FIZIKALNA ANORGANSKA KEMIJA

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Literatura:

G. Wulfsberg, Inorganic Chemistry, University Science Books, 2001.

R. J. Gillespie, P. L. A. Popelier: Chemical Bonding and Molecular Geometry: From Lewis to Electron Densities, Oxford Univ. Press, 2001.

S. F. A. Kettle, Physical Inorganic Chemistry, Oxford Univ. Press, 2000.

7 Tema za pričati o

- Atom
- Veza
- Ioni
- Topljivost
- Oksidacija
- Kompleksi
- Simetrija

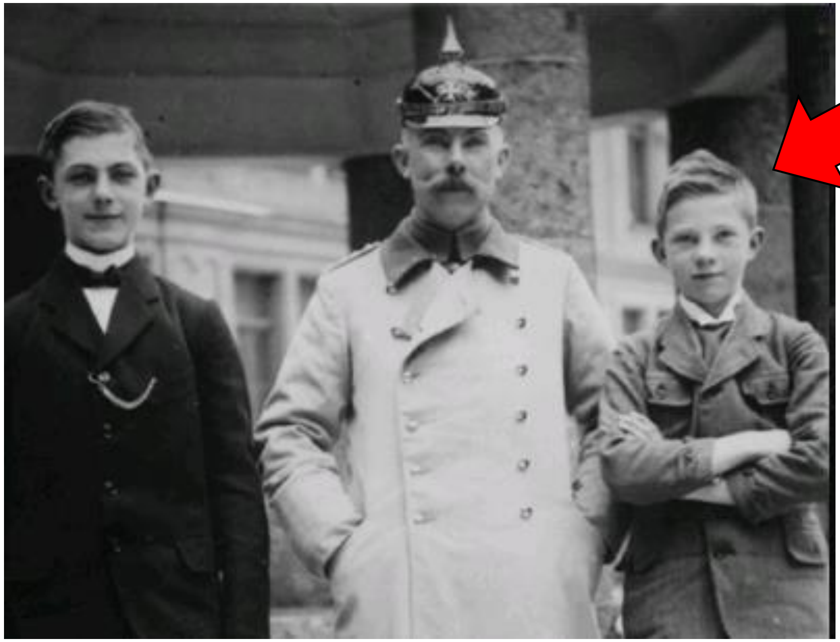
CAPVT I

ATOM

Što je ATOM (NESJEC)

Smallest particle still characterizing a chemical element. It consists of a nucleus of a positive charge (Z is the proton number and) carrying almost all its mass (more than 99.9%) and Z electrons determining its size.

IUPAC



Werner Karl Heisenberg

Tri komplementarna modela atoma

valni

čestični

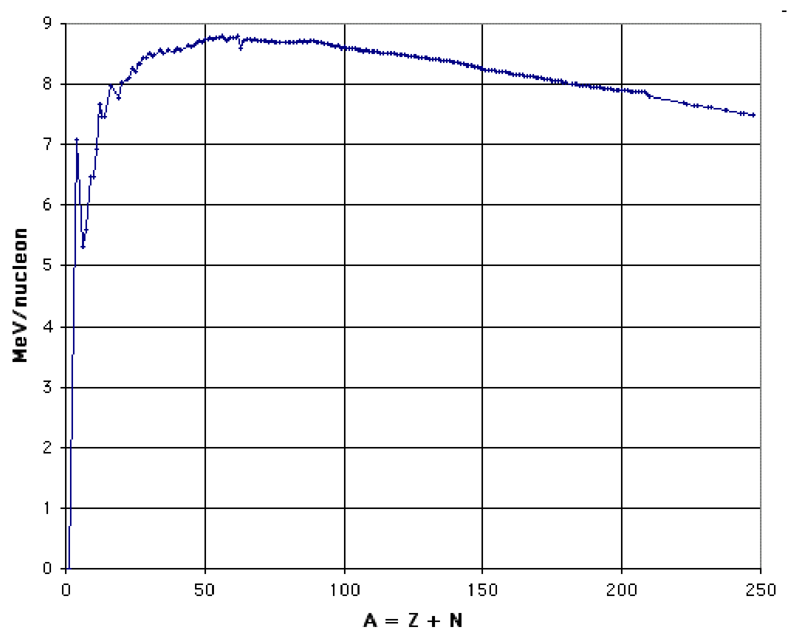
kemijski

Svojstva atoma

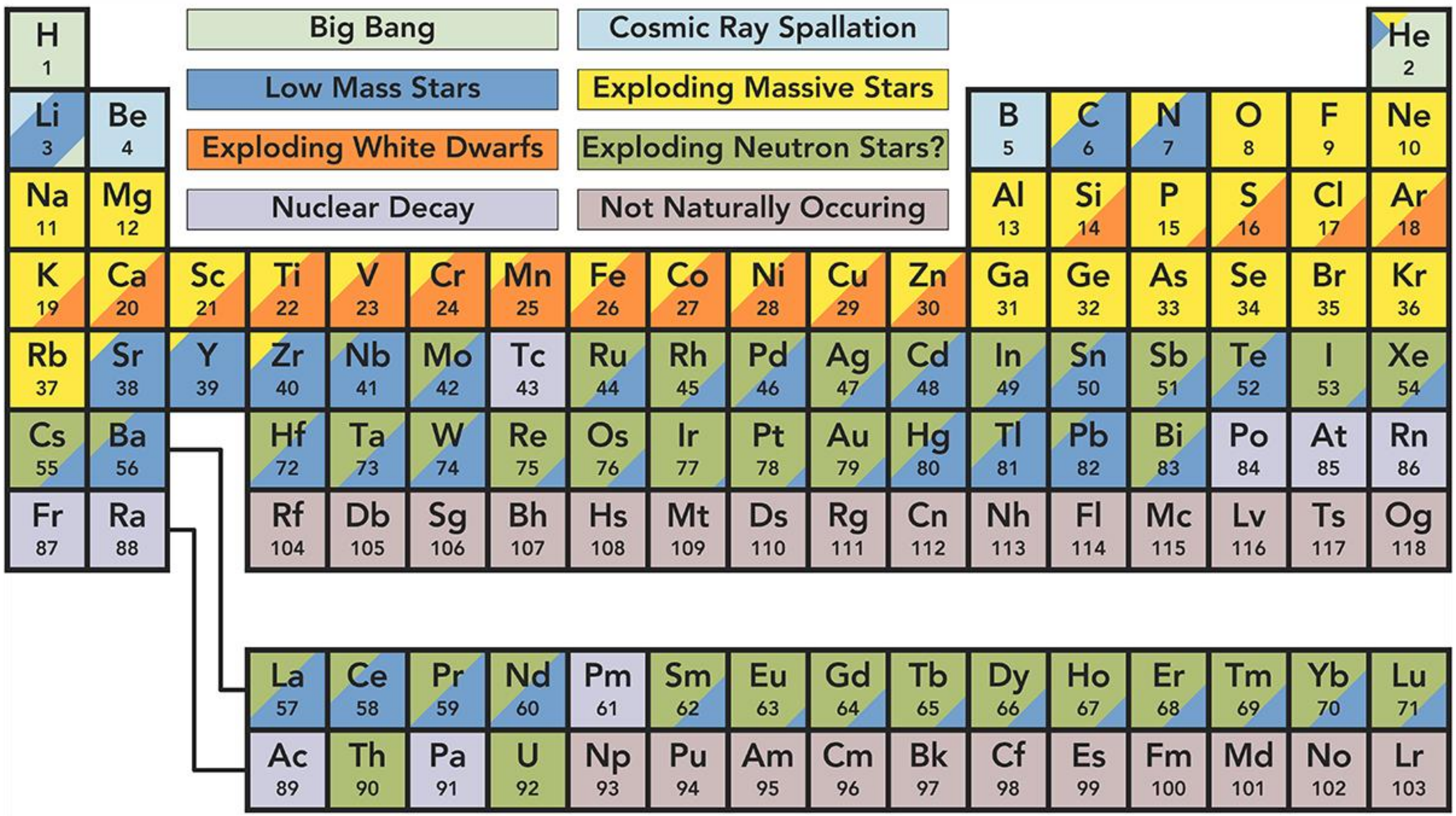
- Nuklearna svojstva
- Masa
- Radijus
- Magnetski moment
- Energija ionizacije
- Elektronski afinitet
- Elektronegativnost

Masa

- Atomska masa (ne brkati s relativnom atomskom masom iliti atomskom težinom) približno jednaka zbroju masa protona i neutrona što sačinjavaju jezgru, ali...

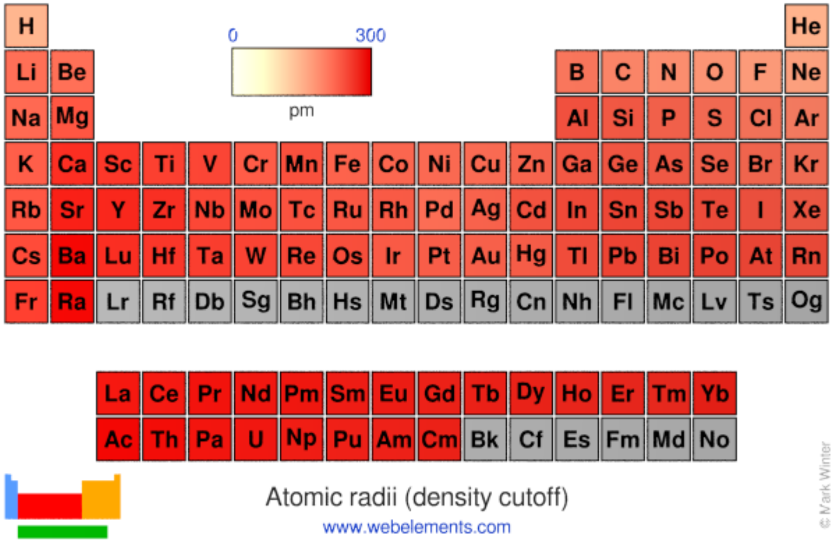


Podrijetlo elemenata



Atomski radijus

- Van der Waalsov
- Bohrov
- Ionski
- Kovalentni
- Metalni


0
300
pm
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Lr Rf Db Sg Bh Hs Mt Ds Rg Cn Nh Fl Mc Lv Ts Og
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No
Atomic radii (density cutoff)
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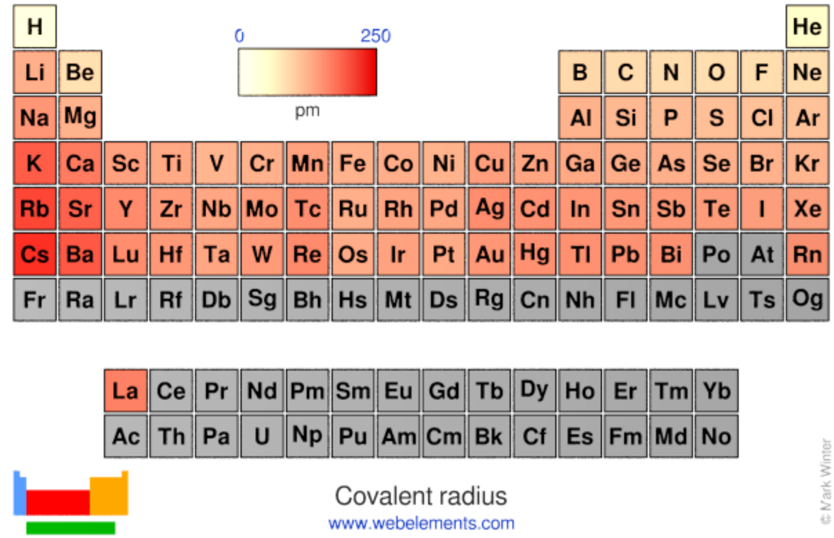
0
250
pm
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Lr Rf Db Sg Bh Hs Mt Ds Rg Cn Nh Fl Mc Lv Ts Og
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No
Covalent radius
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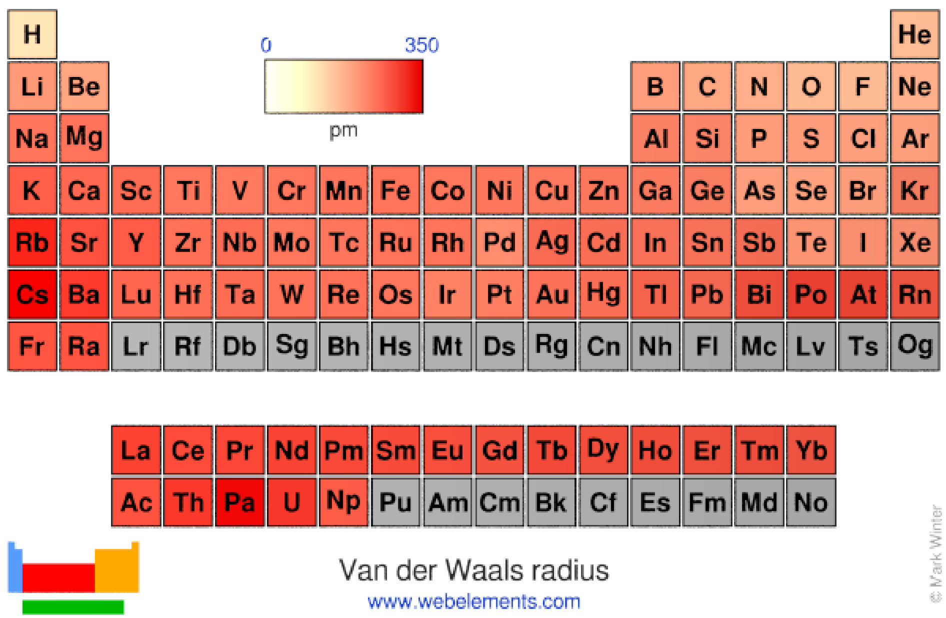
0,001 e/bohr^3


0
350
pm
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Lr Rf Db Sg Bh Hs Mt Ds Rg Cn Nh Fl Mc Lv Ts Og
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No
Van der Waals radius
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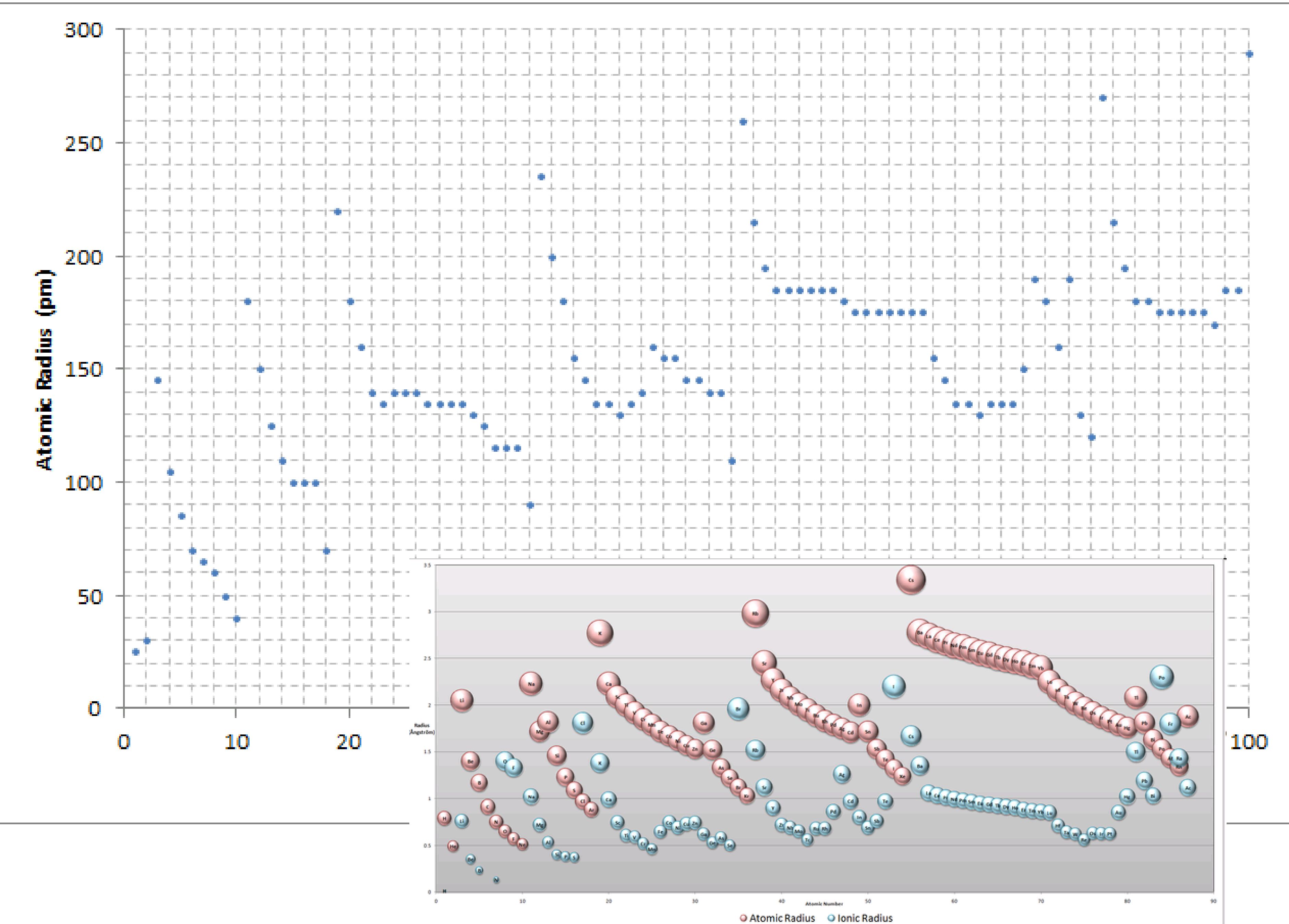
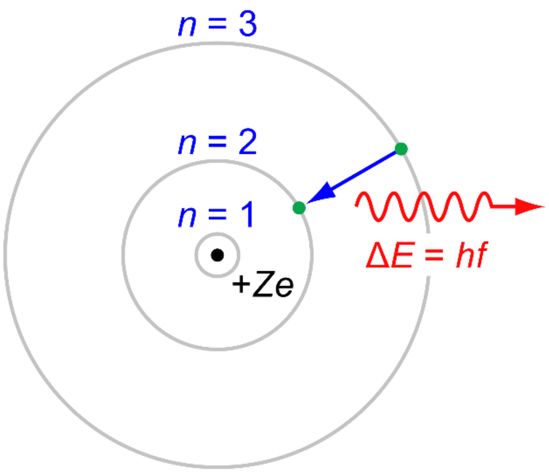


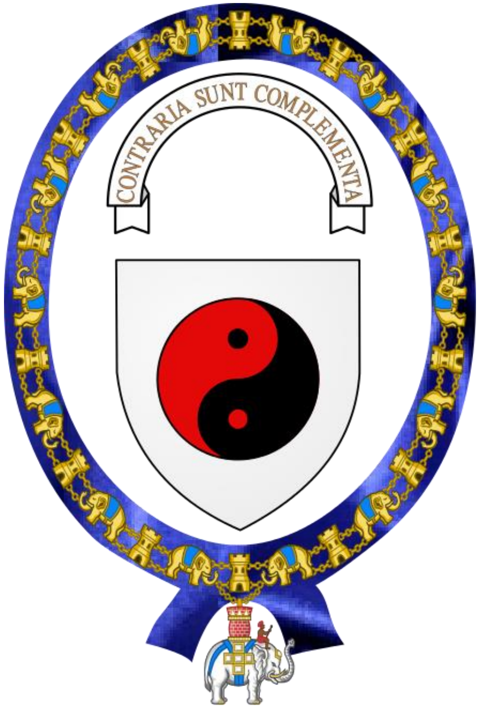
Atomic Radius (pm)
300
250
200
150
100
50
0
0
10
20
100
Atomic Number
Atomic Radius
Ionic Radius



$$\frac{m_e v^2}{r} = \frac{Z k_e e^2}{r^2}$$

$$mvr = L = n\hbar$$

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}$$



Slaterova pravila i Z_{eff}

- Pojedini elektron zasjenjen je od jezgre ostalima i to
- 0,35 e za svaki elektron s isitim *n* i l (s i p se tretiraju kao da su istoga l)
- Ako je elektron s ili p – svi elektroni s *n*-1 zasjanjuju ga s 0,85 e, a ostali s 1 e
- Ako je d ili f – svi elektroni manjega *n* ili l zasjenjuju ga potpuno

Radijus atoma i efektivni naboj

- $r = a_0\,(n^*)^2/\,Z^*$
- a_0=52,9 pm
- n^*=efektivni glavni kvantni broj

$n = 1,\ n^* = 1;$

$n = 2,\ n^* = 2;$

$n = 3,\ n^* = 3;$

$n = 4,\ n^* = 3{,}7;$

$n = 5,\ n^* = 4{,}0;$

$n = 6,\ n^* = 4{,}2$

Skandidna i lantanidna kontrakcija

- B – 85 pm; Al – 125 pm; Ga – 130 pm
- Ti – 140 pm; Zr – 155 pm; Hf – 155 pm

Energija ionizacije

Najmanja energija potrebna da se izbaci jedan elektron iz atoma,

$$X \rightarrow X^{+} + e^{-}$$

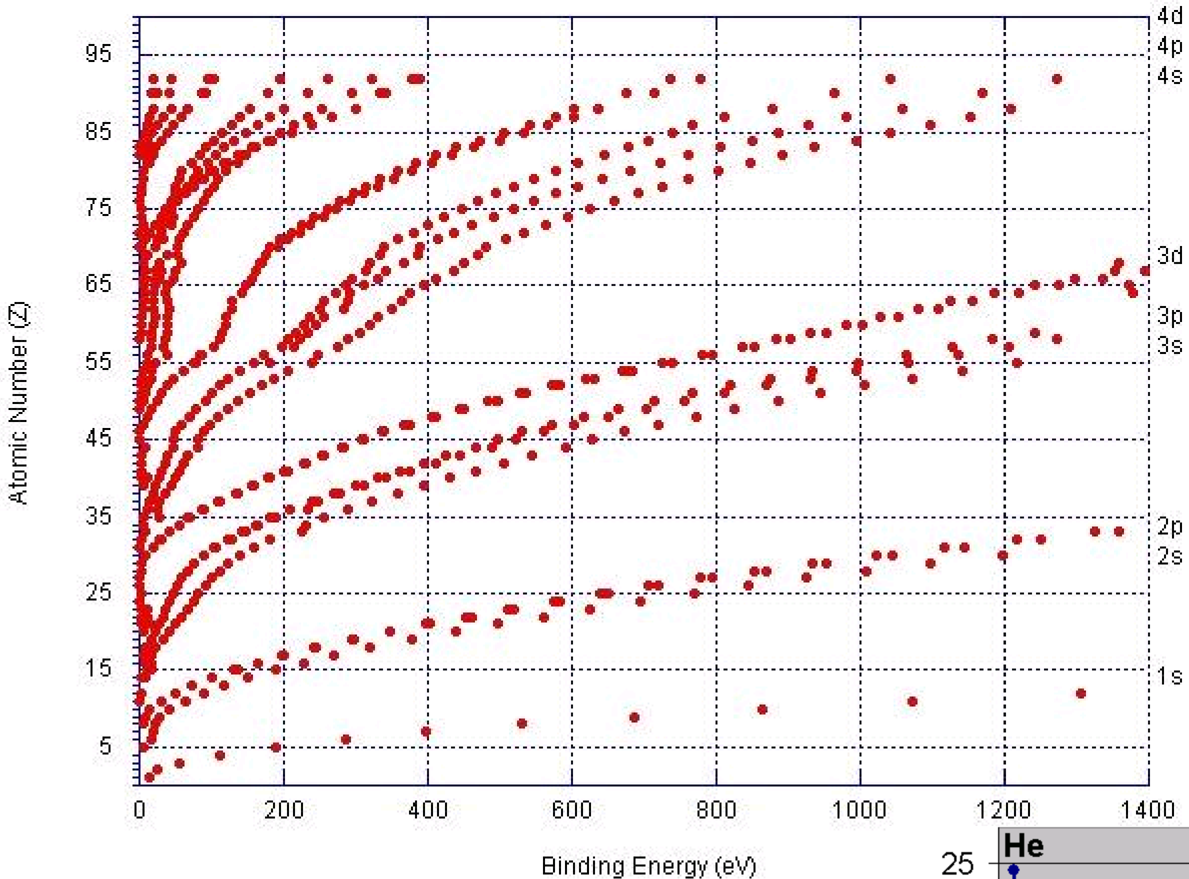
Minimum energy required to eject an electron out of a neutral atom or molecule in its ground state. The adiabatic ionization energy refers to the formation of the molecular ion in its ground vibrational state and the vertical ionization energy applies to the transition to the molecular ion without change in geometry. This quantity was formerly called ionization potential. The second ionization energy of an atom is the energy required to eject the second electron from the atom (energy for the process $X^{+} \rightarrow X^{2+} + e^{-}$*).*

IUPAC

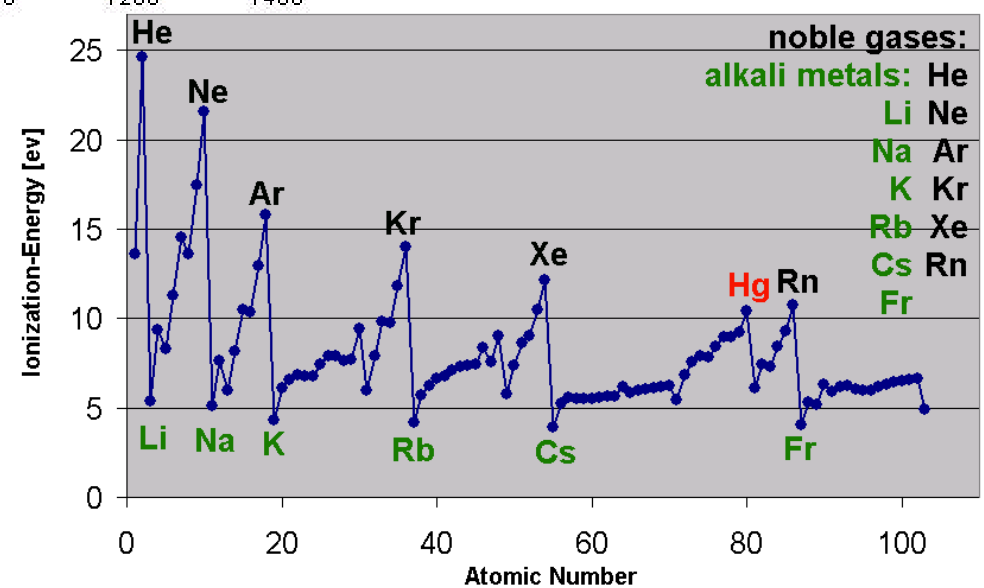
PES

Element	1.	2.	3.	4.	5.	6.	7.
Na	496	4560					
Mg	738	1450	7730				
Al	577	1816	2881	11600			
Si	786	1577	3228	4354	16100		
P	1060	1890	2905	4950	6270	21200	
S	9996	2260	3375	4565	6950	8490	27107
Cl	1256	2295	3850	5160	6560	9360	11000
Ar	1520	2665	3945	5770	7230	8780	12000

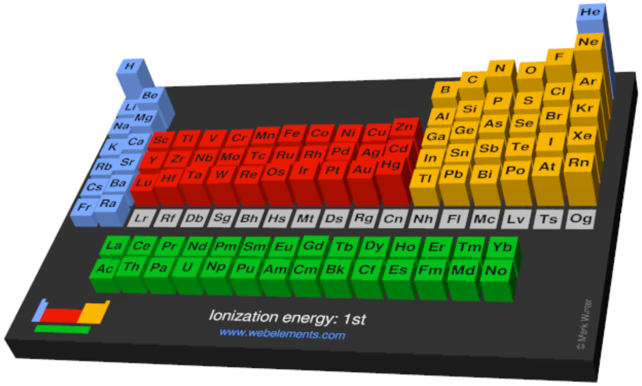
[energije u eV]



Atomic Number (Z)
Binding Energy (eV)
4d
4p
4s
3d
3p
3s
2p
2s
1s



Ionization-Energy [ev]
Atomic Number
noble gases:
alkali metals: He
Li Ne
Na Ar
K Kr
Rb Xe
Cs Rn
Fr
He
Ne
Ar
Kr
Xe
Hg
Rn
Li
Na
K
Rb
Cs
Fr


Ionization energy: 1st
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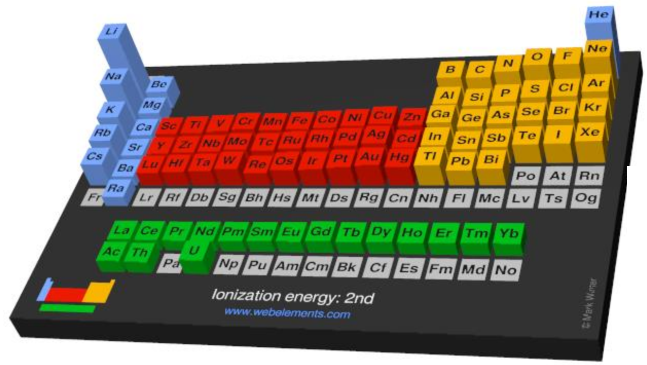
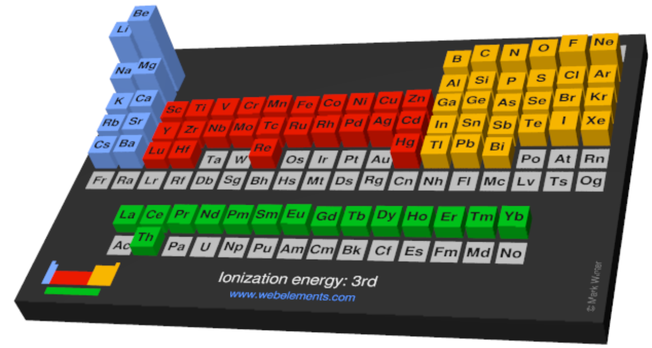

Ionization energy: 2nd
www.webelements.com


Ionization energy: 3rd
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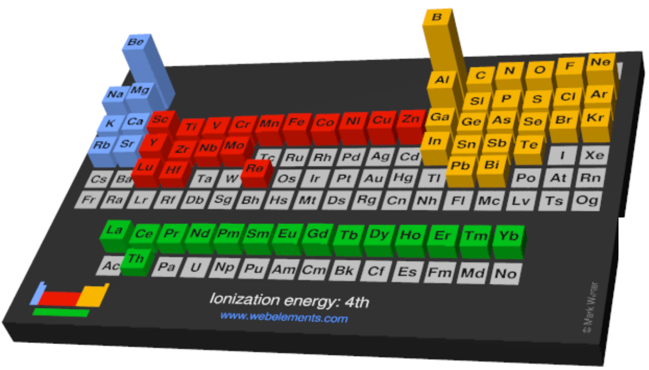
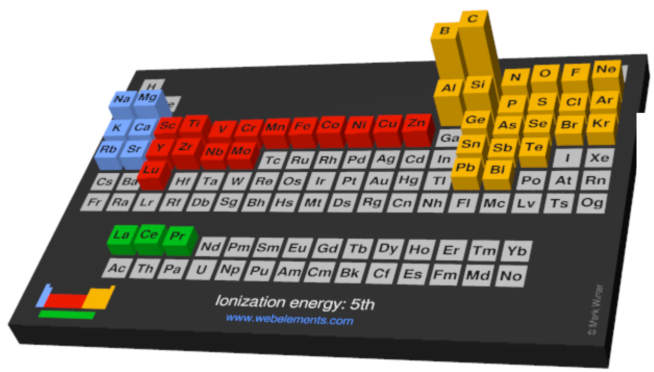
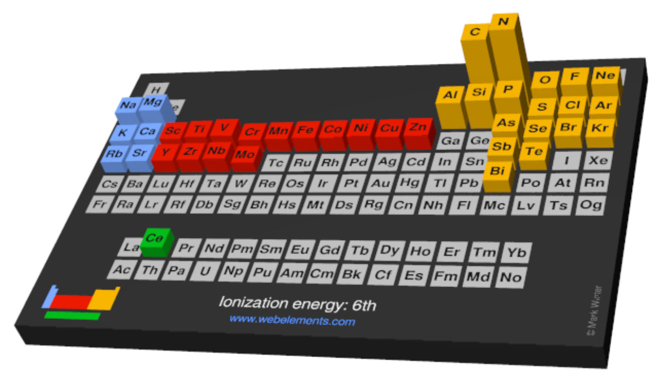
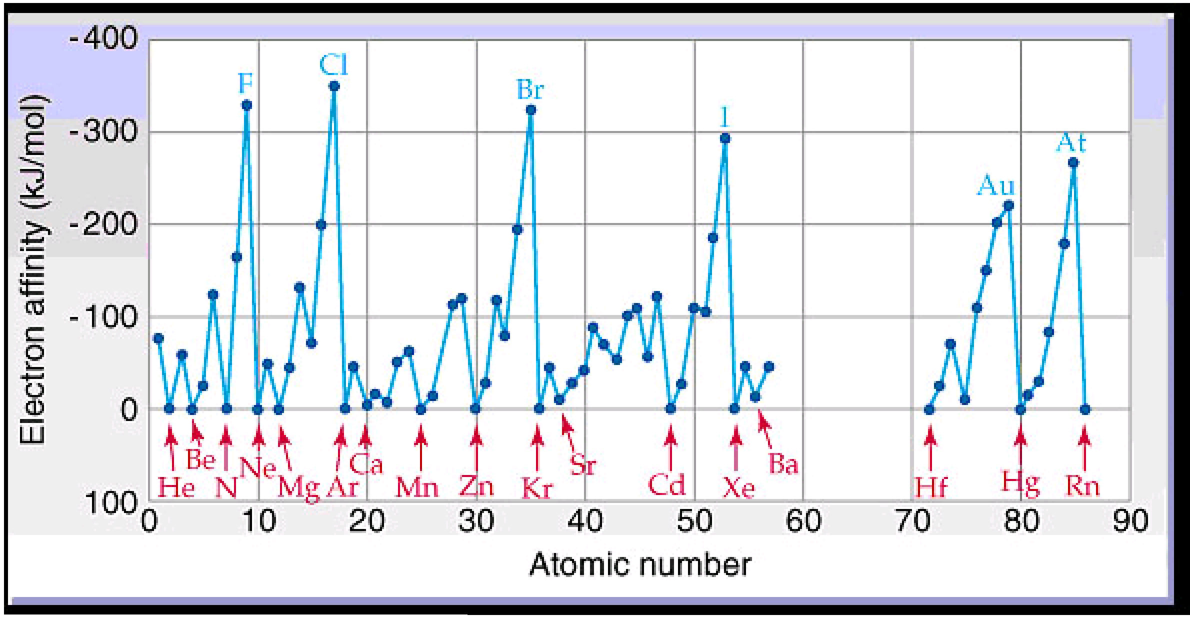

Ionization energy: 4th
www.webelements.com


Ionization energy: 5th
www.webelements.com

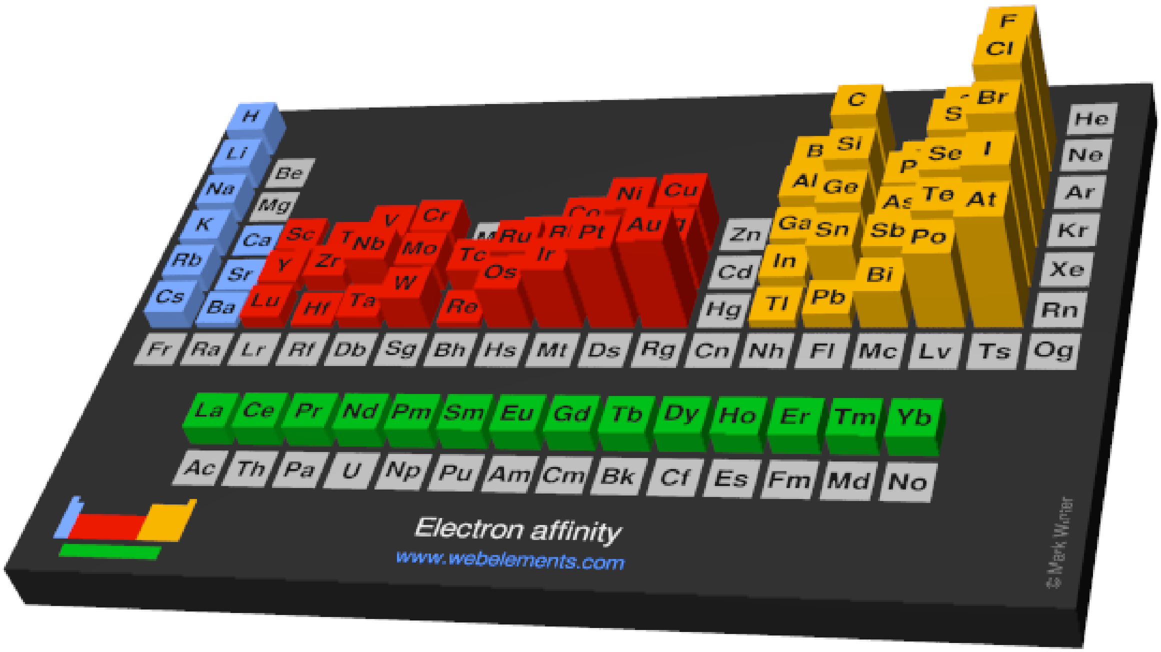

Ionization energy: 6th
www.webelements.com

Elektronski afinitet

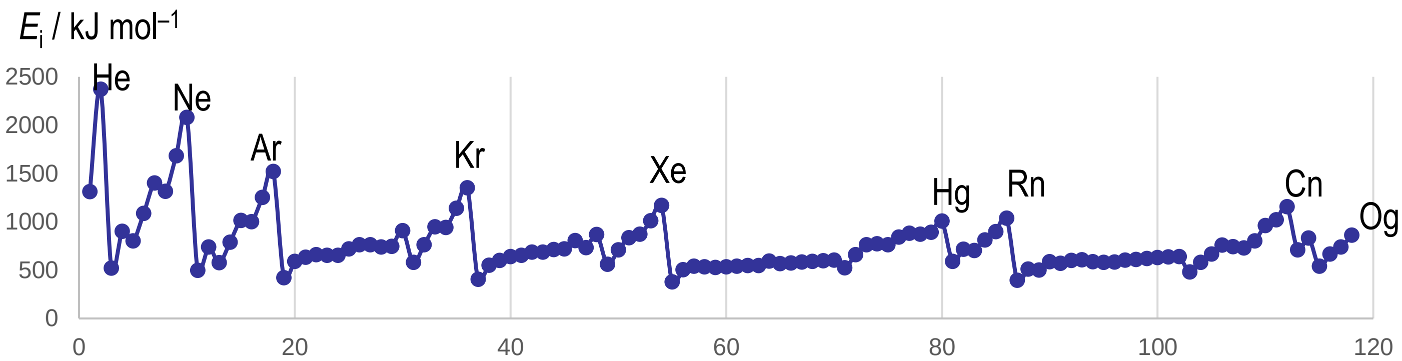
- Energy required to detach an electron from the singly charged negative ion (energy for the process $X^{-} \rightarrow X + e^{-}$). The equivalent more common definition is the energy released when an additional electron is attached to a neutral atom or molecule.



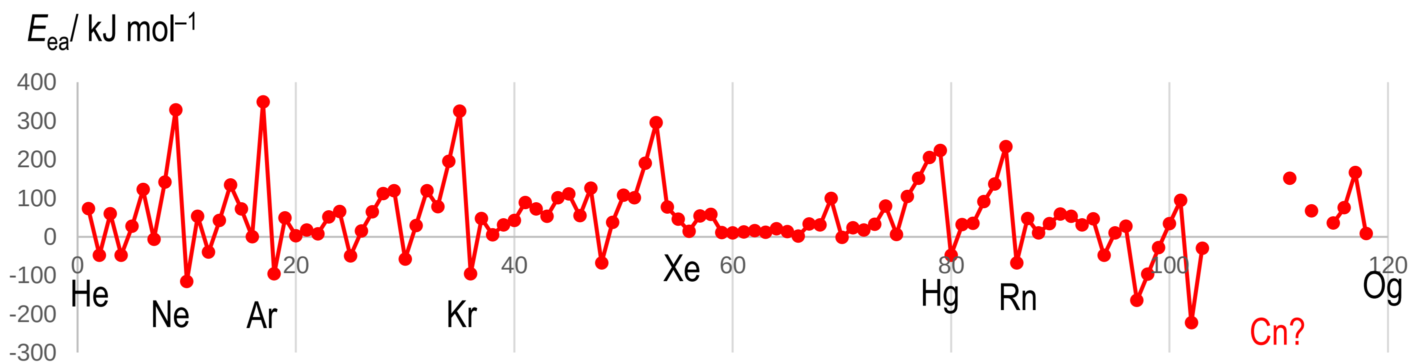
Electron affinity (kJ/mol)
Atomic number
F
Cl
Br
I
Au
At
He
Be
N
Ne
Mg
Ar
Ca
Mn
Zn
Kr
Sr
Cd
Xe
Ba
Hf
Hg
Rn



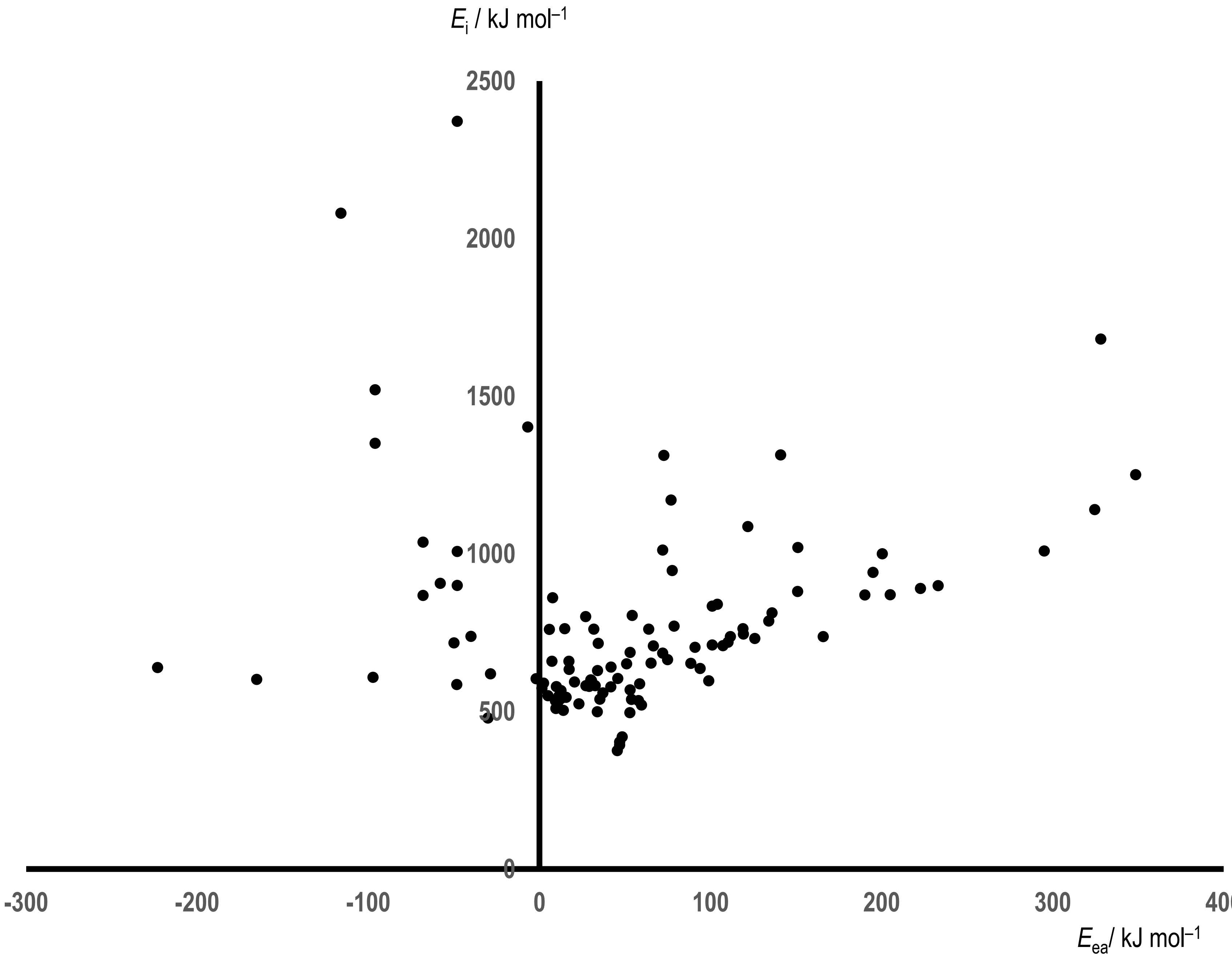
Electron affinity
www.webelements.com



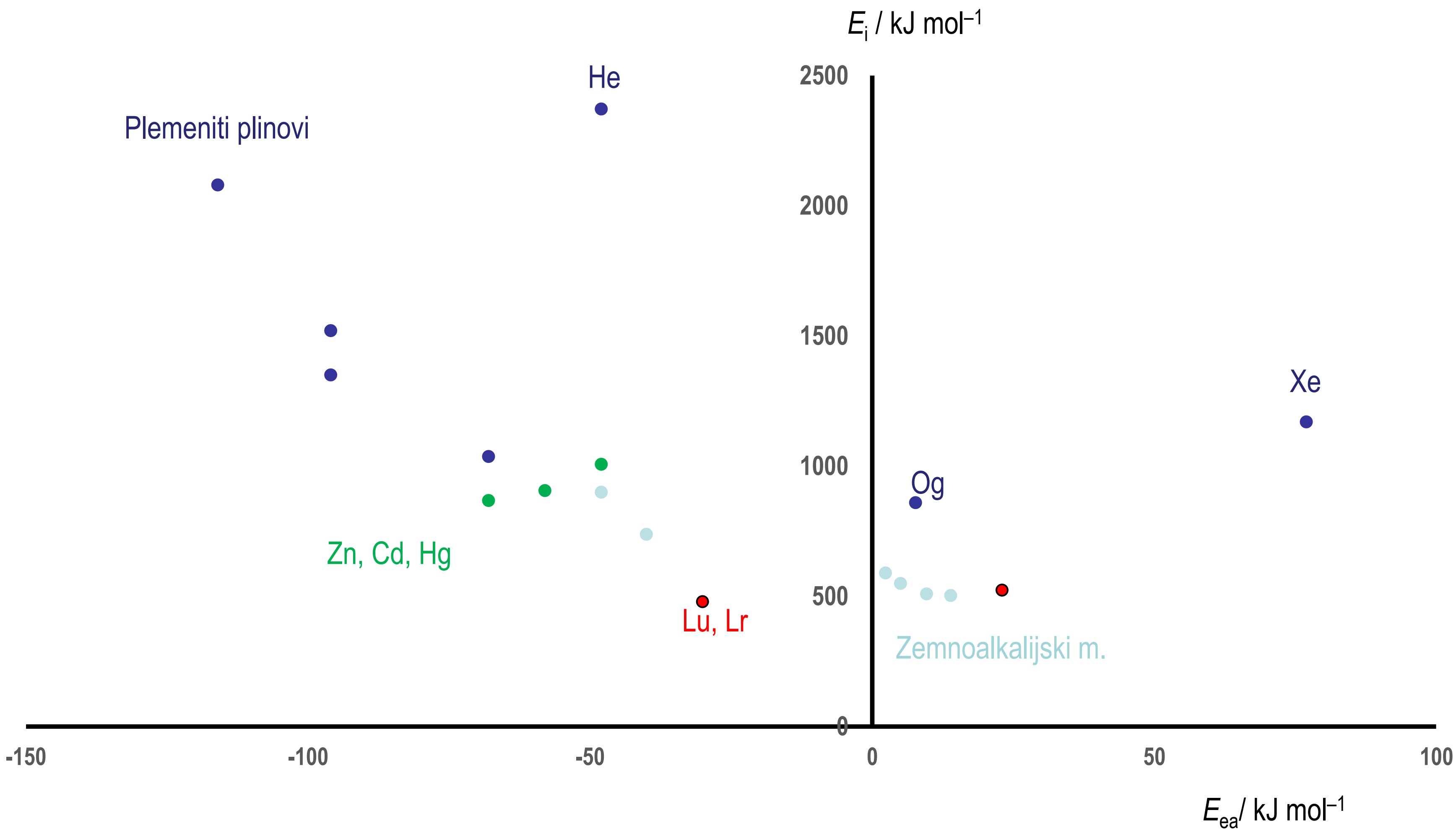
E_i / kJ mol^{-1}
2500
2000
1500
1000
500
0
0
20
40
60
80
100
120
He
Ne
Ar
Kr
Xe
Hg
Rn
Cn
Og



E_{ea}/ kJ mol^{-1}
400
300
200
100
0
-100
-200
-300
0
20
40
60
80
100
120
He
Ne
Ar
Kr
Xe
Hg
Rn
Cn?
Og



E_i / kJ mol^{-1}
2500
2000
1500
1000
500
0
-300
-200
-100
0
100
200
300
400
E_{ea}/ kJ mol^{-1}



E_i / kJ mol^{-1}
2500
2000
1500
1000
500
0
He
Plemeniti plinovi
Xe
Og
Zn, Cd, Hg
Lu, Lr
Zemnoalkalijski m.
-150
-100
-50
0
50
100
E_{ea}/ kJ mol^{-1}

Elektronegativnost

- Moć elektrona da privlači elektrone iz veze

- IUPAC: „Concept introduced by L. Pauling as the power of an atom to attract electrons to itself.“

Pauling:

$$\chi_{\mathrm{A}} - \chi_{\mathrm{B}} = (\mathrm{eV})^{-1/2}\sqrt{E_{\mathrm{d}}(\mathrm{AB}) - \frac{E_{\mathrm{d}}(\mathrm{AA}) + E_{\mathrm{d}}(\mathrm{BB})}{2}}$$

Mulliken:

$$\chi = \frac{E_i + E_a}{2}$$

Gordy:

$$\chi = \frac{eZ_{eff}}{r}$$

Mullikan/Koopmans:

$$\chi = -\frac{E_{HOMO} + E_{LUMO}}{2}$$

Sanderson:

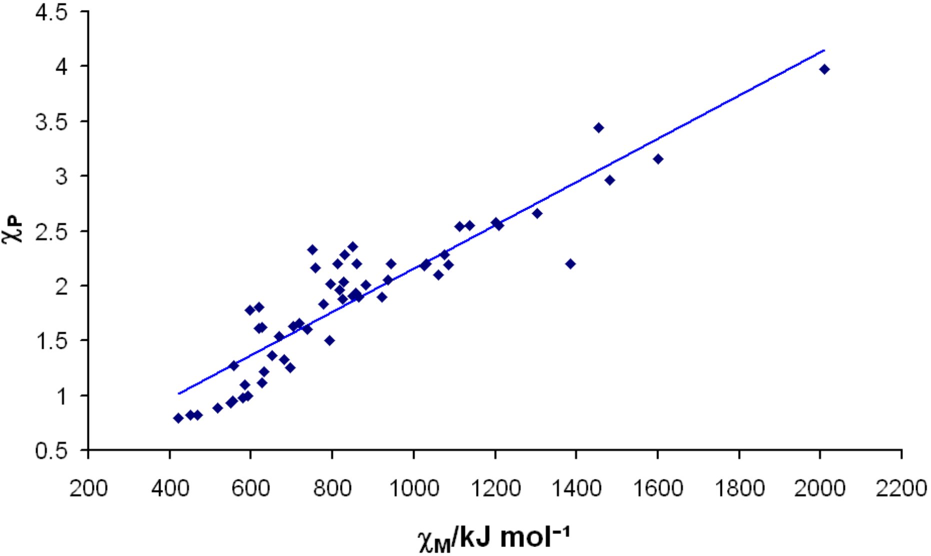
$$\chi = \frac{Z}{r^3 D_{epp}}$$

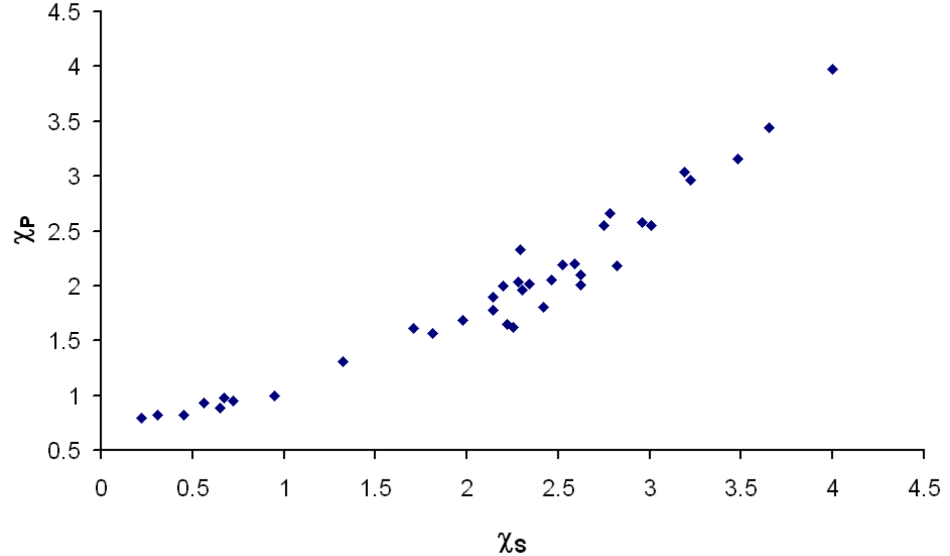
Allred-Rochow:

$$\chi = \frac{Z_{eff}}{r_{kov}^2}$$

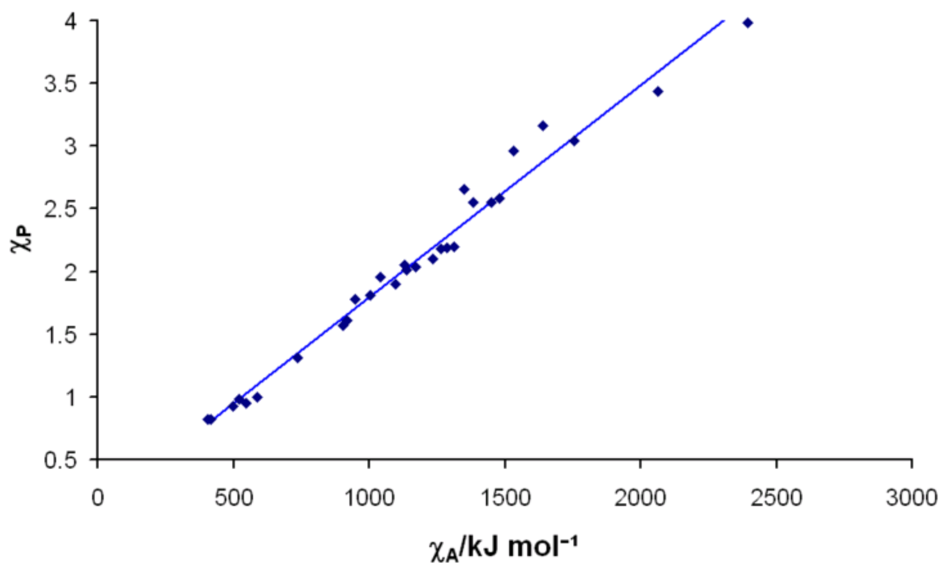
Allen:

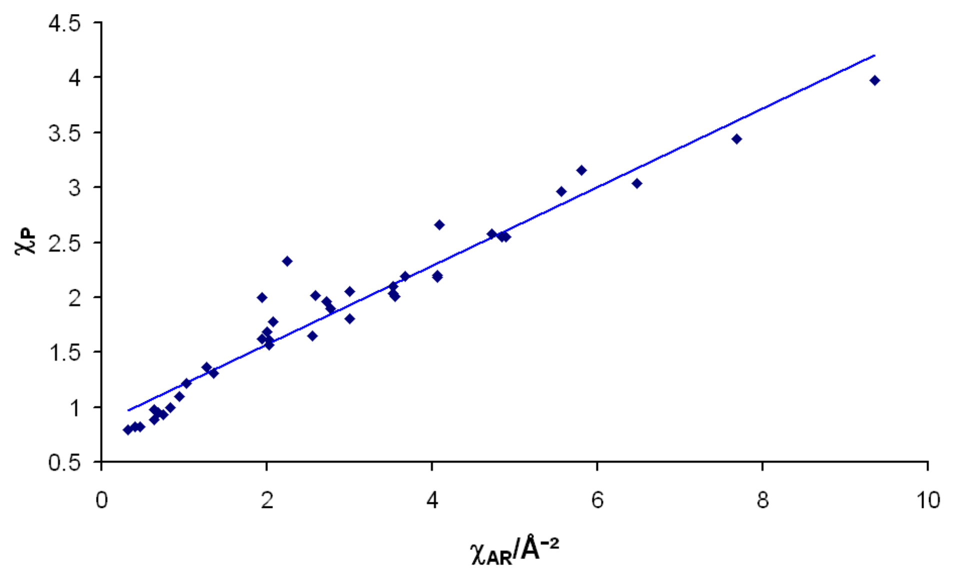
$$\chi = \frac{n(s)E_i(s) + n(p)E_i(p)}{n(s) + n(p)}$$





P = Pauling, **M** = Mulliken, **S** =Sanderson, **A** = Allen, **AR** = Allred–Rochow





Elektronski kemijski potencijal

Unutarmolekulski elektrostatski potencijal nastao uslijed razdiobe elektronske gustoće

Definira elektronska svojstva krutina (vodiča i poluvodiča) – poluvodiči p- i n-tipa

$$\mu(r) = \left[\frac{\partial E[\rho]}{\partial \rho(r)}\right]_{\rho=\rho_{\mathrm{ref}}}$$

$$\mu = -\chi_{\mathrm{M}} = -\frac{E_i + E_a}{2}$$

Princip izjednačavanja elektronegativnostî

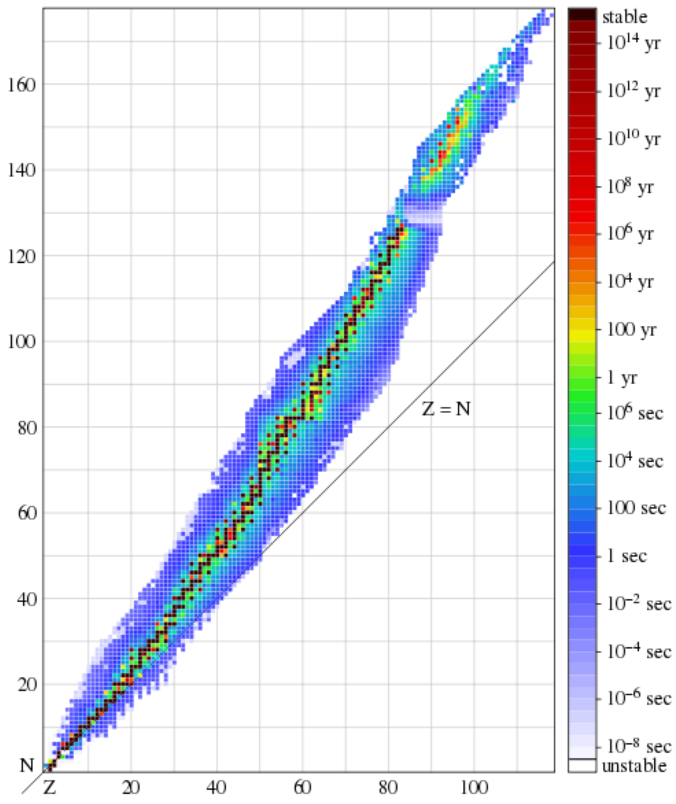
- Sanderson
- Kada se dva ili više atoma različitih elektronegativnosti povezuju kemijskom vezom dolazi do prijenosa naboja pri čemu se mijenjaju elektronegativnosti pojedinih atoma.
- Elektronegativnosti svih atoma u skupini/molekuli se smatraju jednakima prosječnoj elektronegativnosti atome koji skupinu sačinjavaju

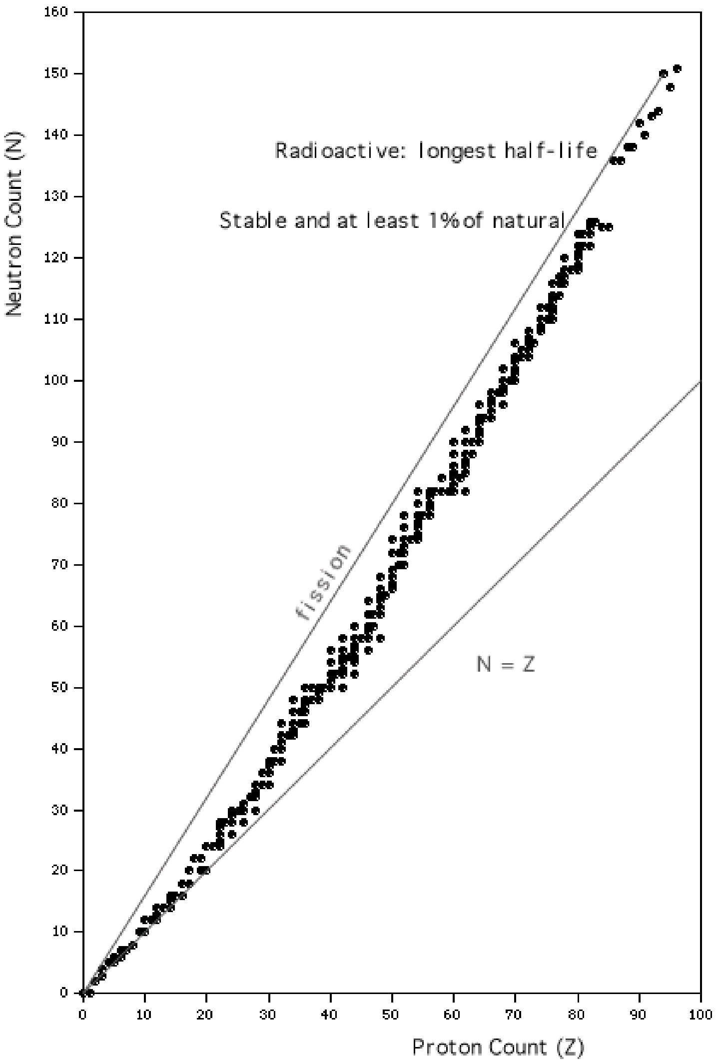
Parcijalni naboji

- Uslijed izjednačavanja elektronegativnosti dolazi do pomaka elektronske gustoće – na pojedinim se atomima javljaju parcijalni naboji
- Sanderson – temeljem razlika u elektronegativnosti polaznih atoma mogu se predvidjeti njihovi parcijalni naboji u spoju
- Parcijalni naboji i ionski radijusi pojedine vrste ovise o drugim vrstama s kojima je ona u vezi
- Parcijalni naboji rijetko izlaze iz raspona $<-e,e>$

Nuklearna svojstva

- Kemičara se u glavnom ne tiču, ali...





Koliko teški mogu atomi biti?

- Čarobne brojke i stabilni otoci

  Model ljusaka – stabilne su one jezgre koje imaju zatvotene nuklearne ljuske

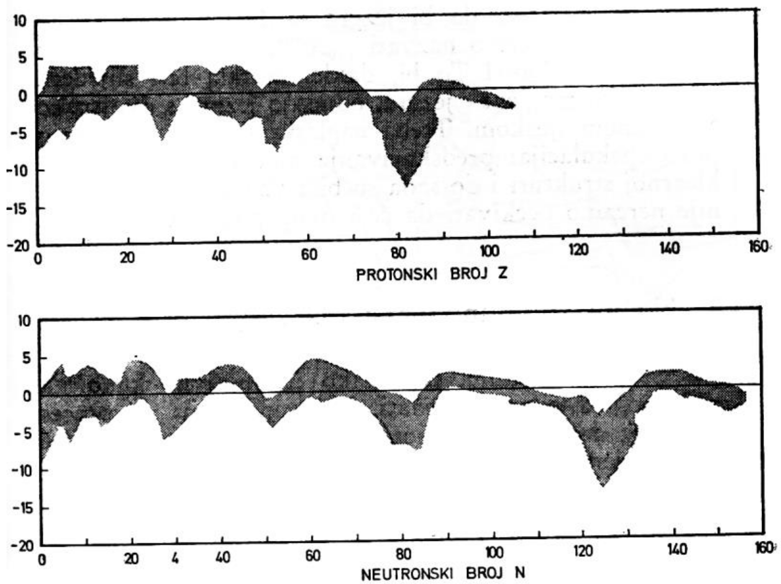
  za kuglastu jezgru:

  N(p) = $2\left(\binom{n}{1}+\binom{n}{2}+\binom{n}{3}\right)$

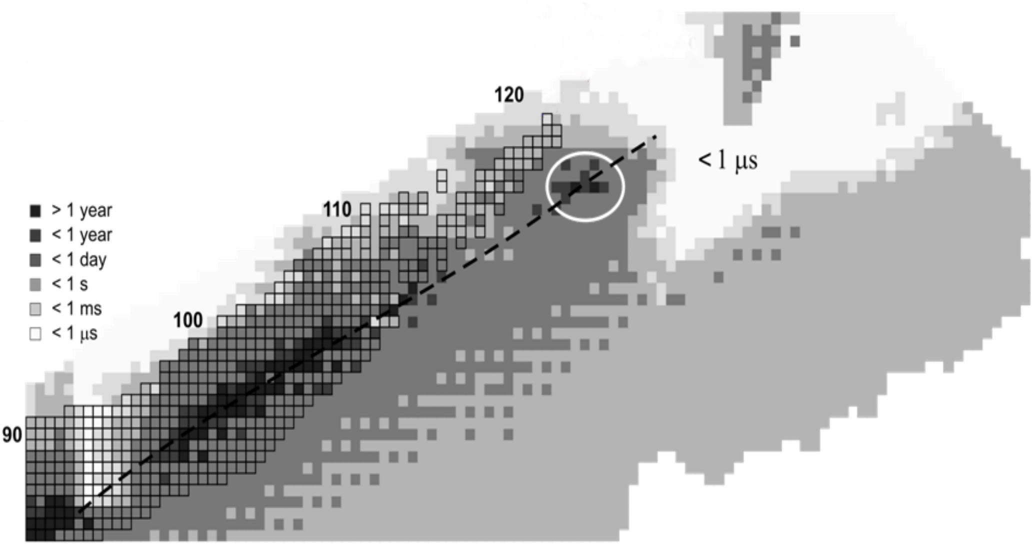
  za stvarnu jezgru (kako se čini...)

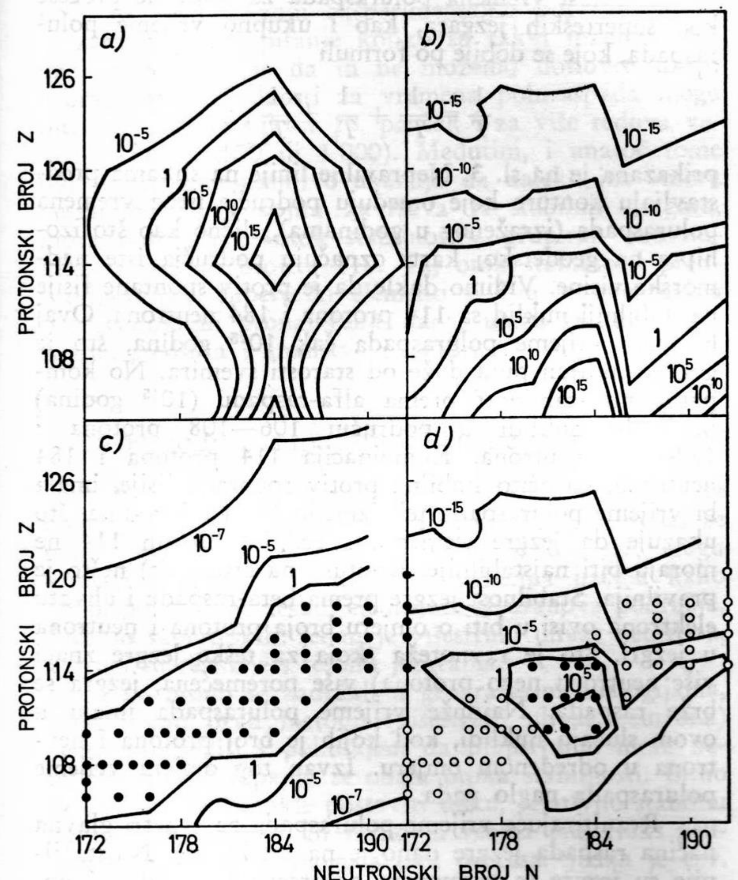
  N(n) = 2, 8, 20, 28, 50, 82, 126, 164, 184, 196, 236, 318...

  N(p) = 2, 8, 20, 28, 50, 82, 114, 122, 124, 164...



Sl. 2. Utjecaj zatvorenosti nukleonskih ljusaka na energiju vezanja jezgri

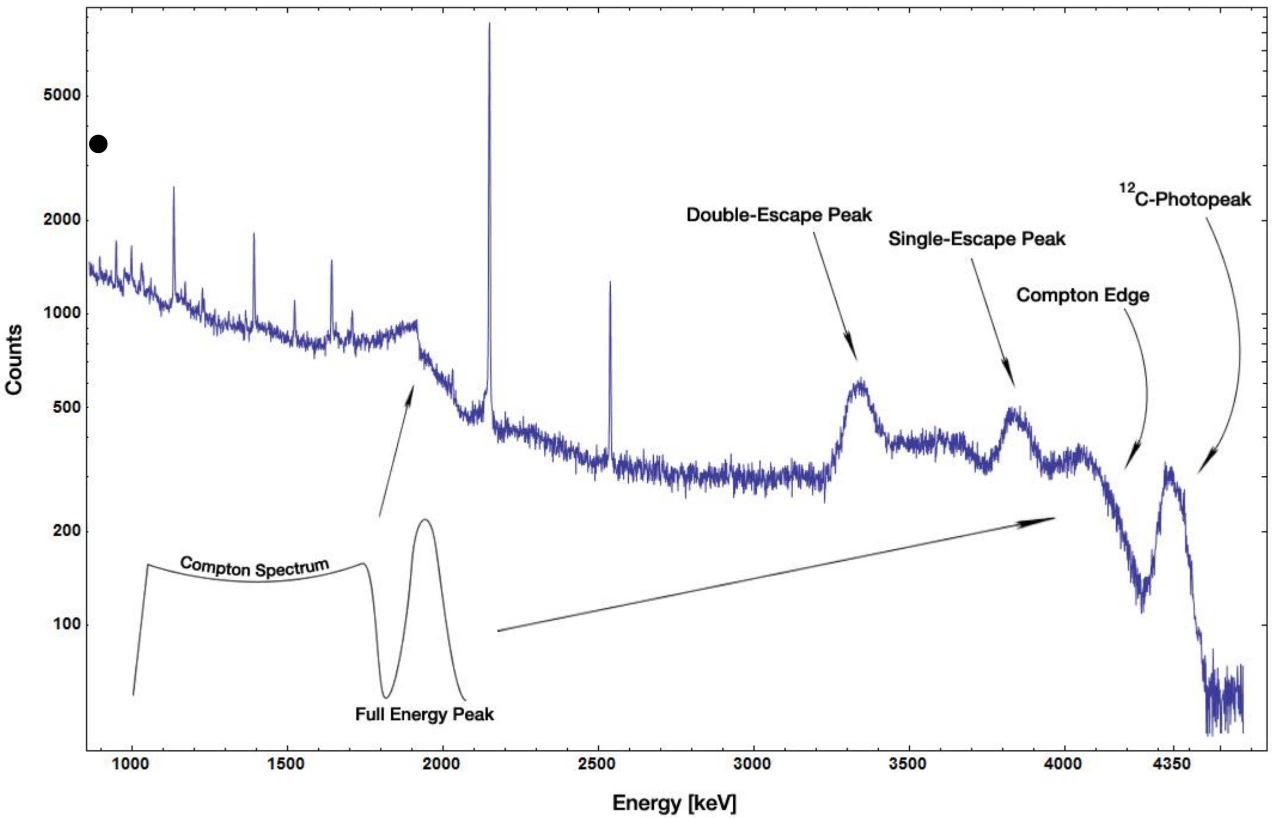




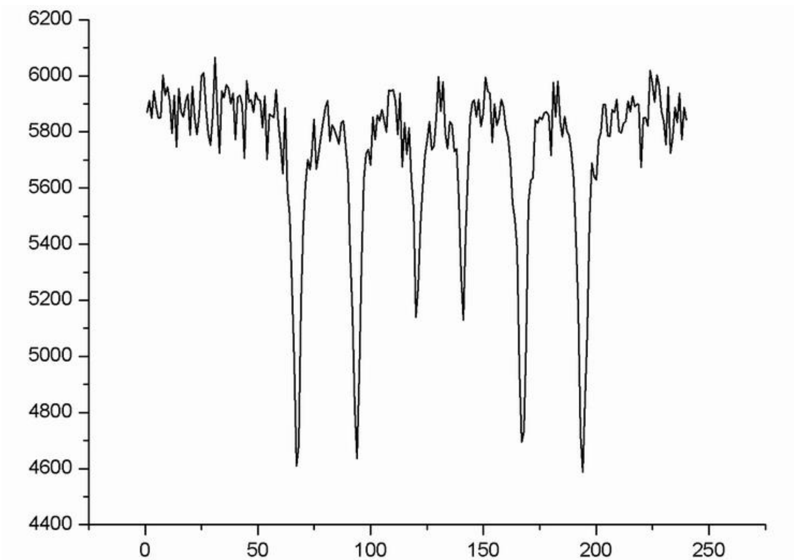
Sl. 3. Vremena poluraspadanja superteških jezgri proračunata iz modela ljusaka. Crtež (a) prikazuje konturnu mapu vremena raspada spontanom fisijom. Brojevi uz linije označavaju vrijeme poluraspada u godinama. Crtež (b) pokazuje to isto za alfa-raspad, a crtež (c) za beta-raspad i uhvat elektrona. Crtež (d) pokazuje rezultirajuće vrijeme poluraspada za sva tri procesa. Puni kružići znače jezgre s vremenom poluraspada dužim od jedne godine, a prazni znače jezgre s vremenom poluraspada kraćim od jedne godine. Promatramo samo jezgre s parnim brojem protona i neutrona; tzv. neparne jezgre znatno su nestabilnije.

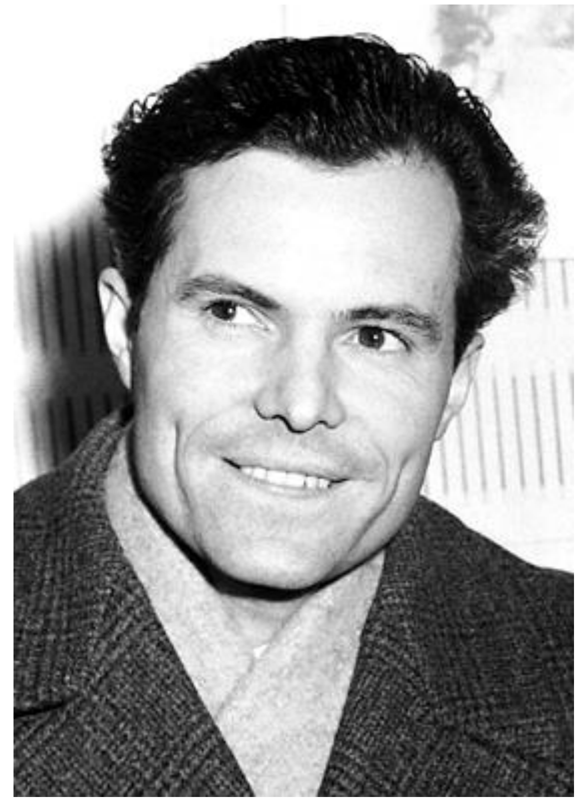
Nuklearni spektri

- Vrlo uske specifične linije
- Male razlike među izobarima
-



Mössbauerova spektroskopija





Rudolf Mössbauer

Teški atomi

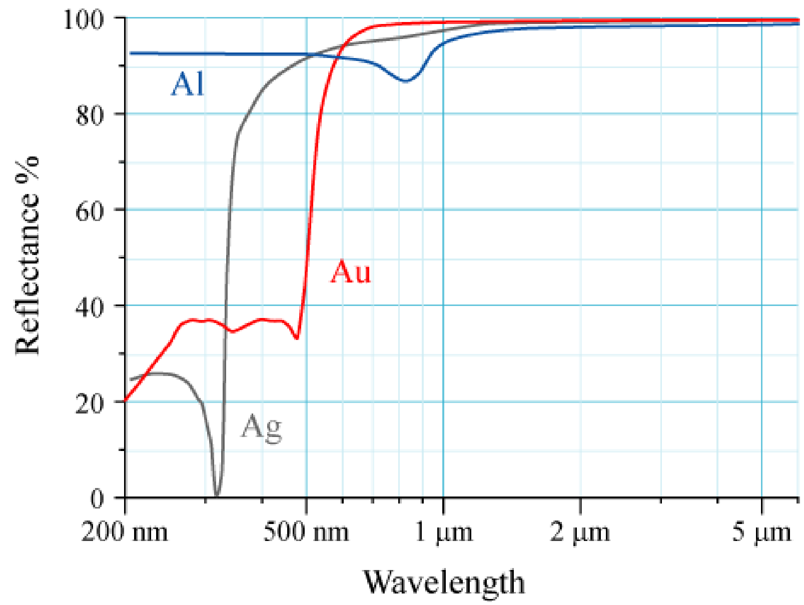
- Relativistička kontrakcija i ekspanzija
  - Porast mase unutarnjih elektrona uslijed povećanja brzine (v(1s) = c za Z=137,036;

$$\mathbf{E}\,[v(1s)] \approx (Z/137)c)$$

  - Elektroni koji prodiru bliže jezgri (s i p) postaju masivniji i približavaju se jezgri – kontrakcija (Au, Hg)
  - Elektroni koji ne prodiru blizu jezgri su jače zasjenjeni – ekspanzija

Neke posljedice relativističkih efekata

- Boja zlata i cezija
  - Raste energija 5d elektrona i opada energija 6d elektrona – mijenja se apsorpcija



- Kapljevitost žive
  - 6s elektroni jako privučeni jezgri – slabe interakcije među atomima

Magnetski moment

- Nuklearni i elektronski
- Elektronski – bitno veći, potječe od nesparenih elektrona

$$\mu_L = -g_L \frac{\mu_B}{\hbar} < \Psi_{n,l,m}|L|\Psi_{n,l,m} >= -\mu_B \sqrt{l(l+1)}.$$

- Nuklearni
  - Protoni i meutroni se sparuju s onima suprotnoga ukupnog kutnog momenta
    - Parni broj i protonâ i neutronâ – magnetski moment je 0
    - Neparni broj jednih a parni drugih – magnetski moment jezgre jednak onomu nesparenog nukleona
    - Neparna oba – magnetski moment kombinacija momeneta dvaju nesparenih