Effective nuclear charge

The hydrogen atom has only 1 electron, the energy level of which is determined by its principal quantum number 'n'. All the orbitals inside this shell have the same energy and the only force experienced by the electron is the attractive force towards the positively charged nucleus.

The situation is, however, different in case of multielectron atoms. The electrons in such atoms experience not only attractive force of the nucleus but also repulsion among themselves and each of their neighbours. The repulsion of outer-shell electrons by the inner-shell electrons is particularly important, as the outer-shell electrons are pushed away from the nucleus due to repulsion of the inner-shell electrons. As a result the nuclear charge felt by the outer-shell electrons is less than what it would ~~be~~ have been if there were no inner electrons. This net charge felt by the valence electrons is termed as the effective nuclear charge, represented by the symbol (Z_{eff}) and the repulsion experienced due to the inner electrons is the "shielding effect." The shielding effect is called so because the inner electrons shield/

screen the outer electrons from experiencing the actual nuclear charge.

$$Z_{eff} = Z_{actual} - \text{electron shielding}$$

or

$$Z_{eff} = Z_{actual} - S \quad (S = \text{screening constant})$$

Consider the example of fluorine (At. No. = 9), there are two electrons in shell 1 ($n=1$) and seven electrons in shell 2 ($n=2$). The seven electrons in $n=2$ will be repelled by two electrons in $n=1$, hence they will experience less attraction than what they would have experienced in the absence of these two electrons. Hence these two inner-shell electrons are shielding or screening the outer electrons from the attractive force of the nucleus, and because of this shielding, the effective attractive force felt by the valence electrons reduces. Shielding effect generally remains the same in the period, as in the period the number of shells is the same and it increases down the group.

Calculation of Screening Constant

In multielectron atoms, the inner electrons shield or screen the outer electrons from the attractive force of nucleus. The effective nuclear charge experienced by the outer electron is

$$Z_{eff} = Z_{actual} - S$$

Z_{actual} = Actual nuclear charge

S = Screening constant

From the radial probability distribution graphs, we know that 2s electrons are more penetrating than 2p. In general, for a given energy level, the penetration of electrons in various subshells is in the following order:

$s > p > d > f$ ------ Order of penetration

Due to greater penetration, s-electrons have maximum screening effect. For a given energy level, the screening effect of electrons in various subshells varies in the order:-

$s > p > d > f$ ---- Order of screening effect

Rules for Calculation of Screening Constant:-(Slater Rules)

1) Electronic configuration of the element is first written and the subshells are grouped in the following order
(1s); (2s,2p); (3s,3p); (3d); (4s,4p); (4d); (4f)------

2) Electrons farther away from the nucleus than electron under consideration do not contribute to the screening constant, S.

(3) The electrons in the same group contribute 0.35 each to the screening constant. In case of 1s, however, the contribution is 0.30.

(4) In case of ns and np groups, all electrons in the next inner shell (n−1) contribute 0.85 each to S and the remaining electrons in the inner shells (n−2) contribute 1.0 each to S.

(5) In case of nd groups, all electrons in the inner shells contribute 1.0 each to the screening constant S. (similar for nf)

Examples:-

* Z_{eff} for 3d- electron in titanium (Z = 22)

Ti (Z = 22) : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^2$

Grouping : $(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^2)(4s^2)$

In case of 3d- electron, the electrons in 4s make no contribution and the electrons in the inner shells make contribution 1.0 each. The second electron in 3d makes a contribution of 0.35.

∴ for 3d electron

$$S = (18 \times 1.0) + (1 \times 0.35) = 18.35$$

$$Z_{eff} = 22 - 18.35 = 3.65$$

* Z_{eff} for 4s- electron in titanium (Z = 22)

In case of 4s- electron, the second electron in 4s- subshell makes contribution of 0.35 to S. All the electrons in the third shell (n−1) make contribution of 0.85

each 1s & and the electrons in the first and second energy levels make a contribution of 1.0 each.

∴ for 4s electron

$$S = (10 \times 1.0) + (10 \times 0.85) + (1 \times 0.35)$$
$$= 18.85$$

$$Z_{eff} = 22 - 18.85 = 3.15$$

* Z_{eff} for 3s or 3p electron in phosphorus atom ($Z=15$)

$P (Z=15): 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

Grouping: $(1s^2)(2s^2, 2p^6)(3s^2, 3p^3)$

four other electrons in the group $(3s^2, 3p^3)$ contribute 4×0.35 and next inner shell contributes 8×0.85 and then the next 2×1.

for a 3s or 3p electron

$$S = (2 \times 1.00) + (8 \times 0.85) + (4 \times 0.35)$$
$$= 2.00 + 6.80 + 1.40 = 10.20$$

$$Z_{eff} = 15 - 10.20$$
$$= 4.80$$

* Z_{eff} experienced by a 2p electron in oxygen atom ($Z=8$)

$O (Z=8): 1s^2, 2s^2, 2p^4$

Group configuration: $(1s^2); (2s^2, 2p^4)$

There are 5 other electrons in the group $(2s^2, 2p^4)$ under consideration which contribute 5×0.35 towards S. Next inner shell contributes 2×0.85.

Thus for 2p electron

$$S = (2 \times 0.85) + 5 \times (0.35) = 3.45$$

$$Z_{eff} = (8 - 3.45) = 4.55$$

* Z_{eff} for 5s electron in Ag atom ($Z=47$)

Ag ($Z=47$) : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^1$

Group configuration : $(1s^2), (2s^2, 2p^6), (3s^2, 3p^6), (3d^{10}), (4s^2, 4p^6)$
$(4d^{10}), (5s^1)$

$$S = (28 \times 1.00) + (18 \times 0.85) + (0 \times 0.35)$$
$$= 43.30$$
$$Z_{eff} = 47 - 43.30 = 3.70$$

* Z_{eff} for 4d electron in Ag atom ($Z=47$)

Ag ($Z=47$) : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^1$

Group configuration: $(1s^2), (2s^2, 2p^6), (3s^2, 3p^6), (3d^{10}), (4s^2, 4p^6)$,
$(4d^{10}) (5s^1)$

$$S = (36 \times 1.00) + (9 \times 0.35) + 0$$
$$= 39.15$$
$$Z_{eff} = 47 - 39.15 = 7.85$$

Z_{eff} for 3d electron in iron atom ($Z=26$)

Fe ($Z=26$) : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$

Group configuration : $(1s^2) (2s^2, 2p^6), (3s^2, 3p^6), (3d^6), (4s^2)$

$$S = (18 \times 1.00) + (5 \times 0.35) + 0$$
$$= 19.75$$
$$Z_{eff} = 26 - 19.75 = 6.25$$

① Group
② Remaining or complete shell
③ Inner shells

Z_{eff} for 4s electron in iron atom ($Z=26$)

Fe ($Z=26$) : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$

Group configuration :- $(1s^2), (2s^2, 2p^6), (3s^2, 3p^6), (3d^6), (4s^2)$

$$S = (10 \times 1.00) + (14 \times 0.85) + (1 \times 0.35)$$
$$= 22.25$$
$$Z_{eff} = 26 - 22.25 = 3.75$$