E_{n_i}^i$ in order to simulate the decreasing separation between the electrons from two levels; this represents the divergence of coulombic interaction with decreasing separation. The exponential factor, $\exp [(E_{n_i}^i - E_v^i)/y]$, in the spin-spin interaction term has a limiting value of unity as E_v^i approaches $E_{n_i}^i$ and thus, simulates this interaction as the electrons with the same spin are forbidden to approach each other very closely due to Pauli's exclusion principle. Taking all these three terms together, the total screening constant Z_0 can be written as,

$$Z_0 = Z_0^* + A \sum_j n_j^i (E_{n_i}^i - E_j^i)^x + B S_v^i \exp [(E_{n_i}^i - E_v^i)/y]. \quad (4)$$

In (4) we would expect A to be positive and B to be negative as the electron-electron coulombic interaction is repulsive whereas the spin-spin interaction stabilises the electronic state.

The various parameters in (4) were calculated for the $2p$ level by a least-square fit (root mean square deviation = 0.022, correlation coefficient = 0.994) of the Z_0 values obtained from experimental ΔE_{2p} data (employing equation 1). The parameters so obtained are as follows: $Z_0^* = 2.6529$, $A = 0.6685$, $B = -1.15946$, $x = -0.4122$ and $y = -384.5$. It is interesting to note that the signs of A and B come out as expected, the latter showing a negative sign. These parameters were then used to calculate the Z_0 versus Z curve shown in figure 1. The marked decrease in Z_0 in the region of $Z = 25$ is due to the spin-spin interaction term; the electron-electron repulsion term would only give a smooth increase from $Z_0 = 3.25$ to $Z_0 = 3.5$ in the region $Z = 20-40$. The spin-spin interaction term becomes dominant in the region of first-row transition metals while it is negligible for $Z > 40$ due to negligible overlap between the core hole and the valence level in this region.

The Z_0 values of $3p$ level obtained from experimental ΔE_{3p} values (figure 2) exhibits a behaviour entirely different from $Z_0(2p)$ values. In view of the large uncertainties in these $Z_0(3p)$ data, we considered it appropriate to omit the spin-spin interaction term in (4), since it would only account for small variations. The parameters obtained by the least-square fit of (4) with the first two terms

alone (root mean square deviation = 0.072, correlation coefficient = 0.956) are as follows:

$$Z_0^* = 7.26072, A = 1.22719 \text{ and } x = -0.5615.$$

We see that Z_0^* value of $3p$ is larger than that for $2p$ as expected. The value of Z_0 for Ar (7.26) calculated from these parameters is indeed very close to the value of Z_0 obtained from experimental ΔE_{3p} value (7.28). The calculated value of ΔE_{3p} in the case of Cl⁻ is also close to the observed value (~ 0.1 eV). We should, however, note that spin-spin interaction may, indeed, become very important in the region of $Z = 19-37$ giving rise to a significant decrease in Z_0 values for these elements. If good data for ΔE_{3p} were available, we feel certain that equation (4) with spin-spin interaction term would predict the exact variation of experimental Z_0 values.

3. Results and discussion

In figures 3 and 4 we have shown how the values of spin-orbit splittings for $2p$ and $3p$ levels calculated from the Dirac equation [equation (1)] employing Z_0

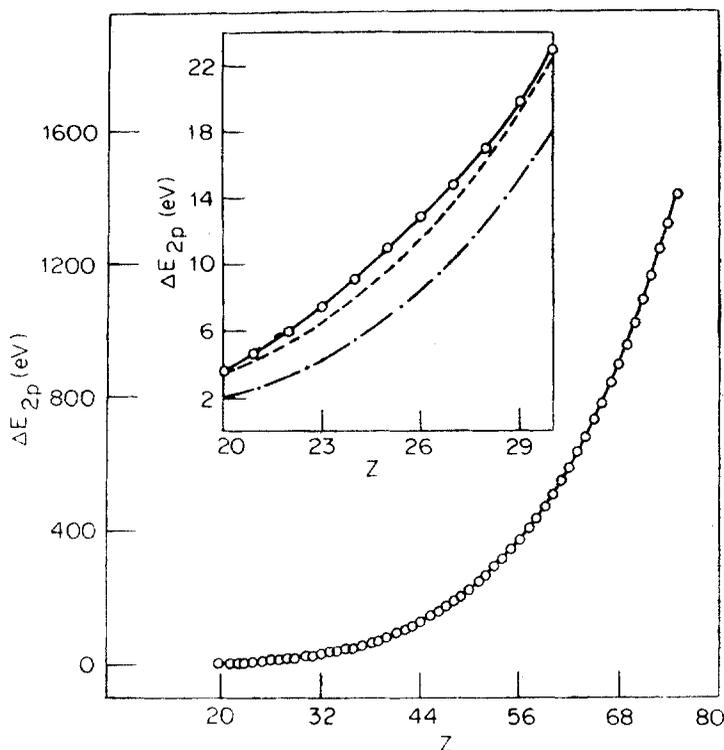


Figure 3. Plot of ΔE_{2p} values against atomic number Z . The solid line is the calculated plot of ΔE_{2p} using Dirac equation incorporating $Z_0(Z)$ according to equation (4). The inset shows the comparison between the values of ΔE_{2p} , predicted according to equation (1) (---), equation (3) (-.-.-) with constant Z_0 and the present model (the solid line); the experimental values are shown as solid circles.

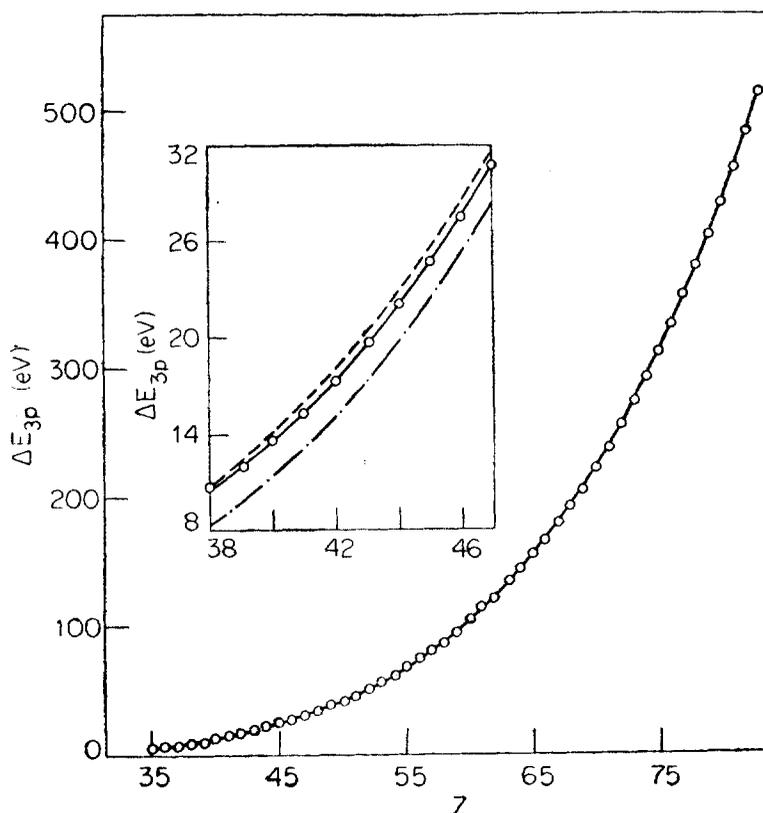


Figure 4. Plot of ΔE_{3p} values against Z . The solid line is the calculated values of ΔE_{3p} according to the present model. The inset shows the comparison between the values of ΔE_{3p} predicted according to equation (1) (---), equation (3) (-·-·-) with constant Z_0 and the present model (the solid line) over a narrow range of Z ; the experimental values of ΔE_{3p} are shown as solid circles.

values given by (4) show excellent agreement with experimental data. In these figures, we have also shown how the description of Z_0 given in terms of (4) gives more reliable predictions of ΔE_{2p} and ΔE_{3p} than when we use (1) or (3) with constant Z_0 values. With constant Z_0 values (1) and (3) give much poorer fits for both ΔE_{2p} (Z range, 20–75) and ΔE_3 (Z range, 35–83) as can be seen from the root mean square deviations given in table 1.

The parameters of (4) for the $2p$ level mentioned earlier were employed to calculate the spin-orbit splittings (ΔE_{2p}) in some of the lighter elements ($Z = 11$ –19). The calculated and experimental values are shown in table 2. We clearly see the success of this model describing the total screening constant from this table.

The description of Z_0 given in (4) appears to be able to explain certain specific variations of spin-orbit splittings found in transition metal systems. Thus, (4) predicts that transition metal ions like Fe^{2+} , Co^{2+} and Co^{3+} should have a higher ΔE_{2p} when they are in the high-spin state than in the low-spin state. The predicted difference varies between 0.4 and 0.8 eV compared to the experimental values which show differences of 0.4–0.6 eV. ΔE_{2p} values calculated for Cr_2O_3 and

Table 1. Root mean square deviations in least-square fits of ΔE_{2p} and ΔE_{3p} values employing different equations.

Level	Range of Z	Equation (1) ^(a)	Equation (3) ^(a)	Present model
2p	20-75	0.771	5.400	0.432
3p	35-83	1.094	2.133	0.803

^(a) The value of constant Z_0 which gave minimum deviation is used in the least-square fit.

Table 2. Calculated and experimental spin-orbit splitting values (in eV) for some elements.

Z	Element	Calculated ΔE_{2p}	Experimental ΔE_{2p} ^(a)
11	Na	0.3	0.3
12	Mg	0.3	0.3
13	Al	0.5	0.4
14	Si	0.9	1.0
15	P	1.4	1.0
16	S	1.6	1.0
17	Cl	1.8	2.0
18	Ar	2.2	2.1
19	K	3.0	2.7
19	K ⁺	2.8	2.7

^(a) The experimental values of ΔE_{2p} are taken from Shirley *et al* (1977).

CrO₃ show a differences of about 0.4 eV between the two compared to an observed difference of 0.8 eV. A lowering of ΔE_{2p} by 0.7eV is predicted for the d^0 state of Mn (Mn⁷⁺) compared to that in Mn²⁺. An increase of ΔE_{2p} by 0.2 eV is predicted in going from Mn to MnO, while the observed change is 0.4 eV. Equation (4) also predicts differences between spin-orbit splittings of elements and their compounds, but we would not expect a quantitative agreement in view of the differences in bonding, crystal field effects and so on.

Acknowledgement

The author is thankful to Professor C N R Rao for suggesting the problem and also for his kind help throughout the course of this work,

References

- Barrie A, Drummond I W and Herd Q C 1974 *J. Electron. Spectrosc. Rel. Phenom.* **5** 217
Bearden J A and Burr A F 1967 *Rev. Mod. Phys.* **39** 125
Dirac P A M 1958 *Principles of quantum mechanics* Ch. XI (Oxford University Press)
Rao C N R, Sarma D D, Vasudevan S and Hegde M S 1979 *Proc. R. Soc. London* **A367** 239
Sarma D D and Rao C N R 1980 *J. Electron Spectrosc. Rel. Phenom.* **20** 25
Shirley D A, Martin R L, Kowalczyk S P, McFeely F R and Ley L 1977 *Phys. Rev.* **B15** 54