Numeri Quantici degli Elettroni

n = **numero quantico principale** ($n \geq 1$): energia, grandezza

l = **numero quantico (del momento angolare) orbitale**: forma
l = 0, 1, 2, 3, 4….n-1 (in totale n valori interi)
La grandezza del momento angolare orbitale è data da $h/2\pi \times \sqrt{\{l(l+1)\}}$

m_l = **numero quantico magnetico**: orientazione
m_l = -l, -l+1, ….0,…l-1, l (in totale 2l+1 valori interi)

s = **numero quantico di spin**: definisce il momento angolare di spin
s = ½
La grandezza del momento angolare di spin è data da $h/2\pi \times \sqrt{\{s(s+1)\}}$

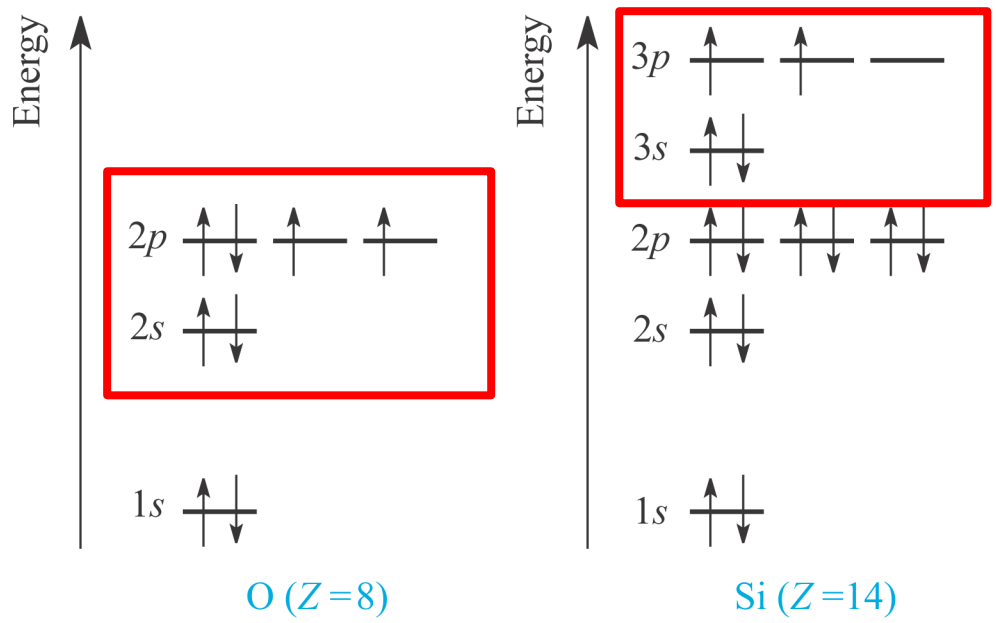
m_s = **numero quantico magnetico di spin**: orientazione
m_s = -1/2, +1/2,

Un orbitale atomico è definito in maniera univoca da 3 numeri quantici n, l, e m_l.
Un elettrone in un orbitale atomico è definito in maniera univoca da 4 numeri quantici: n, l, m_l, m_s.

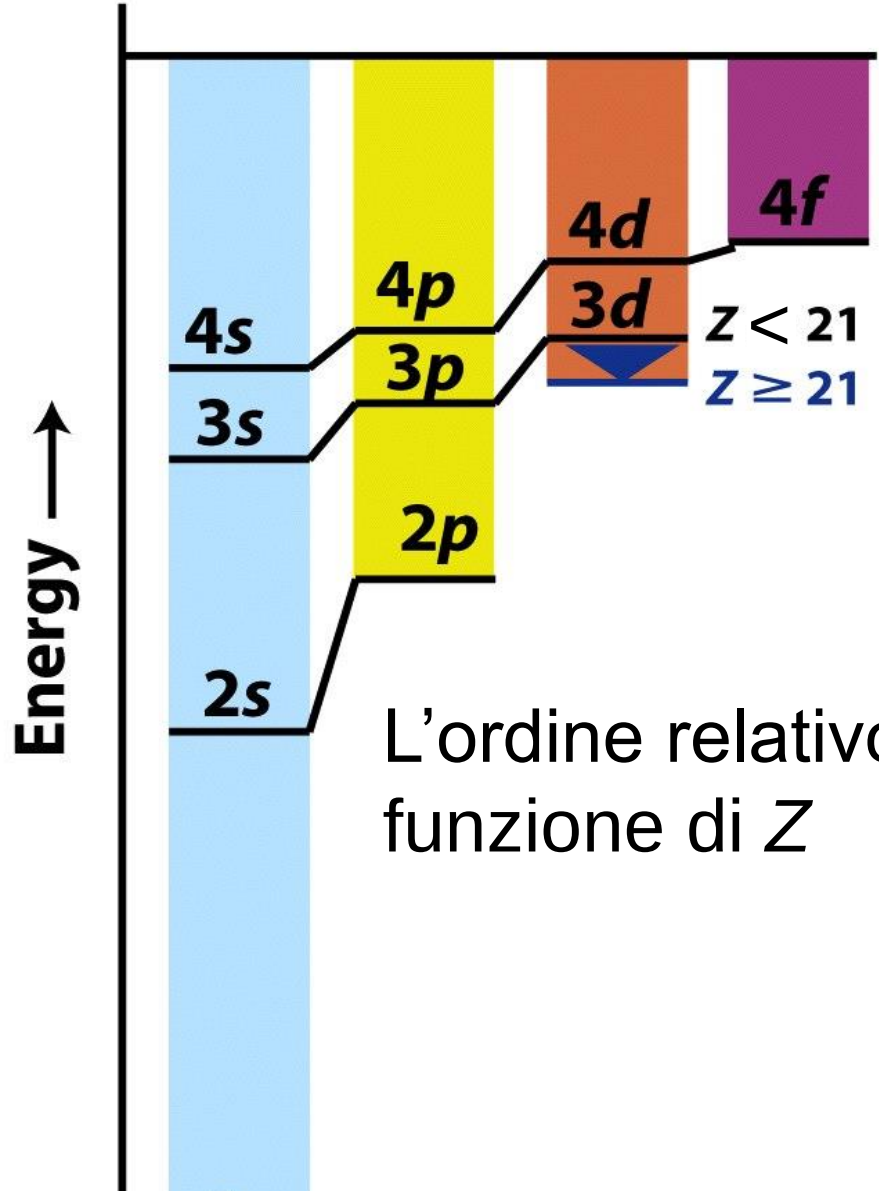
Atomi Polielettronici

Principio di esclusione di Pauli
in un dato atomo non vi possono essere 2 elettroni con la stessa quaterna di numeri quantici

Regola di Hund o della massima molteplicità
in un set di orbitali degeneri gli elettroni non possono avere spin accoppiati in un orbitale finché ogni orbitale nel set non contenga un elettrone, tutti con spin parallelo
(*correlazione di spin*)

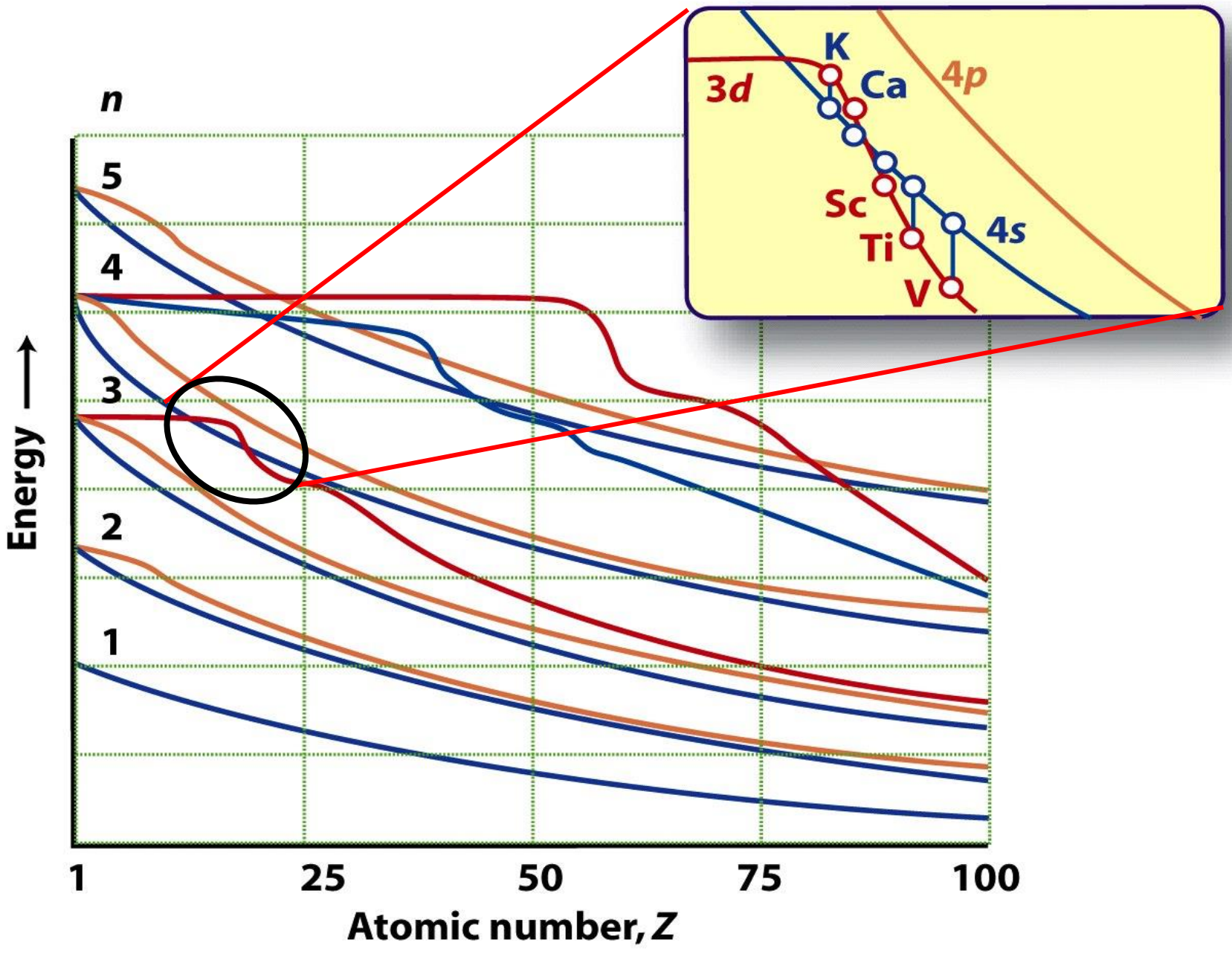

Energy
2p
2s
1s
O (Z = 8)
Energy
3p
3s
2p
2s
1s
Si (Z = 14)

Principio del riempimento progressivo (*Aufbau*)

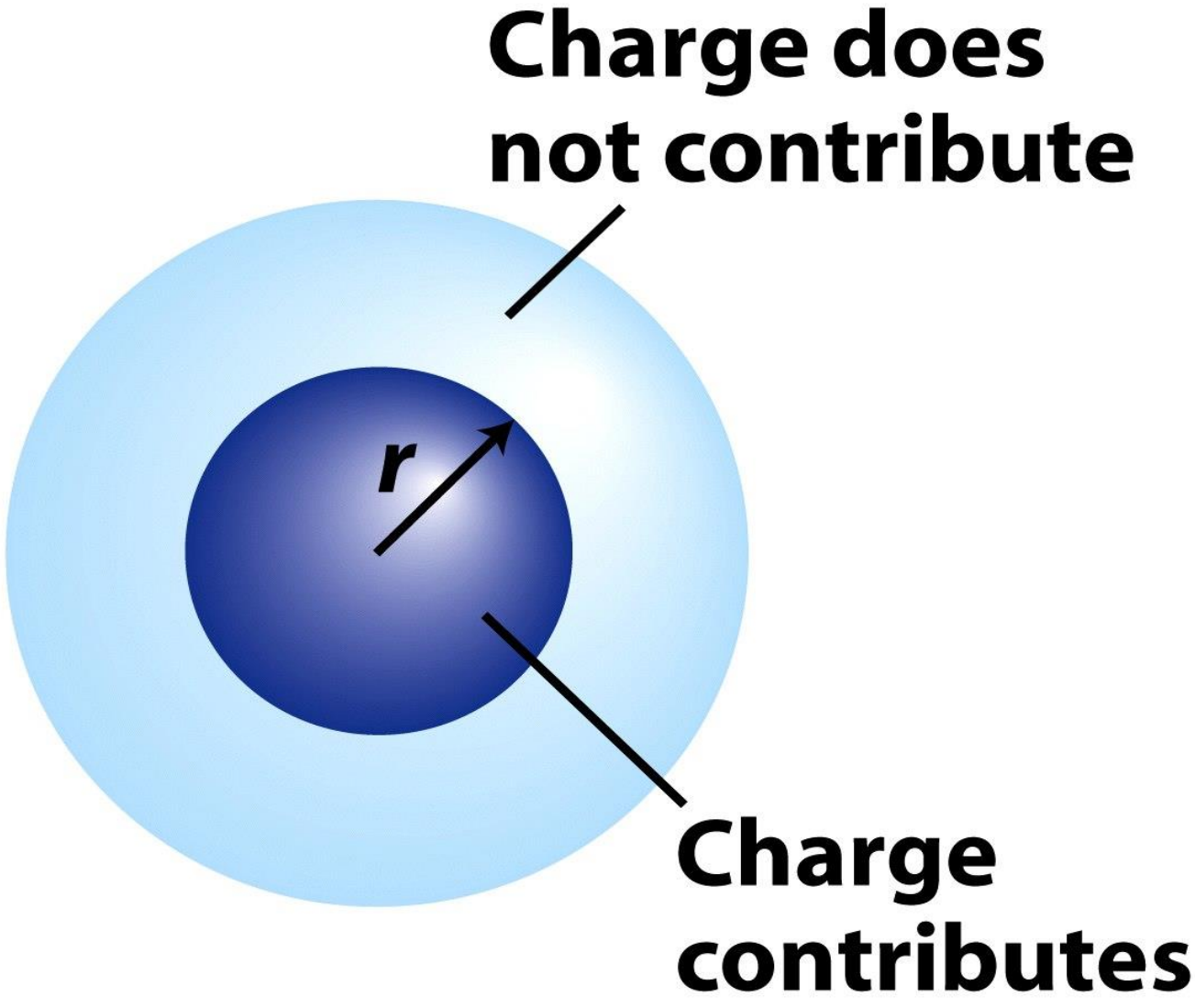


L'ordine relativo può cambiare in funzione di *Z*

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 5d ≈ 4f < 6p < 7s < 6d ≈ 5f


n
5
4
3
2
1
Energy
1
25
50
75
100
Atomic number, Z
3d
4p
4s
K
Ca
Sc
Ti
V

Penetrazione e schermatura



Regole di Slater (ca. 1930)

(empiriche) per il calcolo della **costante di schermo *S***

$$Z_{\text{eff}} = Z - S$$

1. si scrive la configurazione elettronica dell'elemento nel seguente ordine e con questi raggruppamenti: (1*s*) (2*s*, 2*p*) (3*s*, 3*p*) (3*d*) (4*s*, 4*p*) (4*d*) (4*f*) (5*s*, 5*p*)…
2. gli elettroni in ogni gruppo a destra dell'elettrone considerato non contribuiscono a *S*
3. per un elettrone in un orbitale ns o np:

- ogni altro elettrone nello stesso gruppo contribuisce *S* = 0.35;
- ogni elettrone nel livello n-1 contribuisce *S* = 0.85;
- ogni elettrone nei livelli n-2 o inferiori contribuisce *S* = 1

4. per un elettrone in un orbitale nd o nf:

- ogni altro elettrone nello stesso gruppo (nd, nf) contribuisce *S* = 0.35
- ogni elettrone in un gruppo a sinistra di quello considerato contribuisce *S* = 1.

Valori sperimentali di Z_{eff}

Table 1.3 Effective nuclear charges, Z_{eff}

	H							**He**
Z	1							2
1*s*	1.00							1.69
	Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Z	3	4	5	6	7	8	9	10
1*s*	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2*s*	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2*p*			2.42	3.14	3.83	4.45	5.10	5.76
	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
Z	11	12	13	14	15	16	17	18
1*s*	10.63	11.61	12.59	13.57	14.56	15.54	16.52	17.51
2*s*	6.57	7.39	8.21	9.02	9.82	10.63	11.43	12.23
2*p*	6.80	7.83	8.96	9.94	10.96	11.98	12.99	14.01
3*s*	2.51	3.31	4.12	4.90	5.64	6.37	7.07	7.76
3*p*			4.07	4.29	4.89	5.48	6.12	6.76

0.69

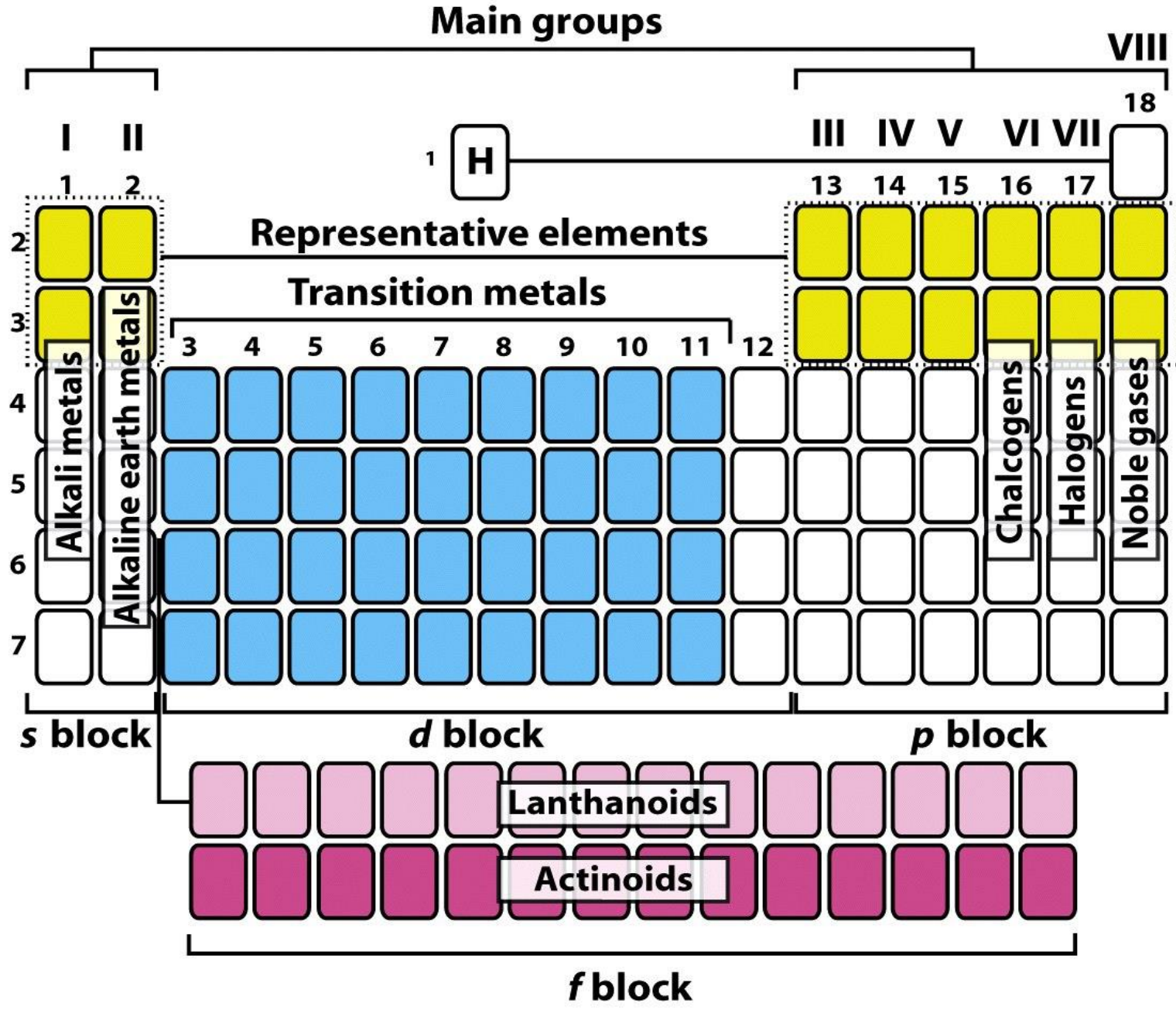
0.62

s-block elements | *d*-block elements | *p*-block elements

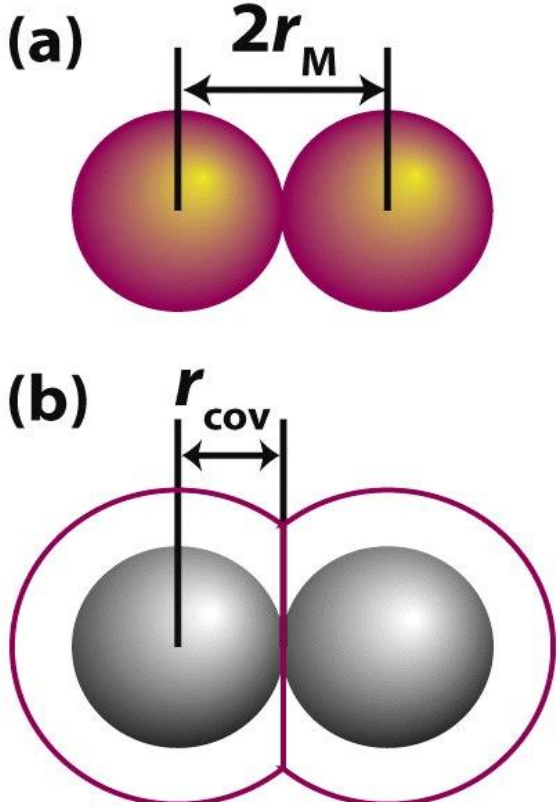
Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57–71 La–Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89–103 Ac–Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub						

f-block elements

Lanthanoids	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinoids	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

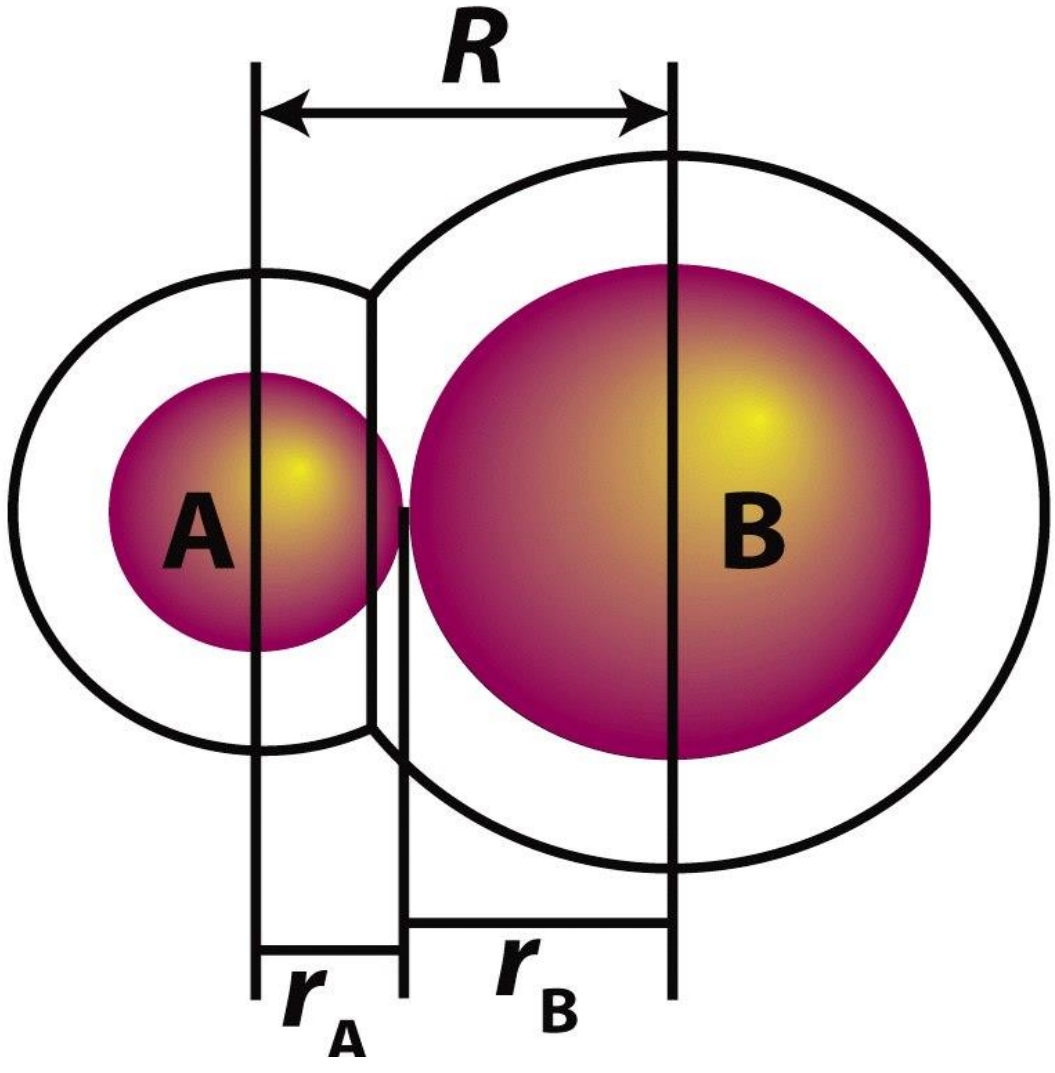

Main groups
VIII
I
II
III
IV
V
VI
VII
18
1
2
13
14
15
16
17
1
H
Representative elements
Transition metals
3
4
5
6
7
8
9
10
11
12
2
3
4
5
6
7
Alkali metals
Alkaline earth metals
Chalcogens
Halogens
Noble gases
s block
d block
p block
Lanthanoids
Actinoids
f block

Raggio Atomico

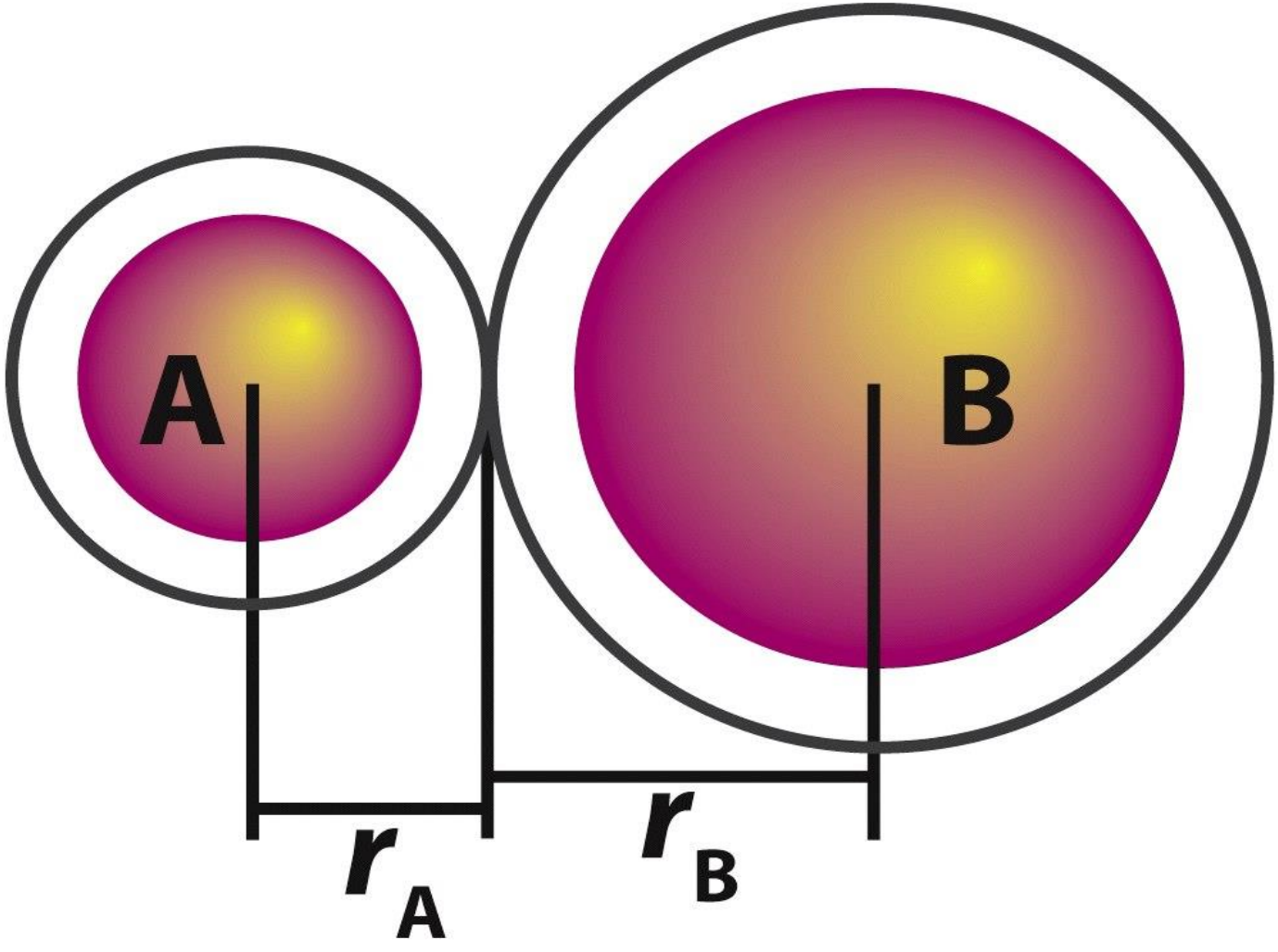


Raggio metallico

Raggio covalente

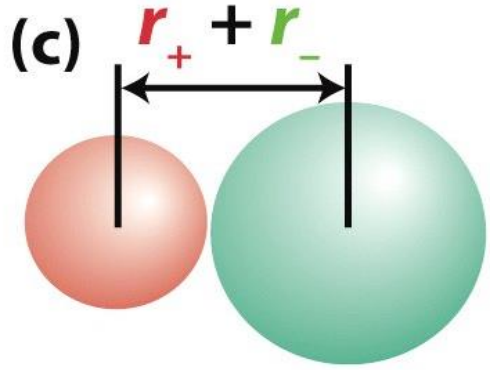


Raggio covalente

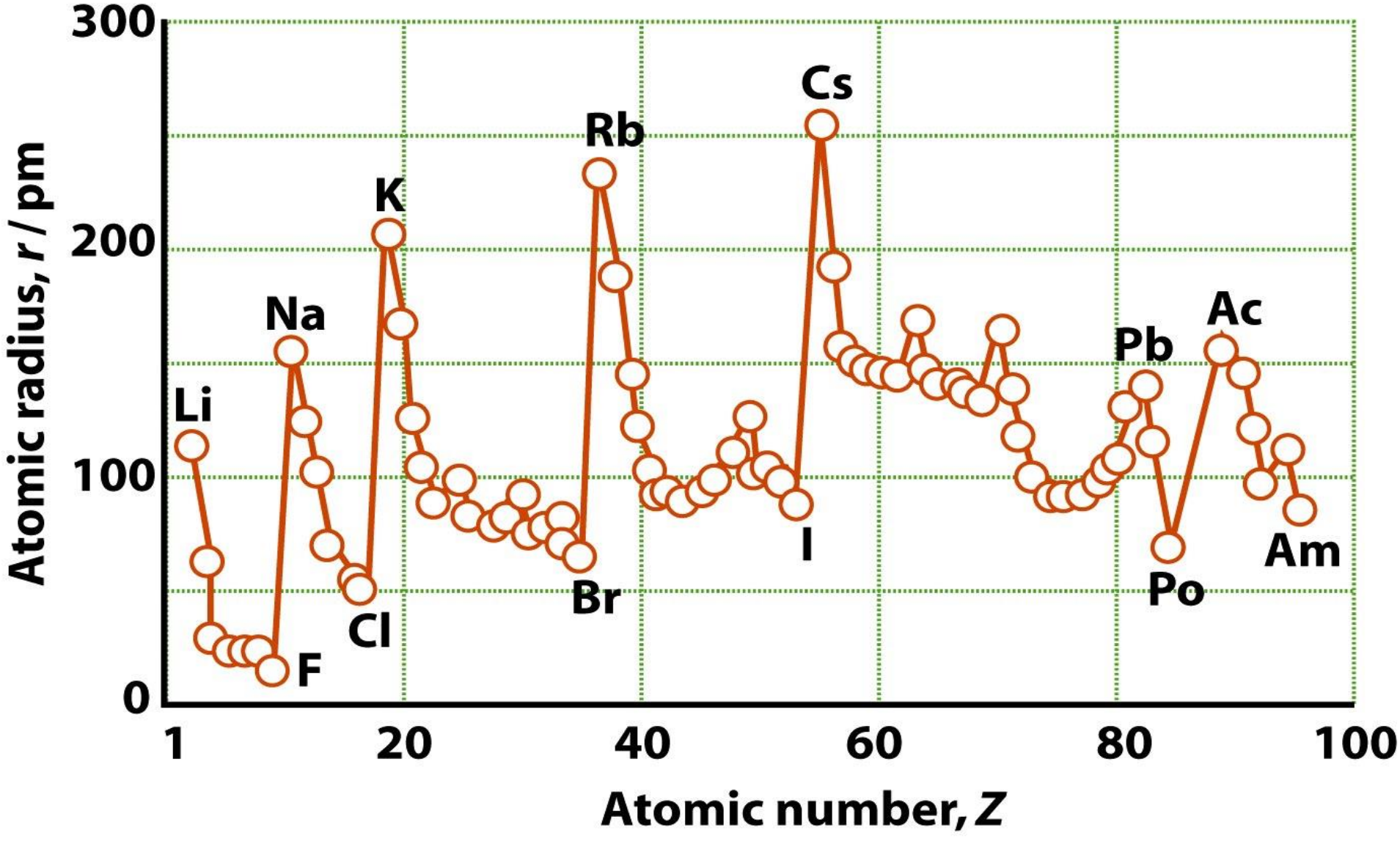


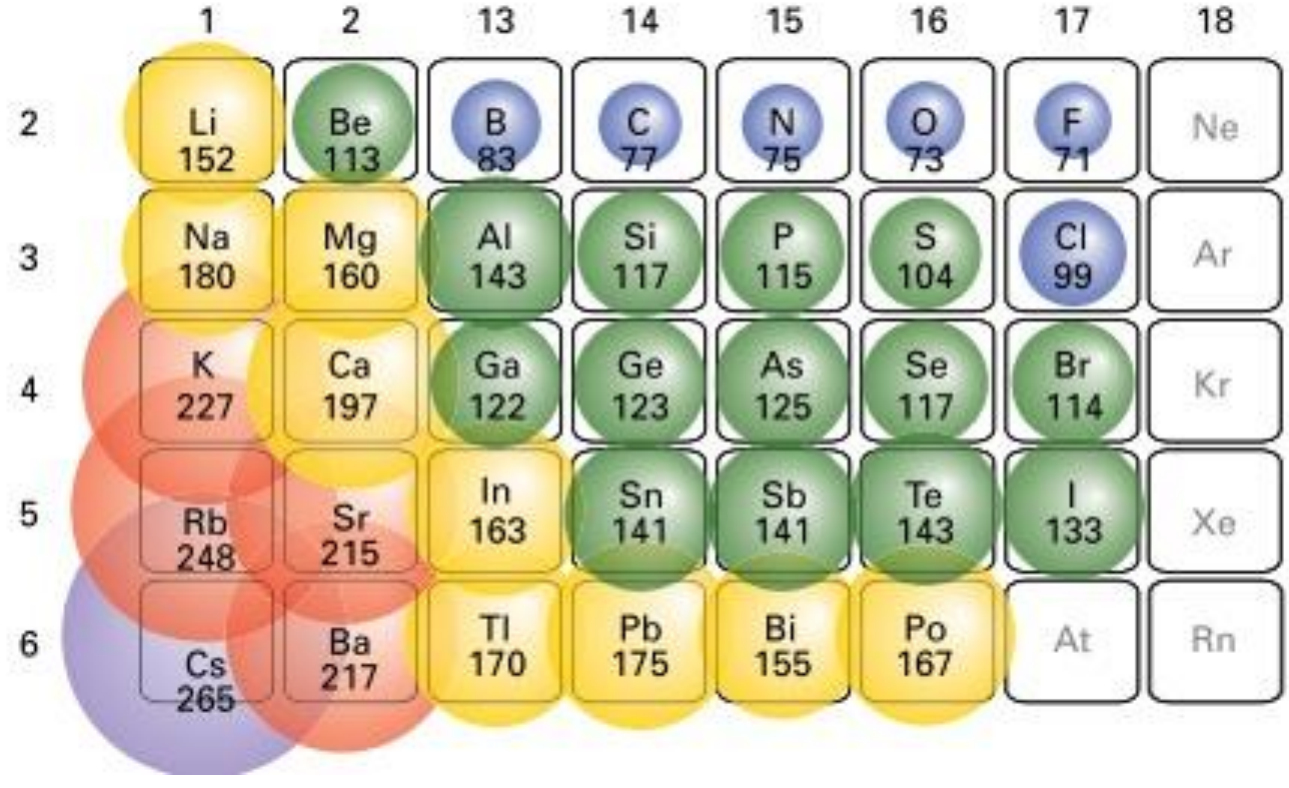
Raggio di van der Waals

Raggio Ionico

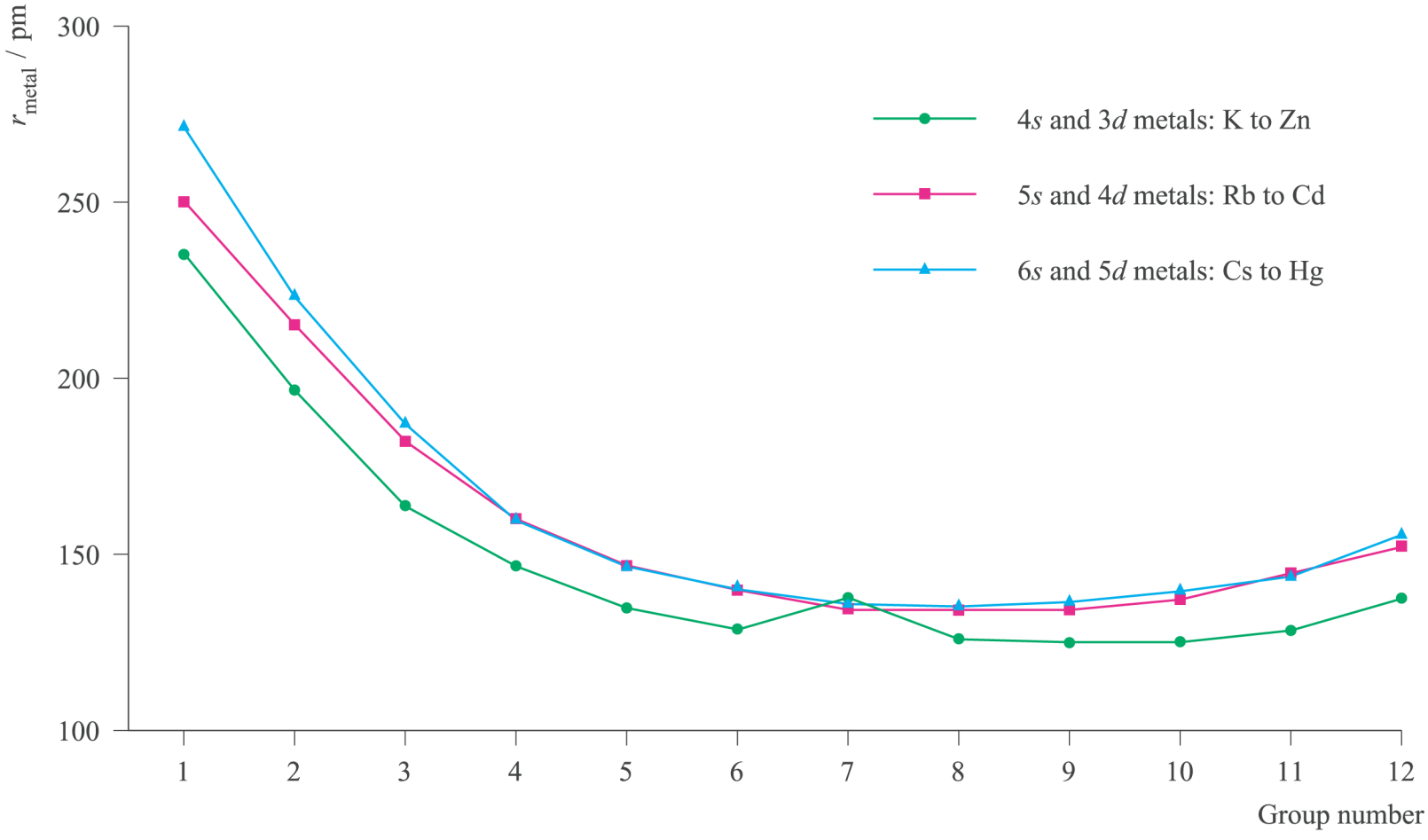


***r* O^{2-} =140 pm**


300
200
100
0
Atomic radius, r / pm
1
20
40
60
80
100
Atomic number, Z
Li
Na
K
Rb
Cs
F
Cl
Br
I
Pb
Po
Ac
Am


1
2
13
14
15
16
17
18
2
3
4
5
6
Li 152
Be 113
B 83
C 77
N 75
O 73
F 71
Ne
Na 180
Mg 160
Al 143
Si 117
P 115
S 104
Cl 99
Ar
K 227
Ca 197
Ga 122
Ge 123
As 125
Se 117
Br 114
Kr
Rb 248
Sr 215
In 163
Sn 141
Sb 141
Te 143
I 133
Xe
Cs 265
Ba 217
Tl 170
Pb 175
Bi 155
Po 167
At
Rn

Raggio atomico



Contrazione lantanidica

Table 1.4 Atomic radii, *r*/pm*

Li	**Be**											**B**	**C**	**N**	**O**	**F**
157	112											88	77	74	66	64
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**
191	160											143	118	110	104	99
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**
235	197	164	147	135	129	137	126	125	125	128	137	153	122	121	117	114
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**
250	215	182	160	147	140	135	134	134	137	144	152	167	158	141	137	133
Cs	**Ba**	**Lu**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**		
272	224	172	159	147	141	137	135	136	139	144	155	171	175	182		

*The values refer to coordination number 12 (see Section 3.2).

Effetti relativistici

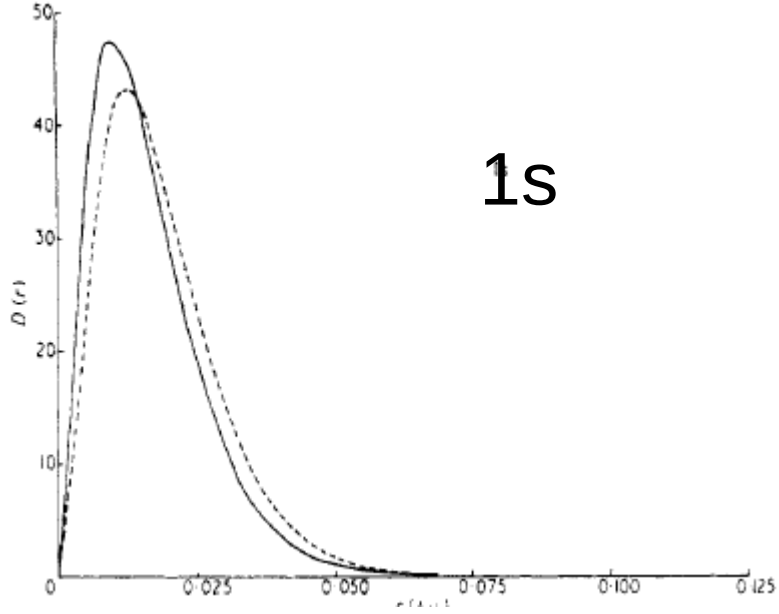
$$m_{\mathrm{rel}} = m_{\mathrm{rest}} / \sqrt{(1 - (v/c)^2)}$$

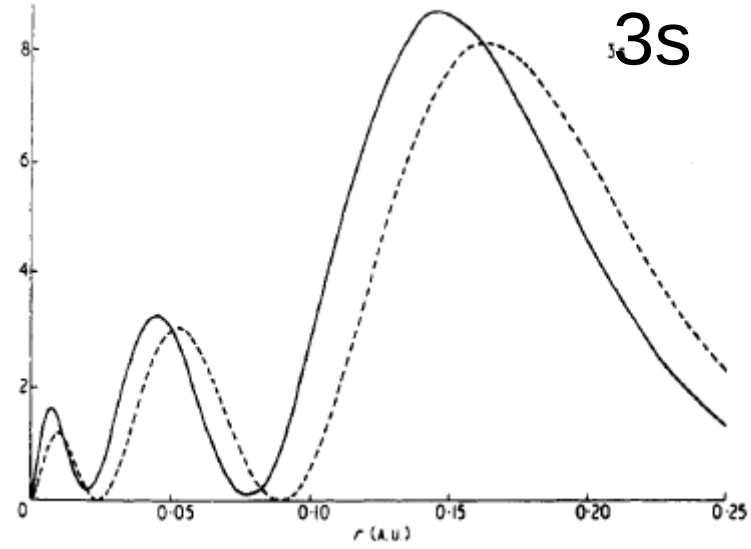
Al crescere della velocità degli elettroni, la massa relativistica aumenta rispetto a quella a riposo

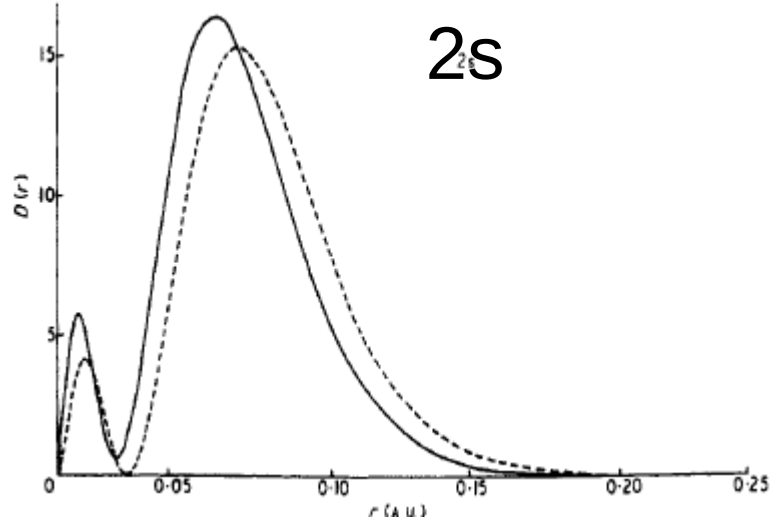
$$a_0 = (4\pi\epsilon_0)(\hbar^2 / me^2)$$

L'aumento di massa comporta una contrazione dell'orbitale, che per gli atomi pesanti come Au e Hg può arrivare al 20%

Densità radiale per $Z = 80$







relativistico

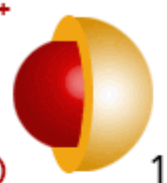
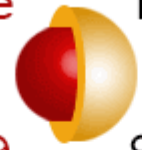
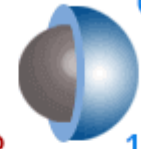
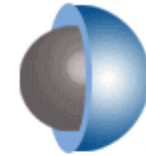
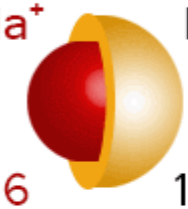
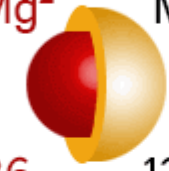
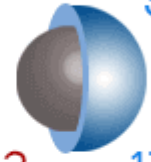
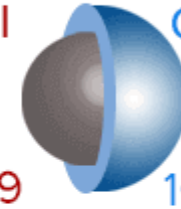
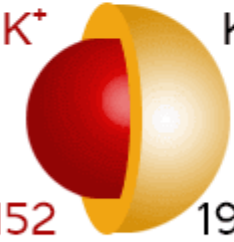
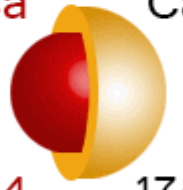
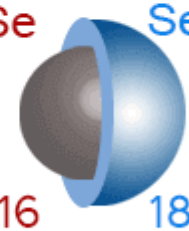
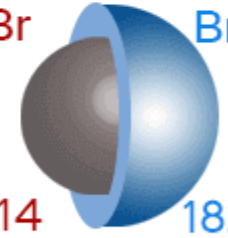
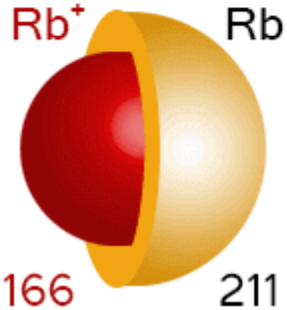
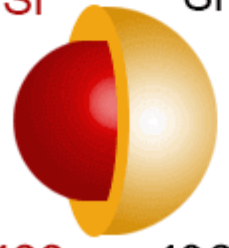
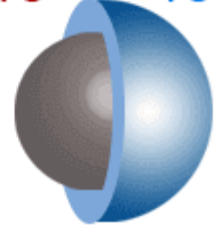
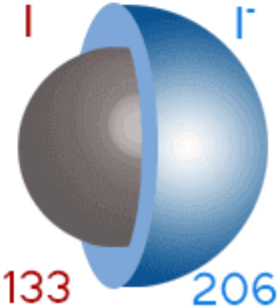
Non-relativistico

Table 1.5 Ionic radii, *r*/pm*

Li^+	Be^{2+}	B^{3+}			N^{3-}	O^{2-}	F^-
59(4)	27(4)	11(4)			146	135(2)	128(2)
76(6)						138(4)	131(4)
						140(6)	133(6)
						142(8)	
Na^+	Mg^{2+}	Al^{3+}			P^{3-}	S^{2-}	Cl^-
99(4)	49(4)	39(4)			212	184(6)	181(6)
102(6)	72(6)	53(6)					
118(8)	89(8)						
K^+	Ca^{2+}	Ga^{3+}			As^{3-}	Se^{2-}	Br^-
138(6)	100(6)	62(6)			222	198(6)	196(6)
151(8)	112(8)						
159(10)	123(10)						
160(12)	134(12)						
Rb^+	Sr^{2+}	In^{3+}	Sn^{2+}	Sn^{4+}		Te^{2-}	I^-
152(6)	118(6)	79(6)	83(6)	69(6)		221(6)	220(6)
160(8)	125(8)	92(8)	93(8)				
173(12)	144(12)						
Cs^+	Ba^{2+}	Tl^{3+}					
167(6)	149(6)	88(6)					
174(8)	156(8)	Tl^+					
188(12)	175(12)	164(6)					

*Numbers in parentheses are the coordination number of the ion. For more values, see *Resource section* 1.

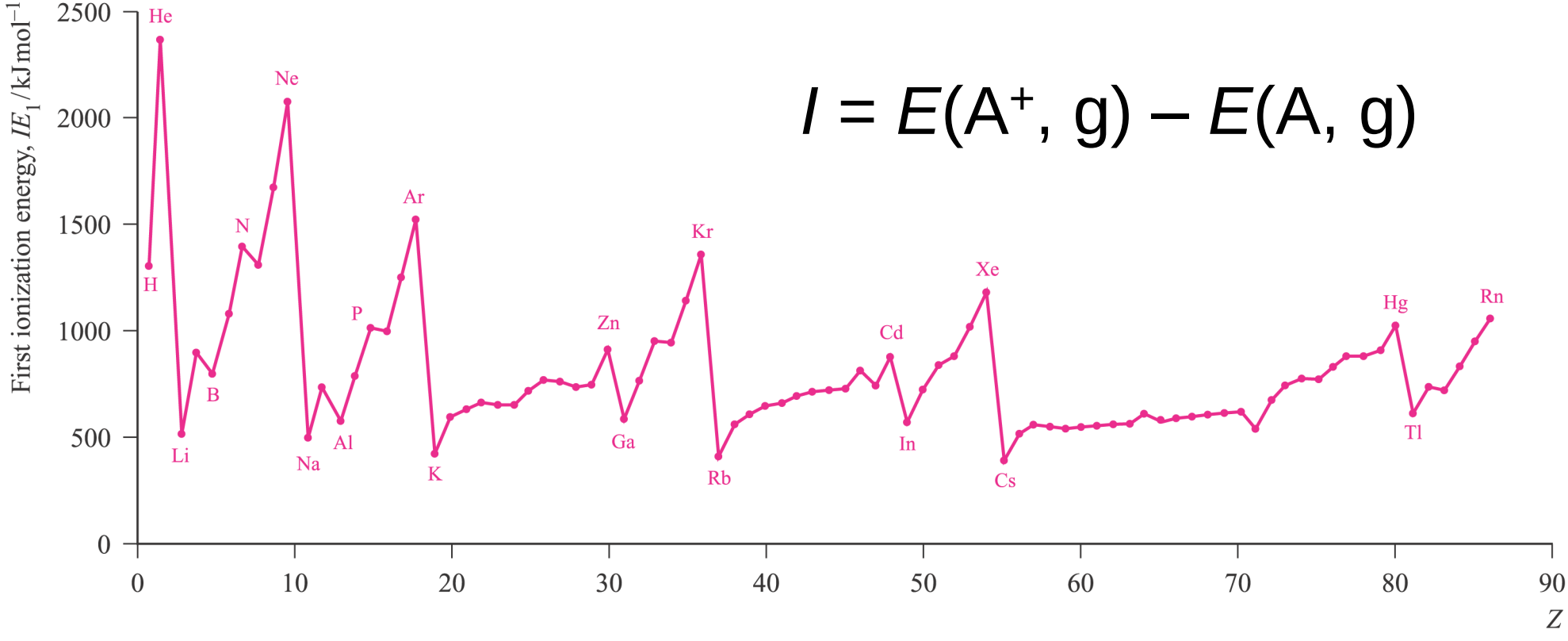
Steps of atoms and their ions in pm

Group 1	Group 2	Group 13	Group 16	Group 17
Li^+  Li 90 134	Be^{2+}  Be 59 90	B^{3+}  B 41 82	O  O^{2-} 73 126	F  F^- 71 119
Na^+  Na 116 154	Mg^{2+}  Mg 86 130	Ai^{3+}  Ai 68 118	S  S^{2-} 102 170	Cl  Cl^- 99 167
K^+  K 152 196	Ca^{2+}  Ca 114 174	Ga^{3+}  Ga 76 126	Se  Se^{2-} 116 184	Br  Br^- 114 182
Rb^+  Rb 166 211	Sr^{2+}  Sr 132 192	In^{3+}  In 94 144	Te  Te^{2-} 135 207	I  I^- 133 206

Energia di Ionizzazione

$$A(g) \rightarrow A^+(g) + e^-(g)$$

$$I = E(A^+, g) - E(A, g)$$



1eV = 96.5 kJ mol^{-1}

Table 1.6 First and second (and some higher) ionization energies of the elements, $I/(\text{kJ mol}^{-1})$

H							**He**
1312							2373
							5259
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
513	899	801	1086	1402	1314	1681	2080
7297	1757	2426	2352	2855	3386	3375	3952
11809	14844	3660	4619	4577	5300	6050	6122
		25018					
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
495	737	577	786	1011	1000	1251	1520
4562	1476	1816	1577	1903	2251	2296	2665
6911	7732	2744	3231	2911	3361	3826	3928
		11574					
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
419	589	579	762	947	941	1139	1351
3051	1145	1979	1537	1798	2044	2103	3314
4410	4910	2963	3302	2734	2974	3500	3565
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
403	549	558	708	834	869	1008	1170
2632	1064	1821	1412	1794	1795	1846	2045
3900	4210	2704	2943	2443	2698	3197	3097
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
375	502	590	716	704	812	926	1036
2420	965	1971	1450	1610	1800	1600	
3400	3619	2878	3080	2466	2700	2900	

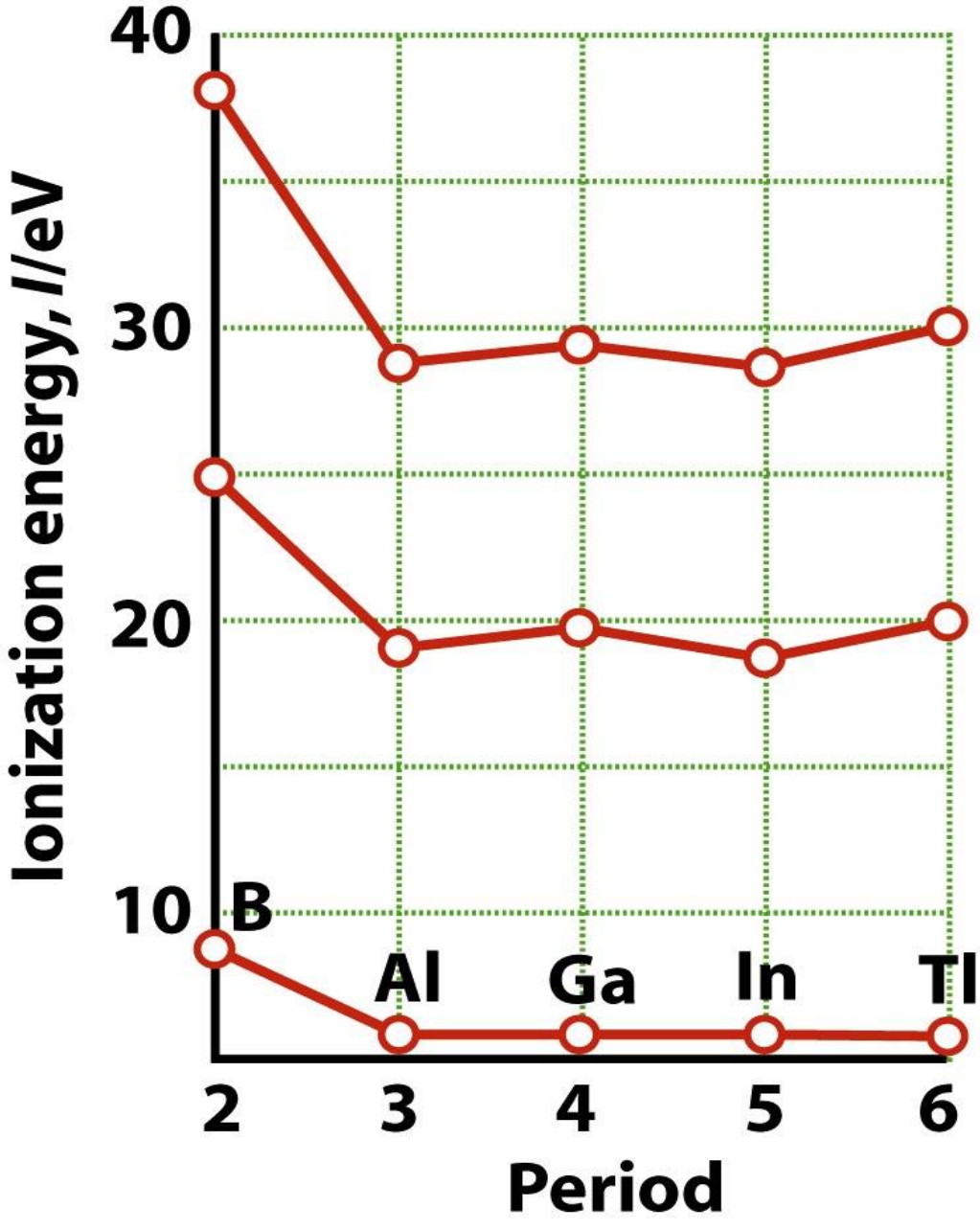

40
30
20
10
Ionization energy, I/eV
B
Al
Ga
In
Tl
2
3
4
5
6
Period

Table 1.7 Electron affinities of the main-group elements, E_a/(kJ mol^{-1})*

$$A(g) + e^-(g) \rightarrow A^-(g)$$

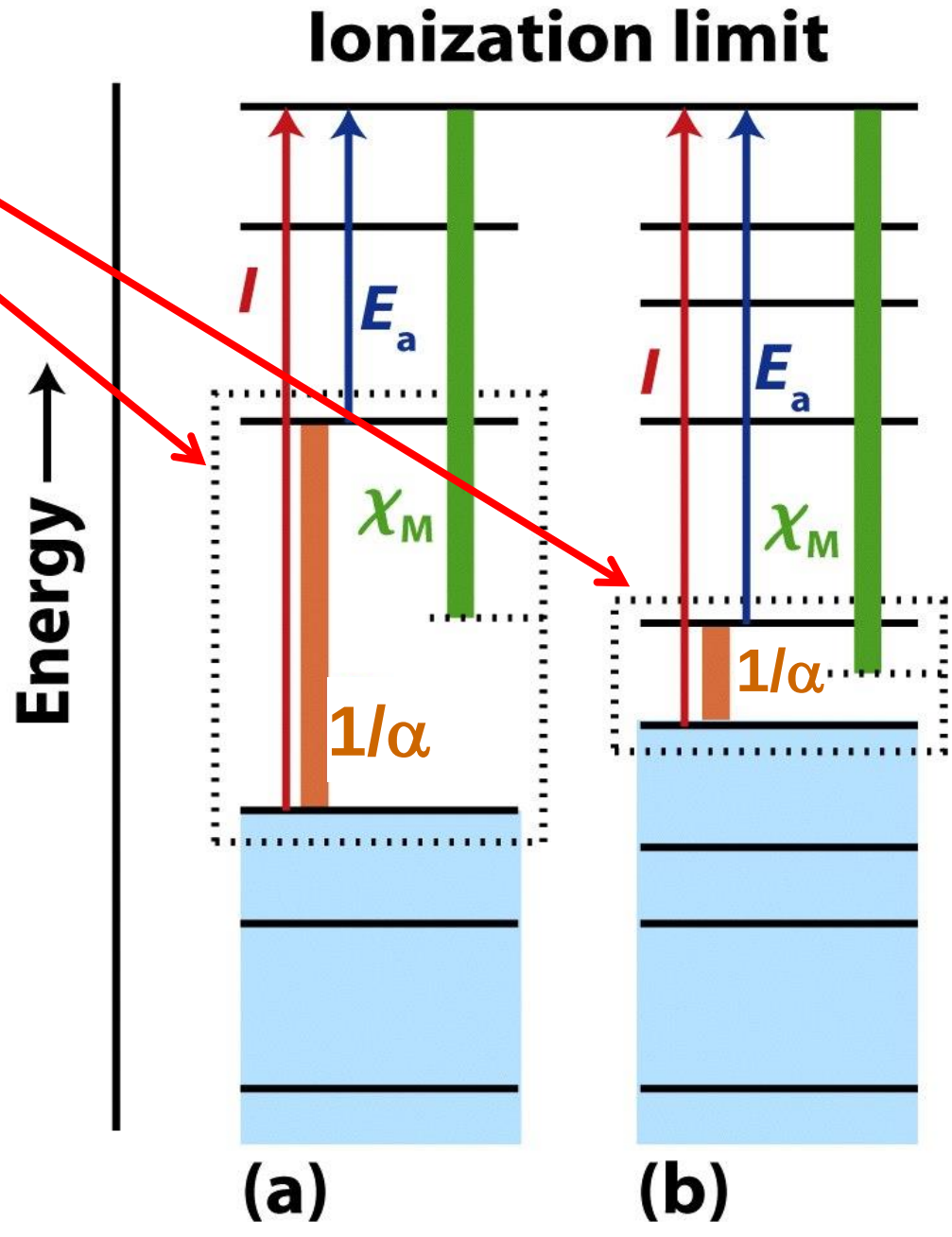
$$E_a = E(A, g) - E(A^-, g)$$

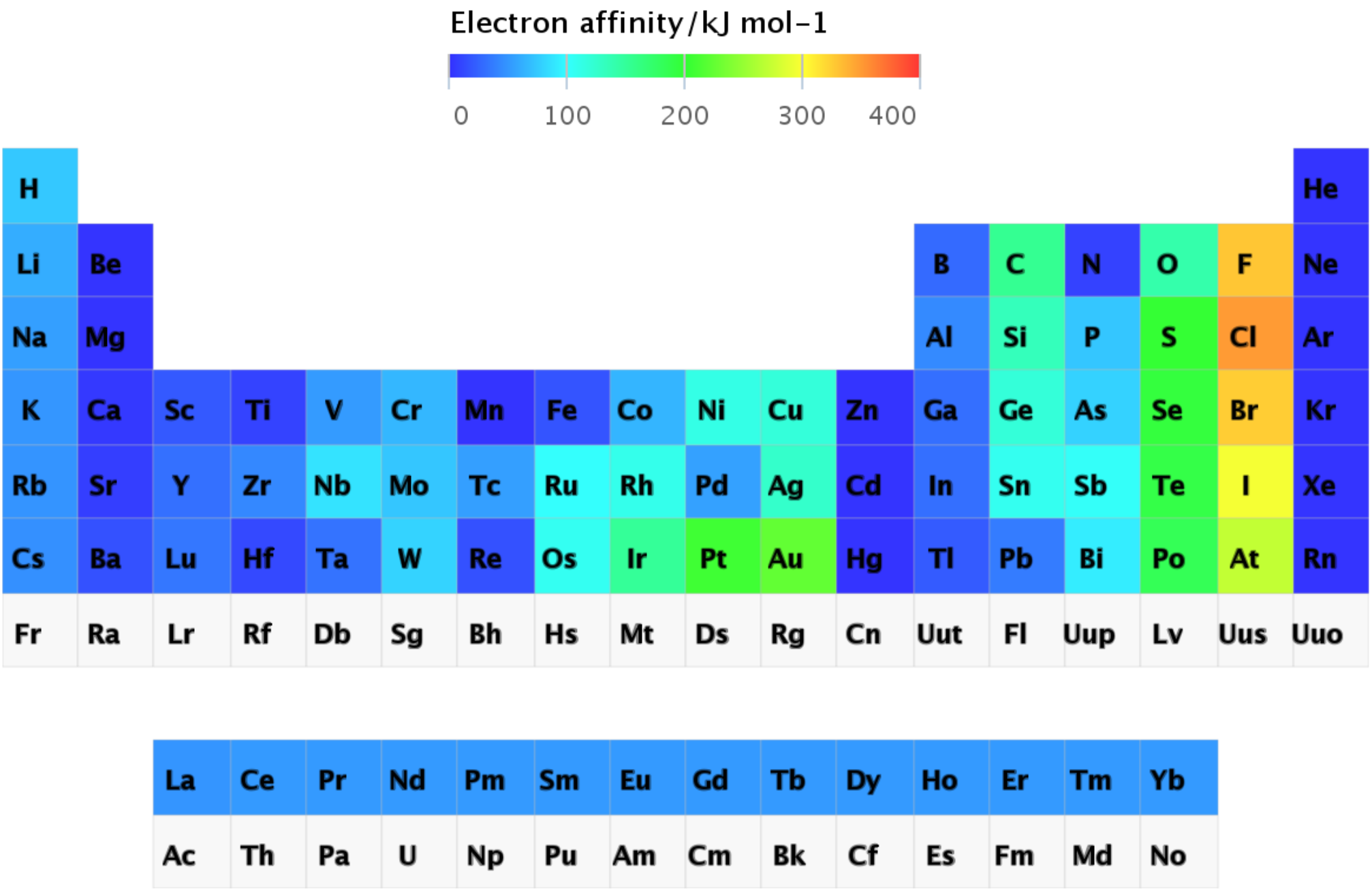
H							**He**
72							−48
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
60	≤0	27	122	−8	141	328	−116
					−780		
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
53	≤0	43	134	72	200	349	−96
					−492		
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
48	2	29	116	78	195	325	−96
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
47	5	29	116	103	190	295	−77

* The first values refer to the formation of the ion X^- from the neutral atom; the second value to the formation of X^{2-} from X^-.

l'affinità elettronica ha segno <u>opposto</u> alla variazione di energia

Orbitali di frontiera





Polarizzabilità e Regole di Fajans

1. cationi piccoli e a carica elevata (e.g. Li^{+}, Mg^{2+}) hanno forte **potere polarizzante**
2. anioni larghi e con carica elevata sono **facilmente polarizzabili** (e.g. I^{-}, Se^{2-}, Te^{2-}, As^{3-}, P^{3-})
3. cationi che non hanno una configurazione elettronica di gas nobile (e.g. quasi tutti quelli dei metalli di transizione) sono più polarizzanti di quelli con guscio chiuso (e.g. cationi dei metalli alcalini o alcalino-terrosi) perché avranno una maggiore Z_{eff}, cioè una carica più alta sulla loro superficie (*cfr* Hg^{2+} e Ca^{2+}, 116 pm).