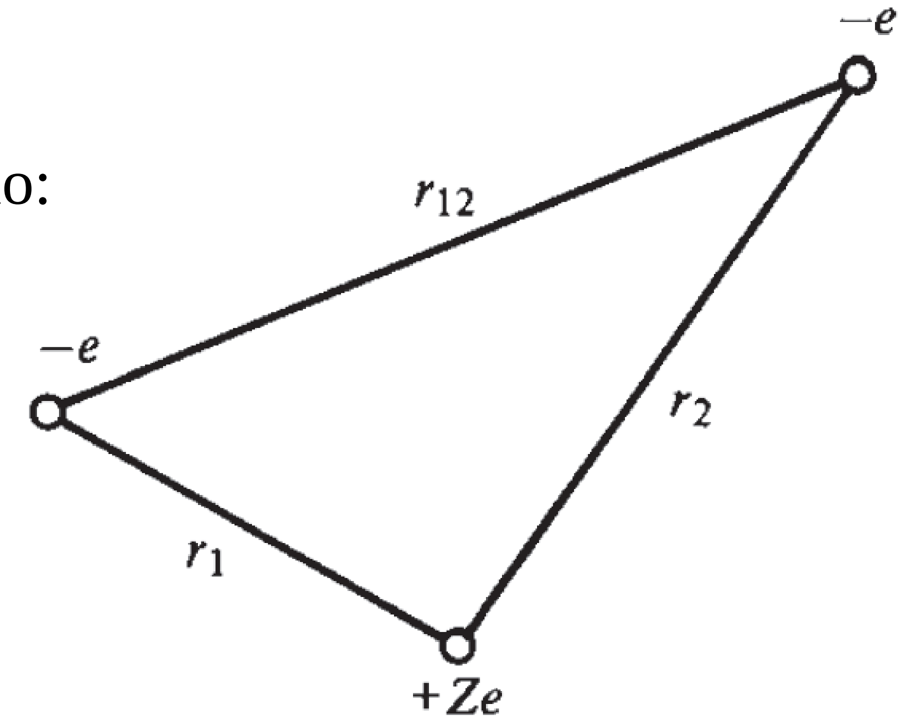
Átomos Polieletrônicos

Por exemplo, átomo de hélio:



equação de Schrödinger:

$$\hat{H}\psi = E\psi$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\left\{\hat{H}_{\mathrm{H}}(1) + \hat{H}_{\mathrm{H}}(2) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right\}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

$$-\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_1^2)\psi(\mathbf{r}_1, \mathbf{r}_2) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi(\mathbf{r}_1, \mathbf{r}_2)$$

$$+ \frac{e^2}{4\pi\varepsilon|\mathbf{r}_1 - \mathbf{r}_2|}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

Unidades Atômicas

Property	Atomic unit	SI Equivalent
mass	mass of an electron, m_e	9.1094×10^{-31} kg
charge	charge on a proton, e	1.6022×10^{-19} C
angular momentum	Planck constant divided by 2π, $\hbar$	1.0546×10^{-34} J·s
distance	Bohr radius, $a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$	5.2918×10^{-11} m
energy	$\dfrac{m_e e^4}{16\pi^2\varepsilon_0^2\hbar^2} = \dfrac{e^2}{4\pi\varepsilon_0 a_0} = E_h$	4.3597×10^{-18} J
permittivity	$4\pi\varepsilon_0$	1.1127×10^{-10} $C^2 \cdot J^{-1} \cdot m^{-1}$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

Aproximação Orbital

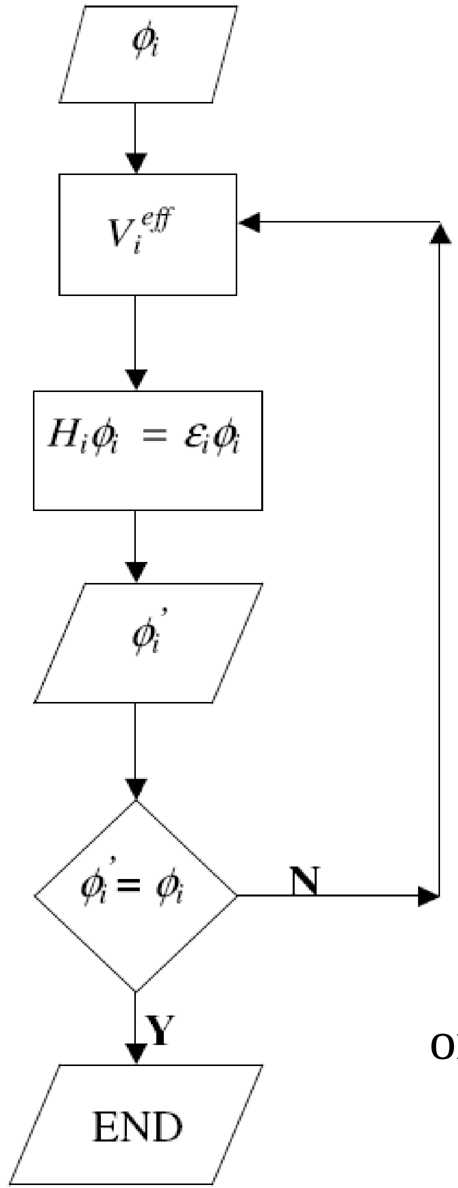
$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$$

$$\hat{H}_1^{\text{eff}}(\mathbf{r}_1)\phi(\mathbf{r}_1) = \epsilon_1\phi(\mathbf{r}_1)$$

$$\hat{H}_1^{\text{eff}}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{\text{eff}}(r_1)$$

$$V_1^{\text{eff}}(r_1) = \int \phi^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi(\mathbf{r}_2)d\mathbf{r}_2$$

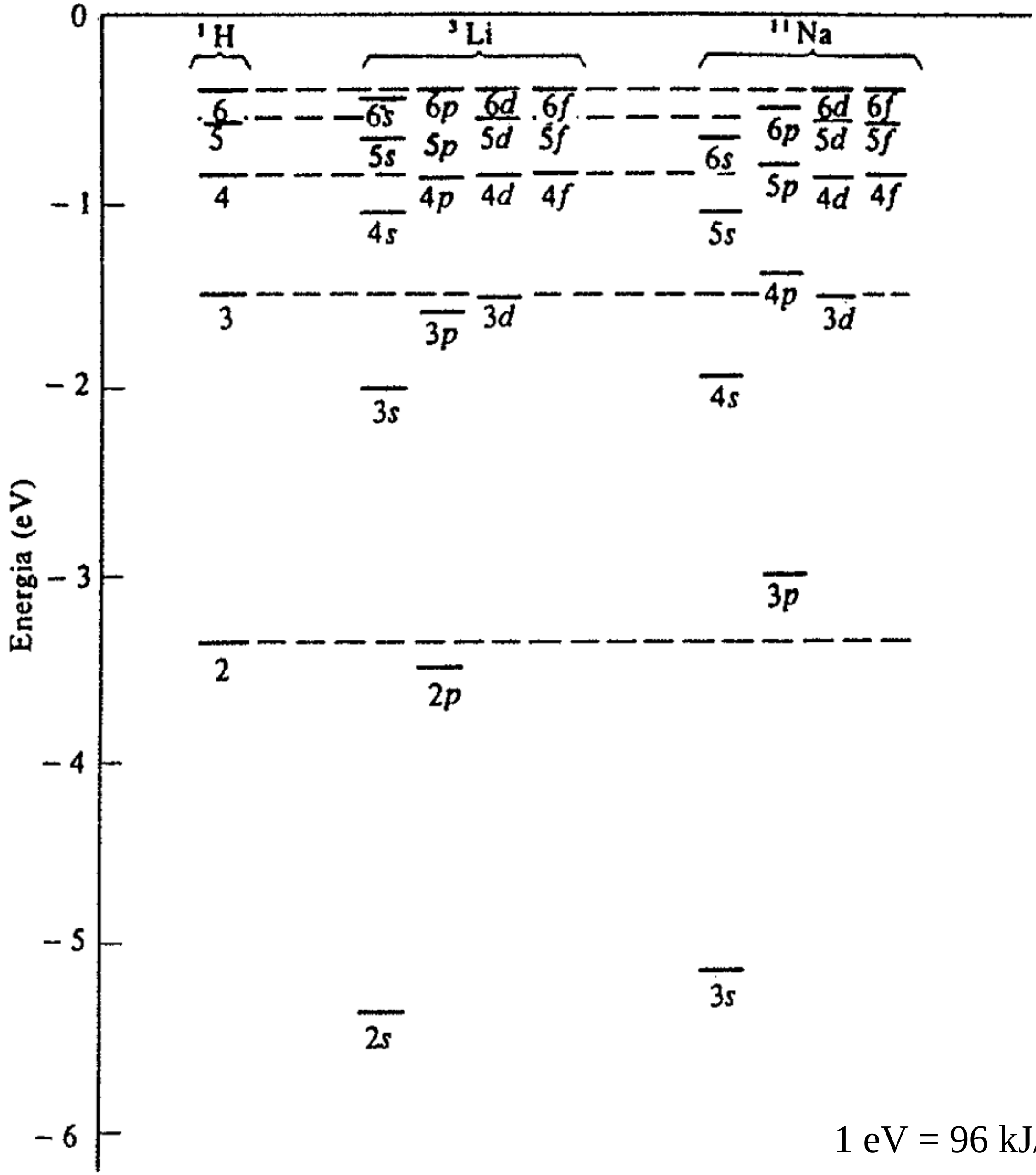
Self-Consistent Field (SCF) Method



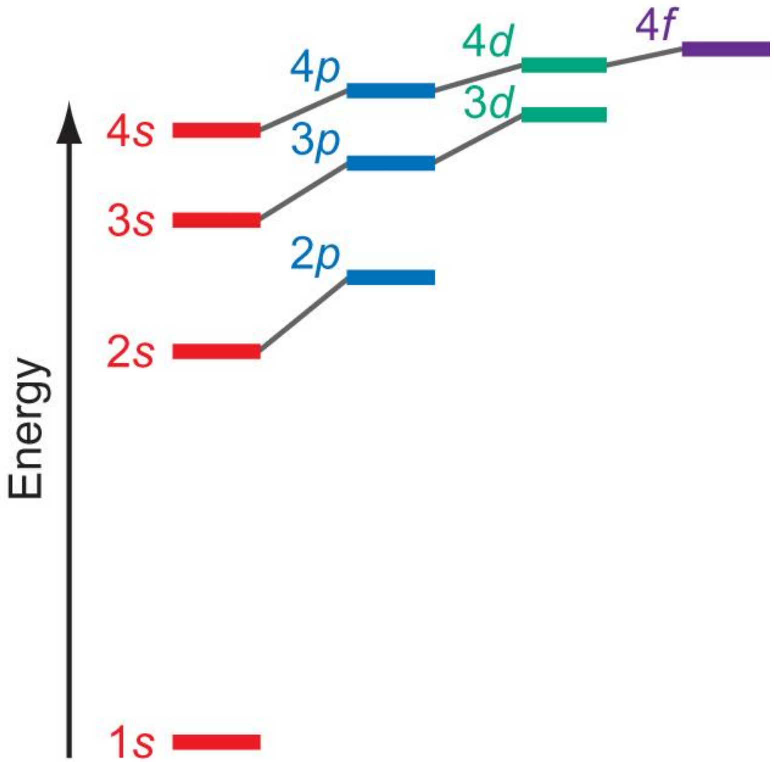
$$V_1^{eff}(r_1) = \int \phi^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi(\mathbf{r}_2)d\mathbf{r}_2$$

orbitais e energias Hartree-Fock

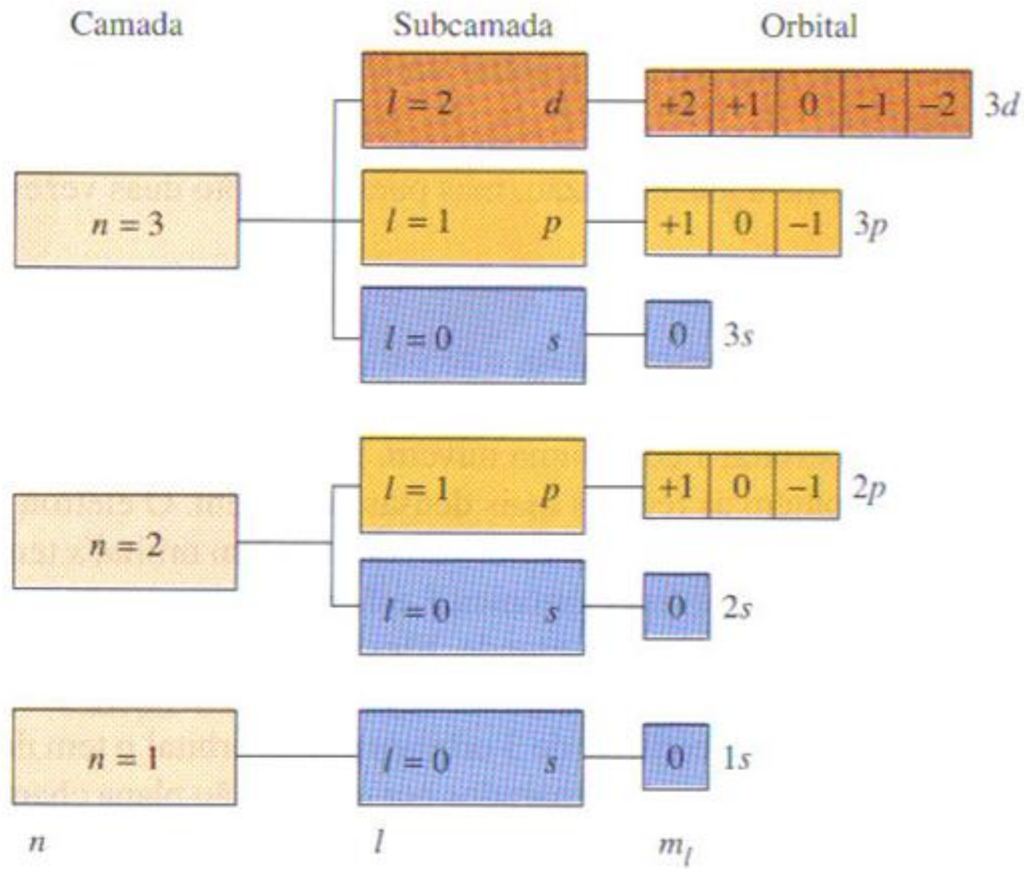
(ϕ_i, ε_i)



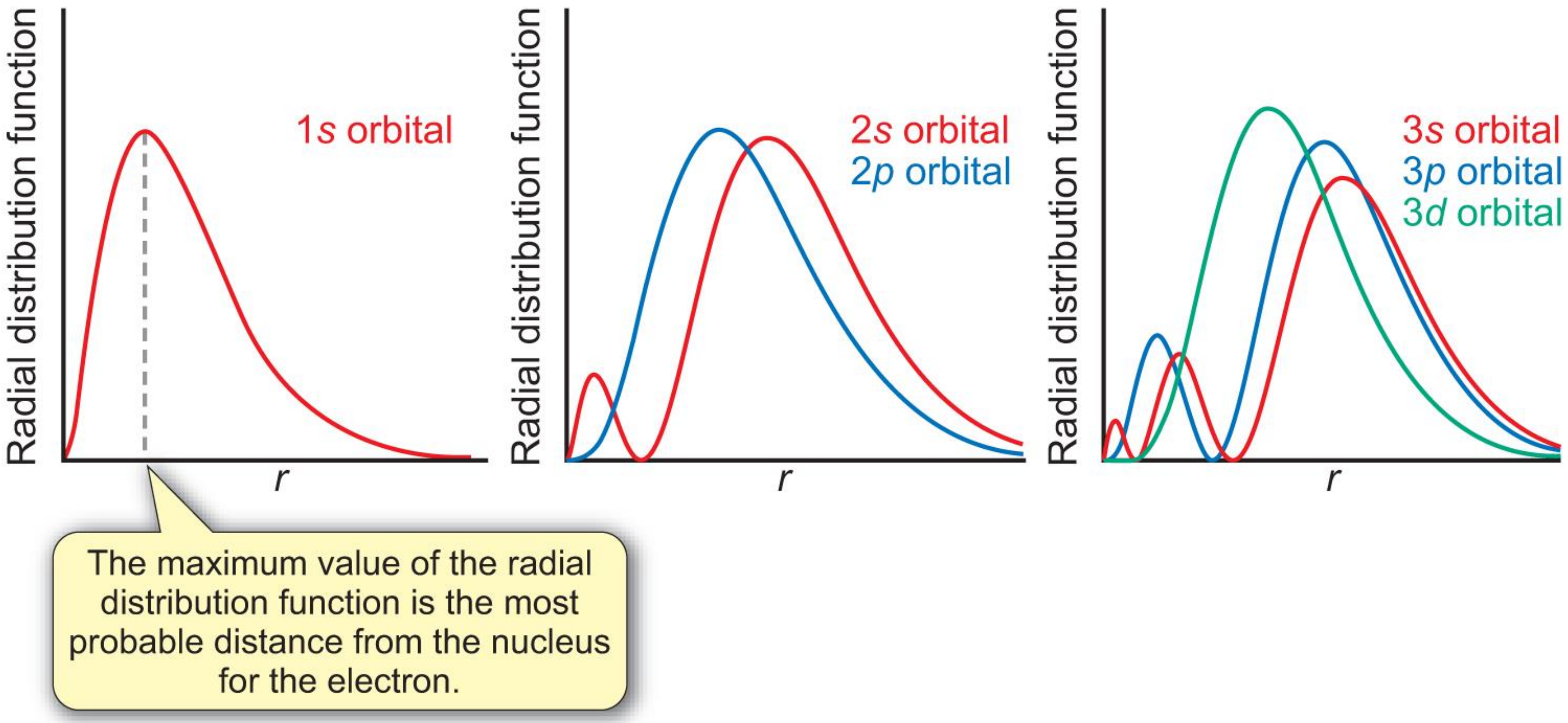
1 eV = 96 kJ/mol = 8100 cm^{-1}



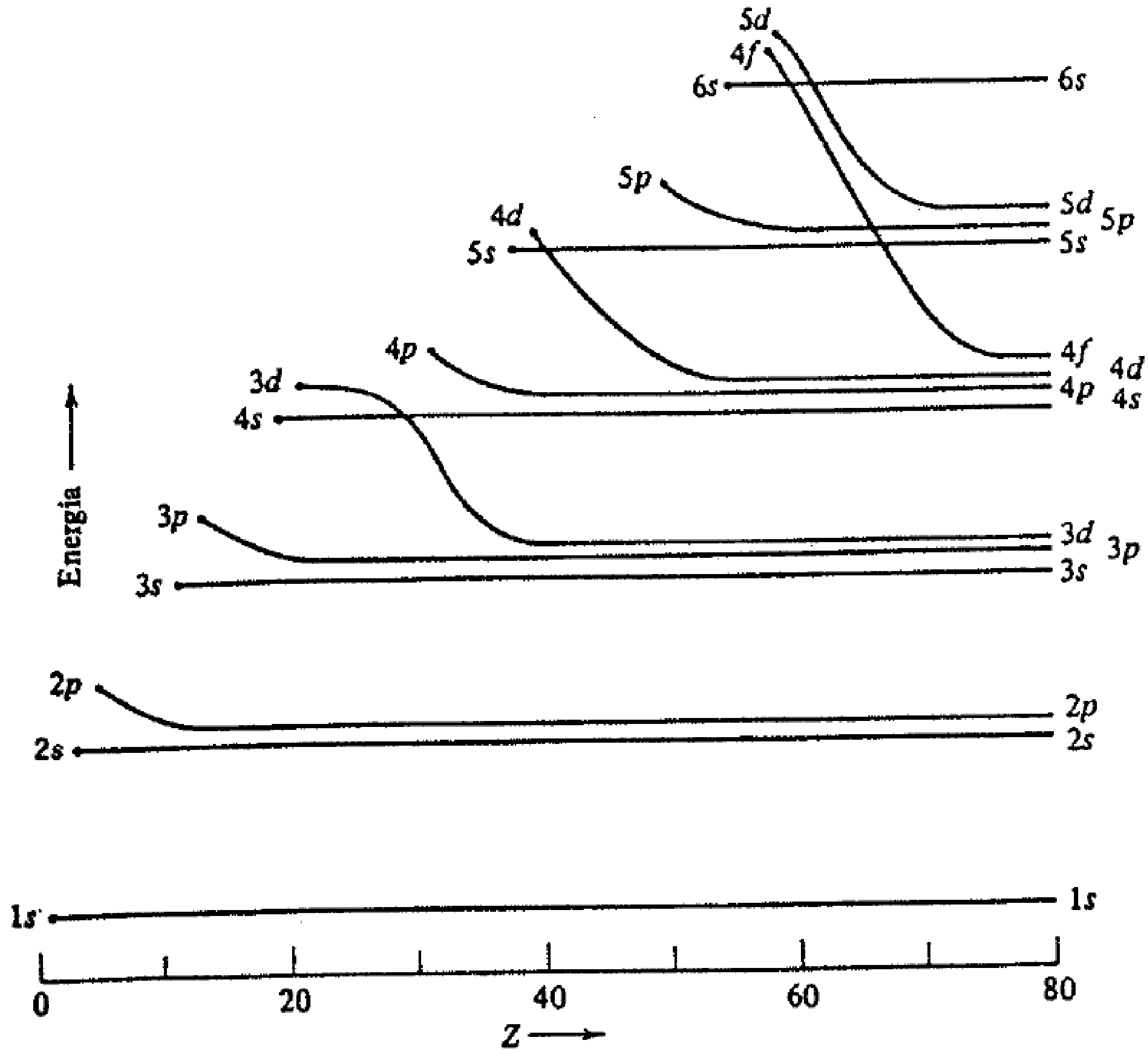
Energy
1s
2s
2p
3s
3p
3d
4s
4p
4d
4f



Camada
Subcamada
Orbital
n = 3
l = 2 d
+2 +1 0 −1 −2 3d
l = 1 p
+1 0 −1 3p
l = 0 s
0 3s
n = 2
l = 1 p
+1 0 −1 2p
l = 0 s
0 2s
n = 1
l = 0 s
0 1s
n
l
m_l



Radial distribution function
1s orbital
r
The maximum value of the radial distribution function is the most probable distance from the nucleus for the electron.
Radial distribution function
2s orbital
2p orbital
r
Radial distribution function
3s orbital
3p orbital
3d orbital
r



5d
4f
6s
6s
5p
5d
5p
4d
5s
5s
4p
4f
4d
3d
4p
4s
4s
3p
3d
3p
3s
3s
Energia
2p
2p
2s
2s
1s
1s
0
20
40
60
80
Z

Aproximação Orbital

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$$

Por exemplo, átomo de hélio, 1s^2: $\psi \approx 1s(1)1s(2)$

Orbital hidrogenóide: função de onda espacial de um elétron.

1s $\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$ $\sigma = Zr/a_0$

$$\psi \approx e^{-\zeta r_1/a_0} e^{-\zeta r_2/a_0}$$

expoente orbital

Por exemplo, orbitais de Slater:

$$S_{nlm}(r, \theta, \phi) = N_{nl} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi)$$

constante de normalização

harmônicos esféricos

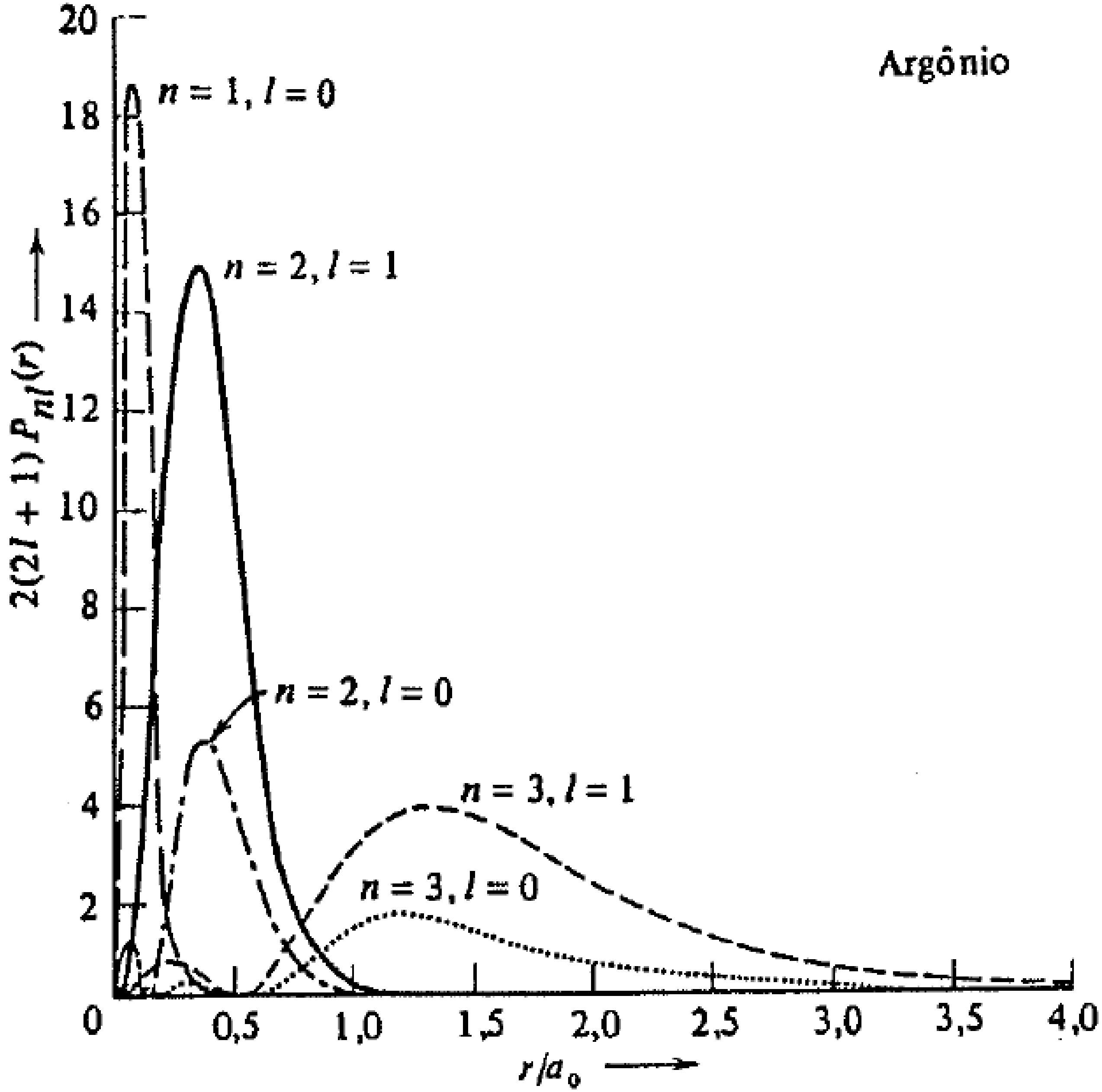
ζ parâmetro ajustável

Estado fundamental do He, $1s^2$:

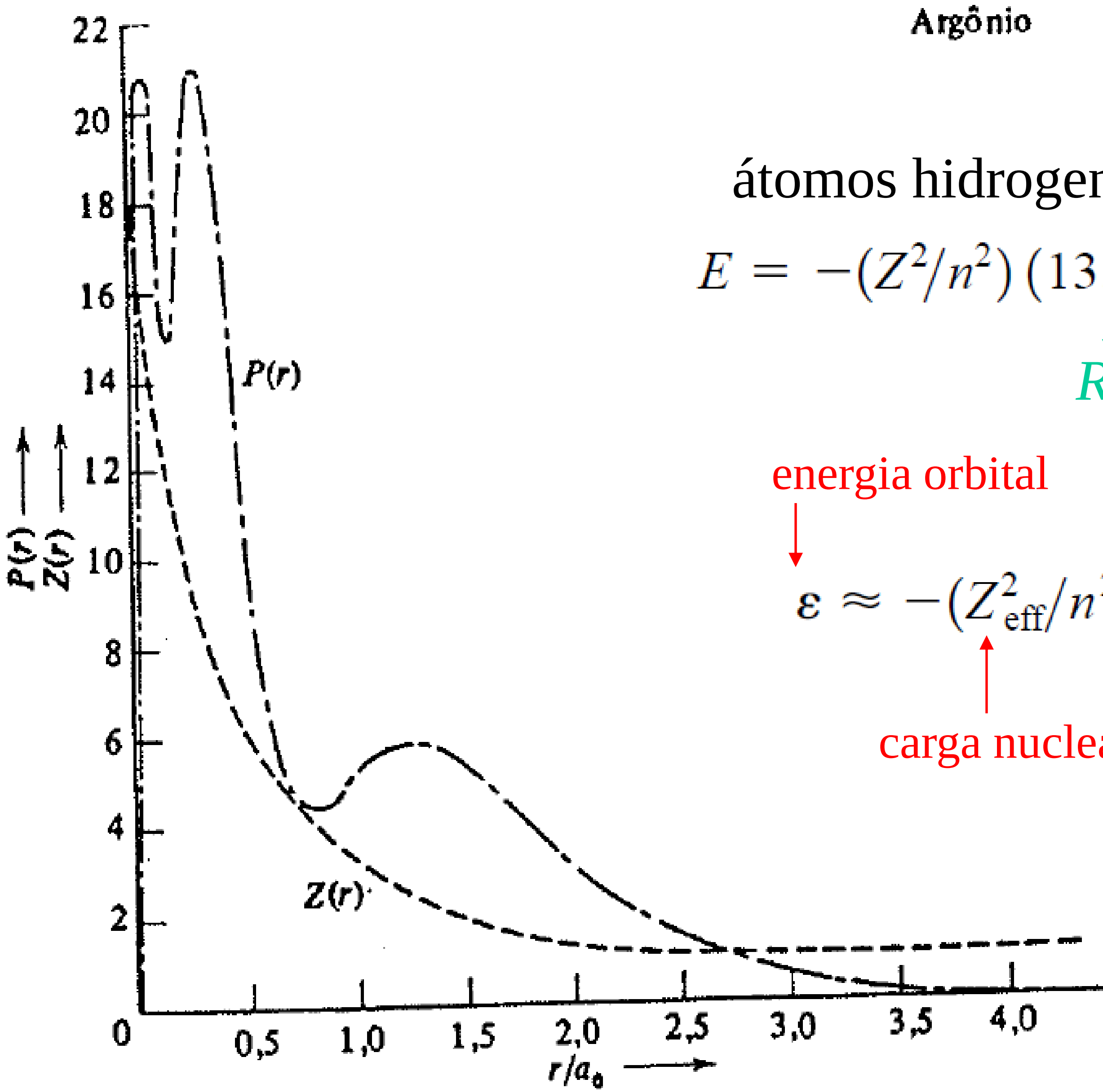
$$\psi = S_{100}(r_1, \theta_1, \phi_1) S_{100}(r_2, \theta_2, \phi_2)$$
$$= \frac{\zeta^3}{\pi} e^{-2\zeta(r_1 + r_2)}$$

$\zeta = 1.6875$ → energia de ionização = 2226 kJ/mol

(experimental, 2376 kJ/mol)



Argônio
$n = 1, l = 0$
$n = 2, l = 1$
$n = 2, l = 0$
$n = 3, l = 1$
$n = 3, l = 0$
$2(2l + 1)\,P_{nl}(r)$
r/a_0
0
2
4
6
8
10
12
14
16
18
20
0,5
1,0
1,5
2,0
2,5
3,0
3,5
4,0



átomos hidrogenóides

$$E = -(Z^2/n^2)(13.60\ \text{eV})$$

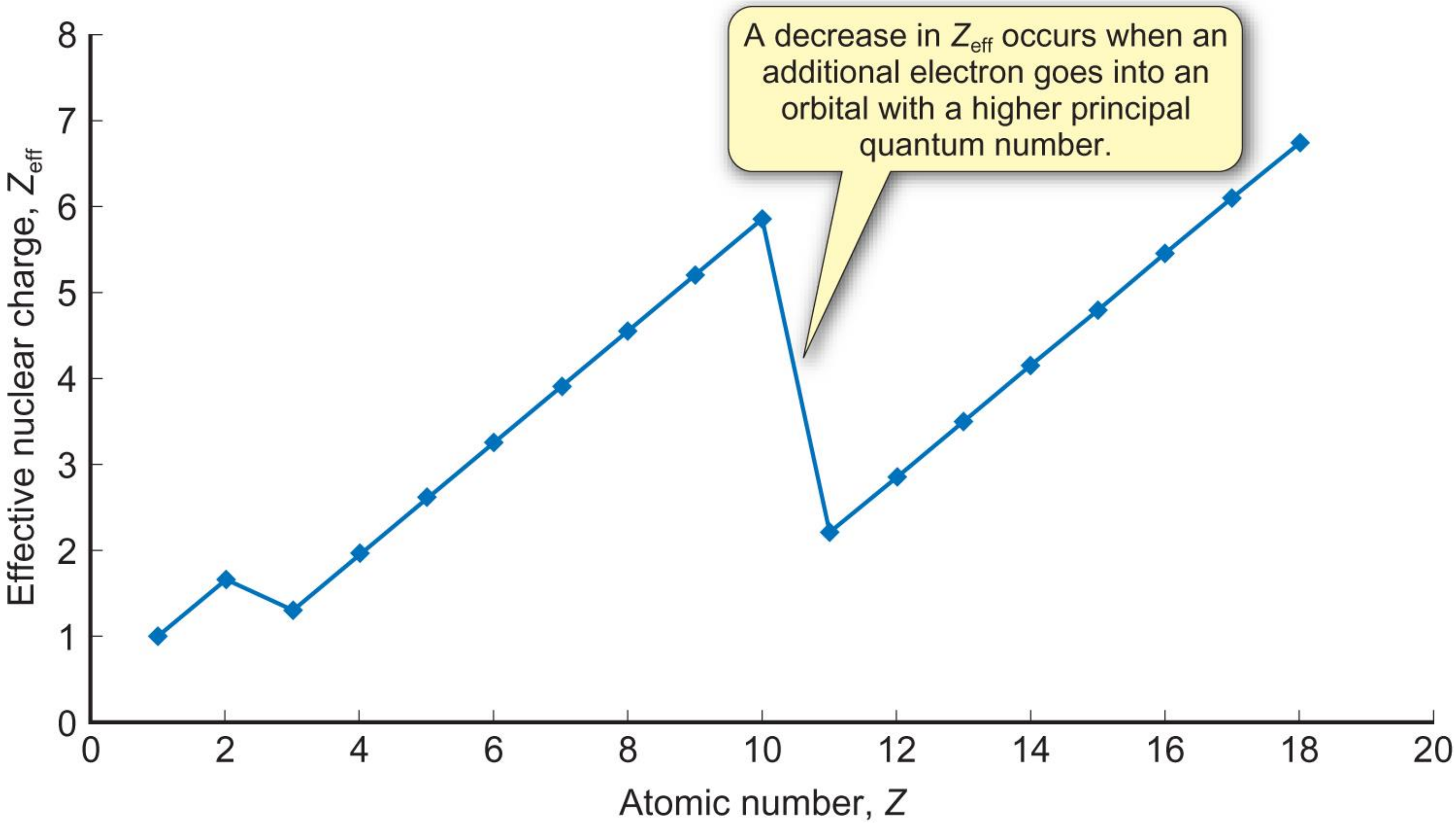
$$\downarrow$$

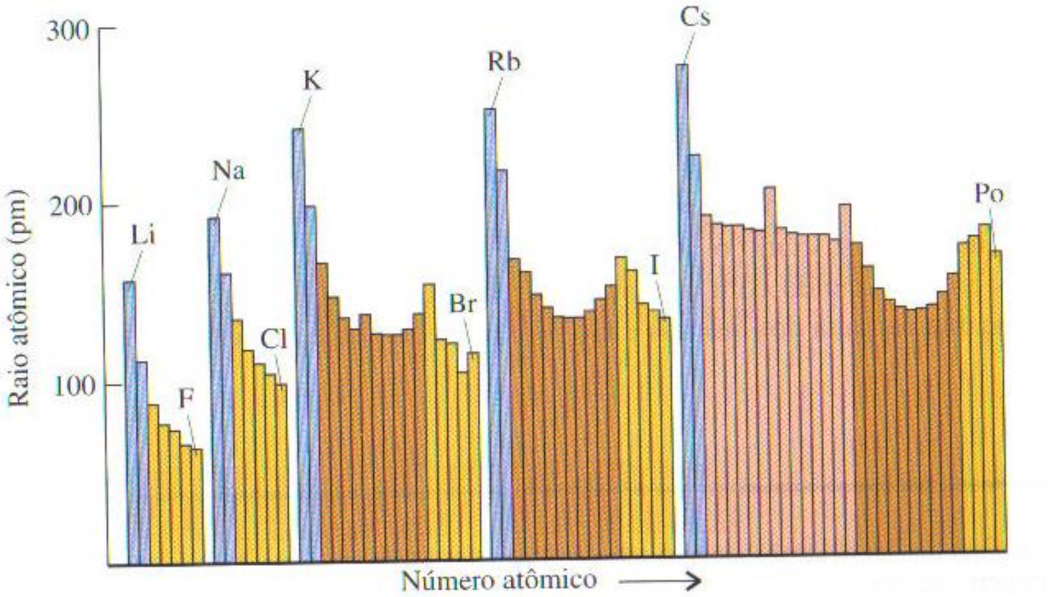
$$R_H$$

energia orbital

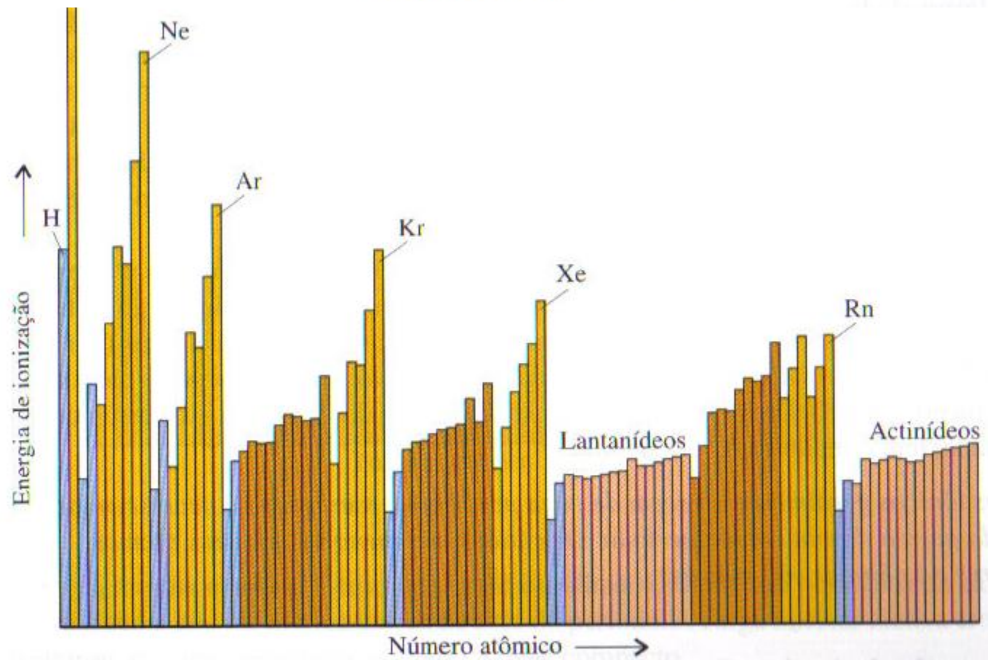
$$\varepsilon \approx -(Z_{\text{eff}}^2/n^2)(13.6\ \text{eV})$$

carga nuclear efetiva

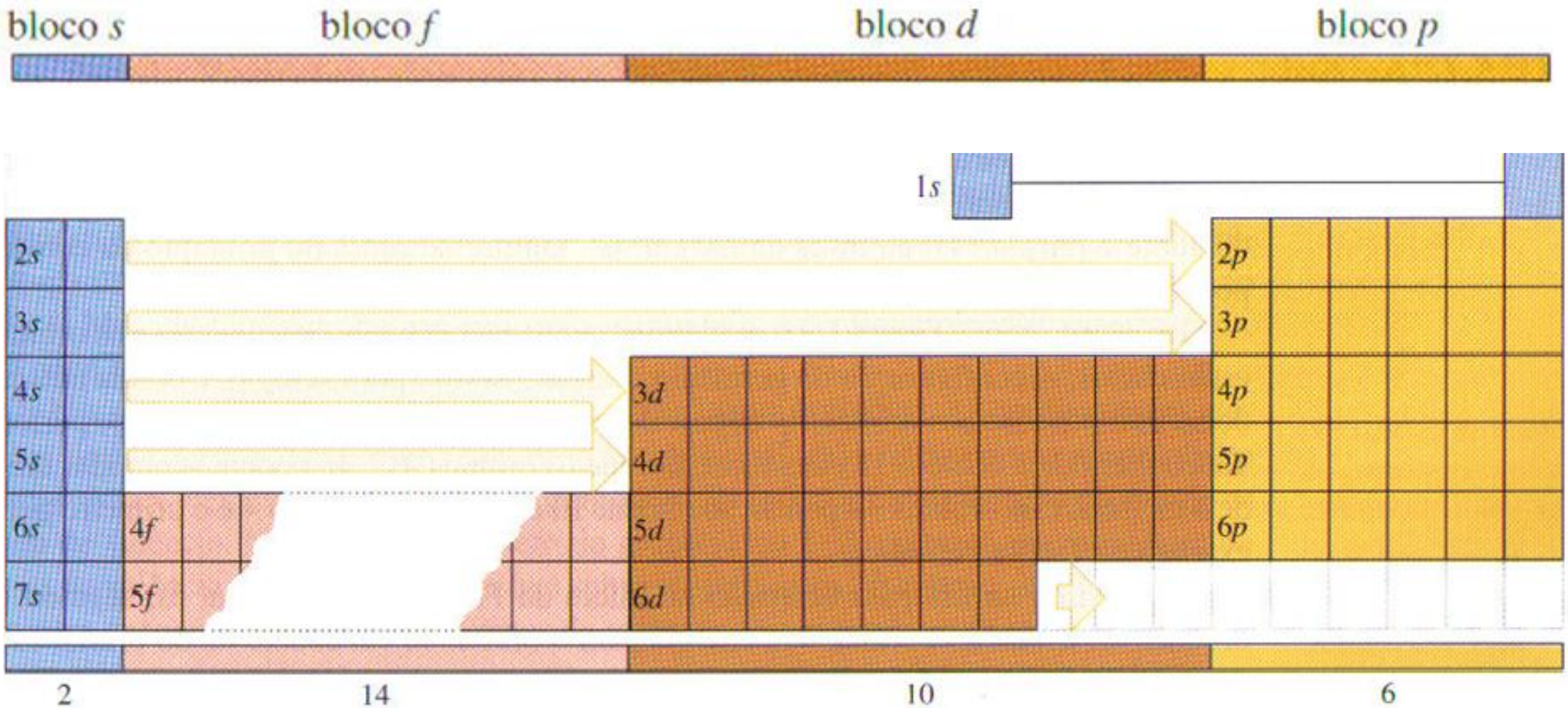

A decrease in Z_{eff} occurs when an additional electron goes into an orbital with a higher principal quantum number.
Effective nuclear charge, Z_{eff}
0
1
2
3
4
5
6
7
8
0
2
4
6
8
10
12
14
16
18
20
Atomic number, Z

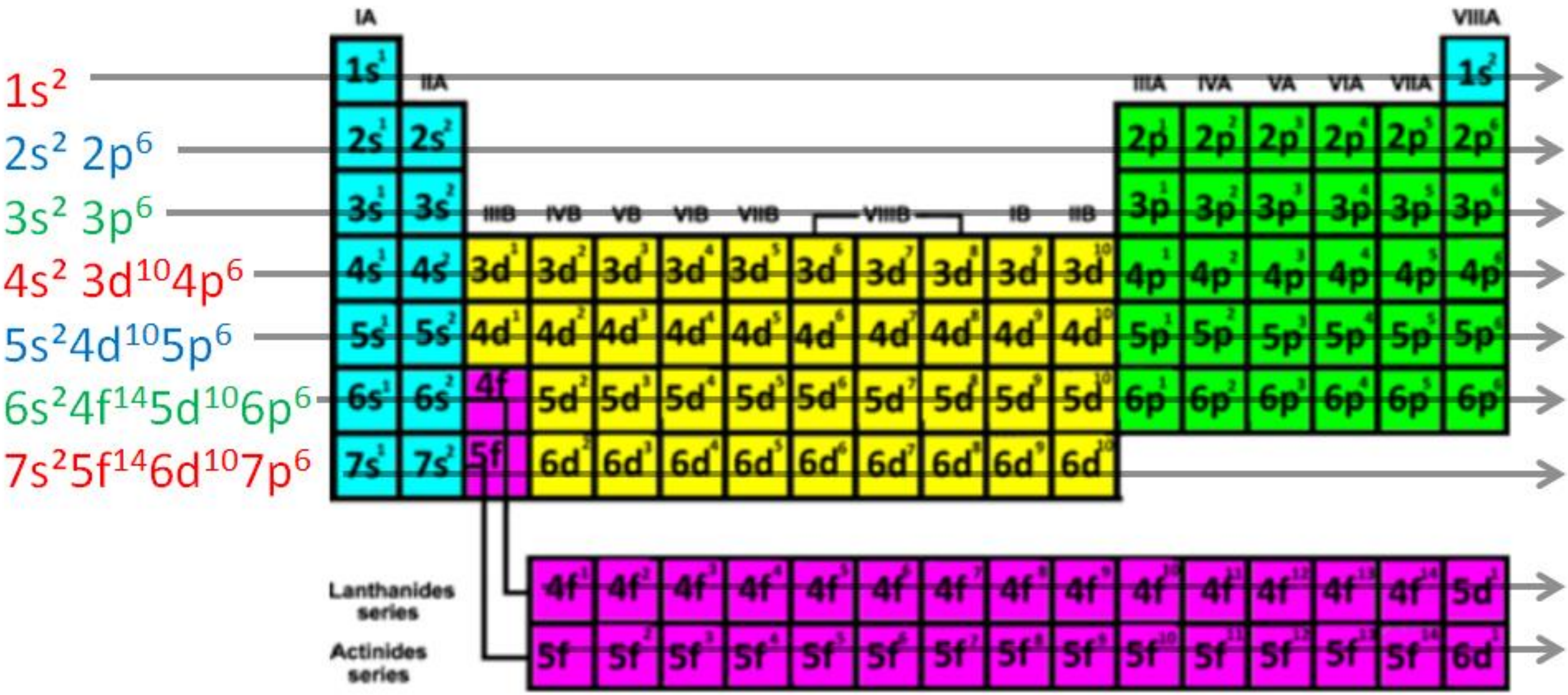


Raio atômico (pm)
300
200
100
Li
F
Na
Cl
K
Br
Rb
I
Cs
Po
Número atômico



Energia de ionização
H
Ne
Ar
Kr
Xe
Rn
Lantanídeos
Actinídeos
Número atômico


bloco s
bloco f
bloco d
bloco p
1s
2s
3s
4s
5s
6s
7s
4f
5f
3d
4d
5d
6d
2p
3p
4p
5p
6p
2
14
10
6


$1s^2$
$2s^2\ 2p^6$
$3s^2\ 3p^6$
$4s^2\ 3d^{10}4p^6$
$5s^24d^{10}5p^6$
$6s^24f^{14}5d^{10}6p^6$
$7s^25f^{14}6d^{10}7p^6$
IA
IIA
IIIB IVB VB VIB VIIB VIIIB IB IIB
IIIA IVA VA VIA VIIA
VIIIA
Lanthanides series
Actinides series

Átomo de Lítio:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\phi_{\cancel{1s}}(\mathbf{r}_3)$$