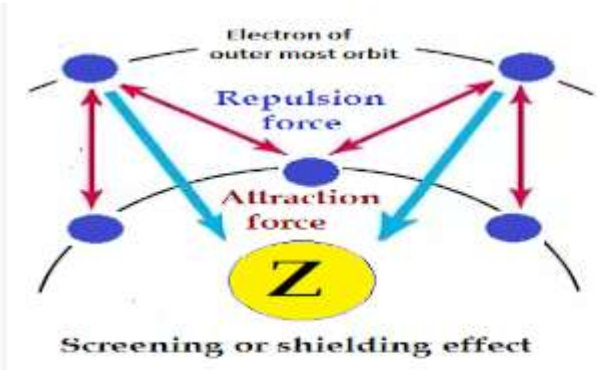
Screening effect or Shielding effect: Slater's method for polyelectronic atoms

SLATER rules make it possible to apply the results of the BOHR model to polyelectronic atoms. When the atomic number increases, the number of core electrons also increases, leading to a decrease in the nucleus's attraction for the outer electrons.



We say that the core electrons shield the nucleus's effect on the outer electrons. In this case, the nucleus affects the outer electrons with a charge Z* or Z_{eff} known as the effective charge.

$$Z^* = Z - \Sigma\sigma i$$

Where Z is the (nuclear charge)= The number of protons in the nucleus of an atom, and σi represent the shielding constant and *value is greater than zero but less than Z.*

Slater formulated the rules that allow us to express this screening effect (σ):

Step 1: Write the electron configuration of the atom in the following form:

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

Step (2): We identify the electron to be studied.

Step (3): Electron in higher group do not shield the electrons in the lower group.

Step (4): We assign the positions of the remaining electrons, (atomic orbital names, and principal quantum number) to be able to determine their shielding values from the following table:

The values of σij are summarized in the following table

	Electrons j that screen i						
The studied electron i	1s	2s2p	3s3p	3d	4s4p	4d	4f
1s	0.31	0	0	0	0	0	0
2s2p	0.85	0.35	0	0	0	0	0
3s3p	1	0.85	0.35	0	0	0	0
3d	1	1	1	0.35	0	0	0
4s4p	1	1	0.85	0.85	0.35	0	0
4d	1	1	1	1	1	0.35	0
4f	1	1	1	1	1	1	0.35

Exp:

Calculating the effective nuclear charge of an electron in the last shell of Chlorine $_{17}Cl$

$$_{17}Cl: 1s^2 2s^2 2p^6 3s^2 3p^5$$

$$\mathbf{Z^*_{3s3p}} = 17 - [(0{,}35 \cdot 6) + (0{,}85 \cdot 8) + (1 \cdot 2)] = \mathbf{6,1}$$

In 1960, Slater introduced an apparent quantum number n* to reduce the differences between experimental values and calculated values. It is necessary to introduce n* starting from the 4th period.

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

Hydrogen-like atom	poly electron atoms
$E_n = \frac{Z^2 E_H}{n^2}$ $r_n = a_0 . \frac{n^2}{Z}$	$E_n = \frac{Z^{*2} E_H}{n^{*2}}$ $r_n = a_0 . \frac{n^{*2}}{Z^*}$

The energy of the atom equals the sum of the orbital energies of all electrons.

Example: Consider the sulfur atom $_{16}S$: $1s2 | 2s^2\ 2p^6 | 3s^2\ 3p^4$,

[$1s^2$]: Each electron in 1s receives the screening effect of the second electron. Its effective charge is $Z_{1s}^* = 16 - \sigma_{1s} = 16 - 0.31 = 15.69$, and its energy is

$$E_1 = \frac{-13{,}6}{n_1^{*2}} Z_{1s}^{*2} = \frac{-13{,}6}{1} \times (15{,}69)^2 = -3347{,}995 \text{ eV}$$

$$Z_{2s,2p}^* = 16 - (7 \times \sigma_{2s,2p} + 2 \times \sigma_{1s}) = 16 - (7 \times 0{,}35 + 2 \times 0{,}85) = 11{,}85$$

$$E_2 = \frac{-13{,}6}{2^2} \times (11{,}85)^2 = -1909{,}746 \text{ eV}$$

$$Z_{3s,3p}^* = 16 - (5 \times 0{,}35 + 8 \times 0{,}85 + 2 \times 1) = 5{,}45$$

$$E_3 = \frac{-13{,}6}{3^2} \times (5{,}45)^2 = -44{,}8838 \text{ eV}$$

$$E_t\,(_{16}S) = 2 * E_1 + 8 * E_2 + 7 * E_3$$

Ionization energy of multi-electron atoms

$A_{(g)} \rightarrow A^+_{(g)} + e^-$

$A^+_{(g)} \rightarrow A^{2+}_{(g)} + e^-$ etc······

$E_i = E_{A+} - E_A$

E_{A+} : énergie totale de A^+ ; E_A : énergie totale de A.

The total energy of the atom will be evaluated by the sum of the individual energies of the electrons.

EXP

Calculating the ionization energy of a chlorine atom.

Cl : $[1\,s^2]: [2\,s^2, 2\,p^6]: [3\,s^2, 3\,p^5]$

$$E_{Cl} = 2\,E_1 + 8\,E_2 + 7\,E_3$$

Cl⁺ : $[1\,s^2]: [2\,s^2, 2\,p^6]: [3\,s^2, 3\,p^4]$

$$E_{Cl^+} = 2\,E_1' + 8\,E_2' + 6E_3'$$

$$E_{I1} = E_{Cl^+} - E_{Cl} = 2\,E_1' + 8\,E_2' + 6E_3' - 2\,E_1 + 8\,E_2 + 7\,E_3 = 6E_3' - 7\,E_3$$

$$Z_{E3}^* = 17 - (6.0{,}35) - (8.0{,}85) - (2\,.1) = 6{,}1$$

$$E_3 = -13{,}6\,.\frac{(6{,}1)^2}{(3)^2} = -56{,}23\ \text{eV}$$

$$Z_{E_3'}^* = 17 - (5.0{,}35) - (8.0{,}85) - (2\,.1) = 6{,}45$$

$$E_3' = -13{,}6\,.\frac{(6{,}45)^2}{(3)^2} = -62{,}866\ eV$$

$$E_{I1} = E_{Cl^+} - E_{Cl} = 6E_3' - 7\,E_3 = 16{,}39\ eV$$