Effective Nuclear Charge

BSc. Semester I

Energy of electron

@ Energy of an electron, $E_n \alpha Z^2/n^2$, n is principal quantum no and Z is actual nuclear charge

@ Energy of H atom, $E_H = 13.6$ eV

@ Energy of helium, $E_{He} = 4E_H = 4 \text{ x } 13.6 = 54.4$ eV, $E_{Obs} = 24.4$ eV

@ Energy of lithium, $E_{Li} = (9/4)\ E_H = 30.5$ eV, $E_{Obs} = 5.4$ eV

@ Energy of beryllium, $E_{Be} = (16/4)\ E_H = 54.4$ eV, $E_{Obs} = 7.3$ eV

@ Z corresponding to E_{Obs} is less than the actual charge.

@ As the orbitals (multielectron atoms) are filled up, the electrons in the inner orbitals shield the electrons in the outer orbitals from the nucleus.

@ Electrons in the outer orbitals do not feel the full force of actual nuclear charge.

@ Decreases the net force on electrons in outer shells (orbital penetration effect)

What is effective nuclear charge?

@ Nuclear charge is generally the atomic number (number of protons) of the species. It is denoted by Z.

@ Effective nuclear charge is the actual charge felt by the outer electrons after taking shielding of the electrons into account. It is denoted by Z^*/Z_{eff}.

@ Z* experienced by all the electrons are not same.

@ Z* is always less than Z.

@ Higher the Z* smaller is the isoelectronic species.

@ Extent to which an orbital of a shell interacts with inner shell is known as penetration effect of the orbital.

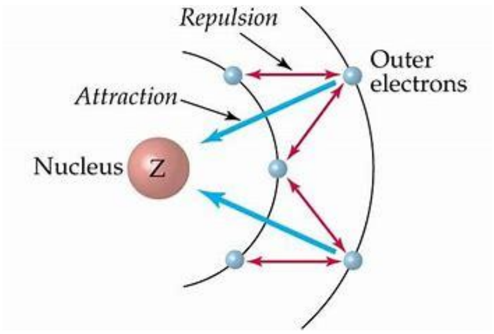
@ Shielding power decreases with decrease in penetrating power. Orbital with higher l values has less penetrating, thereby poor shielding effect. i.e., s > p > d > f.

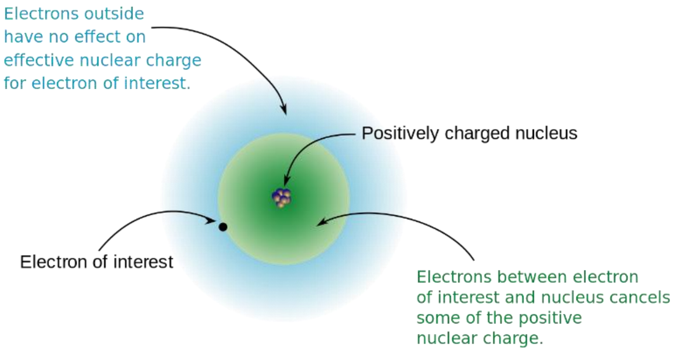
What is screening or shielding effect?

@ The reduction of nuclear charge on the outermost electrons is called shielding or screening effect.

@ Shielding/screening effect is defined as a measure of the extent to which the intervening electrons shield the outer electrons from the nuclear charge.

@ It is denoted by the symbol S/σ.





Slater's rule

@ In 1930, J. C. Slater proposed a set of empirical rules to understand the concept of Effective Nuclear Charge and calculate the Screening or Shielding constant.

@ He proposed a formula for calculation of Effective Nuclear Charge, $Z^* = Z - S$ where S is the Slater's screening constant and Z is the nuclear charge (number of protons)

@ Z* at a particular shell can be estimated by considering shielding of one electron less than the number electrons present in that shell.

@ Z* at the periphery or σ/S at the periphery of an atom, shielding contribution is calculated by considering all the electrons.

Rules

1) The electronic configuration of the atom is written in groupings as:

(1s) (2s,2p) (3s,3p) (3d) (4s,4p) (4d) (4f) (5s,5p)……. etc.

2) Electrons in higher groups do not shield those in lowers groups.

3) If the outermost electron is in s or p orbital,

a) electrons in the same (ns,np) group contribute 0.35, except the 1s where the contribution is 0.30 (for H and He only)

b) electrons in the (n-1) group contribute 0.85

c) electrons in the (n-2) or lower groups contribute 1.00

4) If the outermost electron is in d or f orbital,

a) electrons in the same nd or nf group contribute 0.35

b) electrons in groups to the left contribute 1.00

5) Sum the shielding amounts from steps 2 through 4 and its difference with the nuclear charge gives the effective nuclear charge.

Summarily,

Electron Group	**Contribution to the shielding by each electron**			
	All higher groups	**Same group**	**Groups (n-1)**	**Groups (n-2) or less**
1s	0	0.30	-	-
(ns, np)	0	0.35	0.85	1.00
(nd) or (nf)	0	0.35	1.00	1.00

@ Slater calculated Z* by the values of principal quantum number n. Effective principal quantum number (n*) where n* = n – quantum defect gives more accurate results.

@ The values of n and n* are related as

n	1	2	3	4	5	6
n*	1	2	3	3.7	4.0	4.2

@ Higher the value of n, higher is the quantum defect.

Q.1. Calculate Z* for a valence electron in fluorine.

Soln: Electronic configuration of fluorine is $1s^2 2s^2 2p^5$

Grouping it according to Slater's rule: $(1s^2)\ (2s^2, 2p^5)$

Now, one electron out of the 7 valence electrons becomes the electron of interest. The other remaining 6 valence electrons will contribute 0.35 each towards shielding.

The electrons in (n-1) orbitals i.e., 1s orbital will contribute 0.85 each towards shielding.

S = 0.35 x (No. of electrons in the same shell i.e., n orbital) + 0.85 x (No. of electrons in the (n-1) shell)

S = 0.35 x 6 + 0.85 x 2 = 3.8

Z^* = 9 – 3.8 = 5.2 for a valence electron.

Q 2. Calculate the effective nuclear charge for all electron in Fe atom.

Soln:

The electronic configuration of Fe atom $(1s)^2\ (2s2p)^8\ (3s3p)^8\ (3d)^6\ 4s^2$

For 1s electron, S = 0 + 0.30 x 1 = 0.30 Z* = 26 – 0.30 = 25.70

For 2s2p electron, S = 0 + 0.35 x 7 + 0.85 x 2 = 4.15 Z* = 26 – 4.15 = 21.85

For 3s/3p electron, S = 0 + 0.35 x 7 + 0.85 x 8 + 2 x 1.00 = 11.25 Z* = 26 – 11.25 = 14.75

For 3d electron, S = 0 + 0.35 x 5 + 1.00 x 18 = 19.75 Z* = 26 – 19.75 = 6.25

For 4s electron, S = 0.35 x 1 + 0.85 x 14 + 1.00 x 10 = 22.25 Z* = 26 – 22.25 = 3.75

Q. 3. Calculate the Effective Nuclear Charge in the periphery of Nitrogen (Z = 7)

Soln:

The electronic configuration of Nitrogen is $1s^2\ 2s^2\ 2p^3$

Grouping according to Slater's rule: $(1s^2)\ (2s^2\ 2p^3)$

S = 0.35 x (No. of electrons in the same orbital) + 0.85 x (No. of electrons in the (n-1) orbital

S = 0.35 x 5 + 0.85 x 2 = 3.45

Z* in the periphery of N - atom = Z – S = 7 – 3.45 = 3.55

Q.4. Calculate Z^* for a 6*s* electron in Platinum (Z = 78)

Soln:

Electronic configuration of Platinum (Z=78) is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^8$

Grouping it according to Slater's rule: $(1s^2)\ (2s^2,2p^6)\ (3s^2,3p^6)\ (3d^{10})\ (4s^2,4p^6)\ (4d^{10})\ (4f^{14})\ (5s^2,5p^6)\ (5d^8)\ (6s^2)$

Now, one electron out of the two-valence electron becomes the electron of interest. The other remaining valence electrons will contribute 0.35 each towards shielding.

The electrons in (n-1) orbitals i.e. (6-1) = 5th orbital will contribute 0.85 each towards shielding.

The electrons in (n-2), (n-3), (n-4) …. orbitals will contribute 1.00 each towards shielding.

S = 0.35 x (No. of electrons in the same (n) shell) + 0.85 x (No. of electrons in the (n-1) shell) + 1.00 x (No. of electrons in the (n-2), (n-3) …. orbitals)

S = 0.35 x 1 + 0.85 x 16 + 60 x 1.00 = 73.95

Z^* = Z – S = 78 – 73.95 = 4.15 for a valence electron.

Q.5. Calculate the Effective Nuclear Charge for 4f electrons of Cerium (Z=58)

Soln:

Electronic configuration of Cerium: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^2\ 5s^2\ 5p^6\ 6s^2$

Grouping the orbitals acc. to Slater's $(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)\ (3d^{10})\ (4s^2\ 4p^6)\ (4d^{10})\ (4f^2)\ (5s^2\ 5p^6)\ (6s^2)$

The electrons lying after the 4f electron will not contribute to shielding.

S = 0.35 x (No. of electrons in the same orbital + 1.00 x (all the electrons in the lower orbitals)

S = 0.35 x 1 + 1.00 x 46 = 46.35

Z* = Z – S = 58 – 46.35 = 11.65

Applications of Slater's rule

It provides justification for the sequence of orbitals in the energy level diagram.

Explain the filling of ns-orbital (4s, 5s, 6s…) prior to the filling of (n-1)d orbital (3d, 4d, 5d…).

Let us consider the case of K (Z = 19), in which the last electron is added to 4s orbital.

The configuration of K according to Slater is $(1s^2)$ $(2s^2\ 2p^6)$ $(3s^2\ 3p^6)$ $(4s^1)$

The electrons in the same orbital i.e., n (4s) orbital will contribute 0.35 each, the electrons in (n-1) orbital i.e., 3s and 3p orbitals will contribute S = 0.85 each and all the electrons in (n-2, n-3…. etc.) orbitals i.e. (2s, 2p, 1s) orbitals will contribute S =1.00 each.

S = 0 x 0.35 + 8 x 0.85 + 10 x 1.00 = 16.80

Z* = Z – S = 19 – 16.80 = 2.20

Let us assume that the last electron enters the 3d orbital rather than 4s orbital

The configuration according to Slater is $(1s^2)$ $(2s^2\ 2p^6)$ $(3s^2\ 3p^6)$ $(3d^1)$

The electrons in the same orbital (3d) will contribute S = 0.35 each, whereas the electrons in all the other orbitals will contribute S = 1.00 each.

S = 0 x 0.35 + 18 x 1.00 = 18.00

Z* = Z – S= 19.00 – 18.00 = 1.00

On comparing the Z* of both 4s and 3d orbitals, the 4s electron is under the influence of greater Z*(= 2.20) as compared to 3d electron (= 1.00) in K atom.

So, the electron in 4s orbital will be more attracted by the nucleus and will have lower energy than the 3d electron.

Thus, the last electron will enter in the 4s orbital, rather than the 3d orbital in case of K atom.

Explain why 4s electrons are lost prior to 3d electrons.

Let us consider the case of Vanadium (Z=23) whose electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

After losing 2 electrons, the electronic configuration of V^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$ and not $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

The above Electronic Configuration can be explained by Slater's rules

The Effective Nuclear Charge for 4s electron is calculated as: $(1s^2)$ $(2s^2\ 2p^6)$ $(3s^2\ 3p^6)$ $(3d^3)$ $(4s^2)$

Now, one of the electrons of the 4s orbital becomes electron of interest. The second electron however, will contribute towards shielding effect.

S = 1 x 0.35 + 11 x 0.85 + 10 x 1.00 = 19.70

Z* = Z – S = 23 – 19.70 = 3.30

Now, let us calculate the Effective Nuclear Charge for a 3d electron

According to Slater's rule $(1s^2)$ $(2s^2\ 2p^6)$ $(3s^2\ 3p^6)$ $(3d^3)$ $(4s^2)$

4s orbital lies after the electron under interest and hence its contribution is nil.

One electron of 3d orbital becomes electron of interest. The other two 3d electrons will contribute towards shielding effect.

S = 2 x 0.35 + 18 x 1.00 = 18.70

Z* = Z – S = 23 – 18.70 = 4.30

Comparing the Z* of both the 3d and the 4s electron, it is seen that Z* on 3d electron is 4.30 whereas 4s electron has 3.30

The force of attraction experienced by 3d electrons is more than 4s electrons i.e., 3d electrons are more tightly held to the nucleus.

Thus, the 4s electrons are removed in preference to 3d electrons.

Explain why size of a cation is always smaller than its neutral atom.

Let's take the example of Lithium atom and Lithium ion

The Electronic configuration of Lithium atom is $1s^2\ 2s^1$

According to Slater's $(1s^2)$ $(2s^1)$

As 2s orbital has only one electron, it becomes the electron of interest.

Only the 1s electrons will contribute towards shielding.

S = 2 x 0.85 = 1.70, Z* = Z – S = 3 – 1.70 = 1.30

The Electronic Configuration of Lithium (Li^+) ion is $1s^2$

Grouping according to Slater: $(1s^2)$

In this case, one of the 1s electrons becomes electron of interest and the other 1s electron contributes towards shielding

S = 1 x 0.30 = 0.30, Z* = Z – S = 3 – 0.30 = 2.70

Effective nuclear charge of Li^+ ion is more than Li atom.

So, the size of Li^+ ion is smaller than Li atom.

Explains why an anion is always larger than its neutral atom

Taking the example of Chlorine atom and Chlorine ion.

In case of Chlorine atom (Z = 17), the electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

Grouping it according to Slater's rule $(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^5)$

$S = 6 \times 0.35 + 8 \times 0.85 + 2 \times 1.00 = 10.90$

$Z^* = Z - S = 17 - 10.90 = 6.10$

In case of Chlorine ion Cl^- The electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Grouping it according to Slater's rule $(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)$

$S = 7 \times 0.35 + 8 \times 0.85 + 2 \times 1.00 = 11.25$

$Z^* = Z - S = 17 - 11.25 = 5.75$

Effective nuclear charge on Cl atom is more than Cl^- ion.

So, the size of Cl^- ion is larger than Cl atom.

Explains the successive ionization energies of elements

Let us consider the case of Al

Electronic configuration of Al $(1s^2)\ (2s^22p^6)\ (3s^23p^1)$

$S = 2 \times 0.35 + 8 \times 0.85 + n2 \times 1.00 = 9.50$

$Z^* = 13 - 9.5 = 3.5$

Electronic configuration of Al^+ $(1s^2)\ (2s^22p^6)\ (3s^2)$

$S = 1 \times 0.35 + 8 \times 0.85 + n2 \times 1.00 = 9.15$

$Z^* = 13 - 9.15 = 3.85$

Electronic configuration of Al^{2+} $(1s^2)\ (2s^22p^6)\ (3s^1)$

$S = 8 \times 0.85 + n2 \times 1.00 = 8.80$

$Z^* = 13 - 8.80 = 4.20$

Z^* in order $Al^{2+} > Al^+ > Al$, thus $IE_3 > IE_2 > IE_1$

Periodic variation of effective nuclear charge

Effective nuclear charge felt by both K and L shell electrons increase from Li to F (variation in atomic and ionic radii along a period).

Similar trend is also followed by third and subsequent period as well.

Effective nuclear charge for K electrons is more than L electron.

In moving down the group, the number of principal shell increases as well as the nuclear charge.

The effective nuclear charge also increases down the group.

The effect is more pronounced from 2nd principal shell to 3rd principal shell.

Calculation of Ionization energy and Electron affinity

According to Slater's treatment, the energy of an electron in an atom is given by, $E = -[me^4Z^{*2}/8\epsilon_o h^2 n^{*2}] = -[13.6\ Z^{*2}/n^{*2}]$ eV, Z* and n* are effective nuclear charge and effective principal quantum number respectively.

The energy of all the electrons in an atom/ion is the summation of Z^{*2}/n^{*2} terms for each electron.

This is the amount of energy required to remove the electrons from the atom/ion to infinity.

The IE of an atom/ion (M) is equal to the difference of its corresponding energy before and after ionization i.e., $IE = E_{M+} - E_M$

Similarly, electron affinity of an atom/ion (X) is given by $EA = E_{X-} - E_X$

Q. Calculate the first IE of Li applying Slater's rule

Soln: Electronic configuration of Li and Li^+ are $1s^22s^1$ and $1s^2$ respectively

$$E_{Li} = [-13.6\ (Z^*/n^*)^2_{2s1} + \{-13.6\ (Z^*/n^*)^2_{1s2}\}]$$

$$= [-13.6\ (Z^*/n^*)^2_{2s1} - \{13.6\ (Z^*/n^*)^2_{1s2}\}]$$

$$E_{Li+} = [\{-13.6\ (Z^*/n^*)^2_{1s2}\}]$$

Z* has to be calculated separately for each type of electrons.

Thus, $\mathbf{IE = E_{Li+} - E_{Li}} = [-13.6\ (Z^*/n^*)^2_{2s1}]$

For Li, Z* for the 1s electron is same in Li and Li^+ (since 2s electron in Li does not screen the inner 1s electron)

For the 2s electron n=2, n*=2 and $Z^* = 3 - S = 3 - 2 \times 0.85 = 1.30$

Hence, $IE = -13.6 \times (1.3/2)^2 = -5.75$ eV

Therefore, the first IE for Li is 5.75 eV (exp. value 5.40 eV)

Q. Calculate the electron affinity of fluorine applying Slater's rule

Soln: Electronic configuration of F and F^- are $1s^22s^22s^5$ and $1s^22s^22s^6$ respectively i.e., $1s^2(2s2s)^7$ and $1s^2(2s2s)^8$

$E_F = [\{-13.6(Z^*/n^*)^2_{(2s2p)7}\} + \{-13.6\ (Z^*/n^*)^2_{1s2}\}]$

$= [-\{13.6(Z^*/n^*)^2_{(2s2p)7}\} - \{13.6\ (Z^*/n^*)^2_{1s2}\}]$

$E_F = [\{-13.6(Z^*/n^*)^2_{(2s2p)8}\} + \{-13.6\ (Z^*/n^*)^2_{1s2}\}]$

$= [-\{13.6(Z^*/n^*)^2_{(2s2p)8}\} - \{13.6\ (Z^*/n^*)^2_{1s2}\}]$

Thus, $\mathbf{IE = E_{F-} - E_F}$

$= [-\{13.6(Z^*/n^*)^2_{(2s2p)8}\}] - [-\{13.6(Z^*/n^*)^2_{(2s2p)7}\}]$

$= [-13.6\ \{9-(7x0.35+2x0.85) + 13.6\ \{9-(6x.35+2x0.85)]$

$= [-13.6x4.85 + 13.6x5.20] = 13.6x0.35 = 13.6(5.20-4.85) = 4.76$ eV

Therefore, the first EA for F is 3.80 eV

Q Calculate the first IE of oxygen using Slater's rule. (14.16 eV)

Calculation of Electronegativity - Allred-Rochow Scale

According to Allred-Rochow, an atom will attract an electron in the valence shell.

Proposed a relationship between the tendency to attract electrons (χ) and effective nuclear charge (Z^*).

Electronegativity, $\chi = 0.359(Z^*/r^2) + 0.744$

Numerical constants 0.359 and 0.744 are arbitrarily chosen to give desired range, r is the covalent radius of the atom.

Q. Calculate the electronegativity of Si using AR scale if its covalent radius is 1.175Å.

Limitations of Slater's Rule

@ Slater grouped both s and p orbitals together for calculating effective nuclear charge, which is incorrect. This is because radial probability distribution curves show that s orbitals are more penetrating than p orbitals. So, the s orbitals should shield to a greater extent as compared to p orbital.

@ According to Slater, all the s, p, d and f electrons present in shell or energy level lower than (n-1) shell will shield the outer n electrons with equal contribution of S=1.00 each. This is not justified as energetically different orbitals should not contribute equally.

@ Slater's rules are less reliable for heavier elements.

Problems for Practice

Q. 1. Calculate Z^* for

(a) valence electron in N

(b) 4s and 3d electron in V

(c) 3p electron in P

(d) 4s electron in Co

(e) 3d electron in Mn

(f) valence electron in Mg

(g) 3d and 4s electron in Ni

(h) 5s, 5p and 4d electron in Sn

(i) 3d and 4s electron in Zn

(j) 5d electron in Platinum (Z = 78)

Q. 2. Calculate Z* at the periphery of Cr atom.

Q. 3. What will be the expected trend in Z* going from C to O?

Q. 4. Calculate the first and second IE of Li using Slater's rule

Q. 5. Calculate Z* for a 3p electron in P, S, Cl and Ar. Is the calculated value of Z* consistent with the relative sizes of these atoms.

Q.6. A 2p electron in O^{2-}, F^{-}, Na^{+} and Mg^{2+}. Is the calculated value of Z* consistent with the relative sizes of these ions.

Q.7. A 4s and a 3d electron of Cu. Which type of electron is more likely to be lost when Cu forms a positive ion?

Q. 8. A 4f electron in Ce, Pr and Nd. There is a decrease in size, commonly known as the lanthanide contraction, with increase in atomic number in the lanthanides. Are your values of Z* is consistent with this trend.