Fundamental processes: Atomic Physics

CERN Accelerator School: Ion Sources
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Outline and intro

- Electrons in an atom
- Electron configurations
- Periodic table of elements
- Ionization energies
- Negative ions – electron affinity
- Atomic processes in ion sources
- Ways to ionize atoms:
  - Hot surface
  - Particle impact
  - Photons

- Interest of atomic physics:
  - study of the atom as an isolated system of electrons and an atomic nucleus
  - Processes: atom ionization and excitation by photons or collisions with particles
- Atomic physics for ion sources:
  - Energy required for ionization
  - Efficiency of ionization

Physical quantities and units

- Kinetic energy of charged particles is measured in *electron volts* (eV).
- 1 eV: energy acquired by singly charged particle moving through potential of 1 Volt.

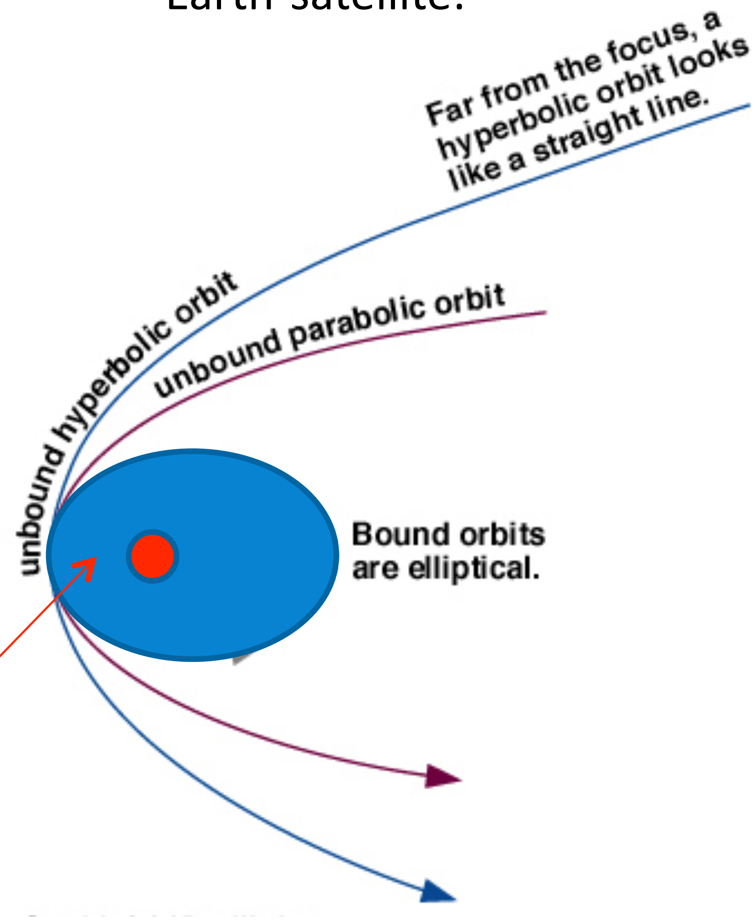
- 1 eV = e * (1 Volt) = $1.6022 \cdot 10^{-19}$ J
- Mass of electron: $m_e = 9.109 \cdot 10^{-31}$ kg
- Mass of proton: $m_p = 1.672 \cdot 10^{-27}$ kg
- Atomic mass unit = 1/12 carbon-12 mass: 1 u = $1.6606 \cdot 10^{-27}$ kg
- Elementary charge of particle is e = $1.6022 \cdot 10^{-19}$ C (or A*s)

- Electron with 1 eV kinetic energy is moving with a velocity of about 594 km/s
- 1eV = thermal energy at 11 600 K

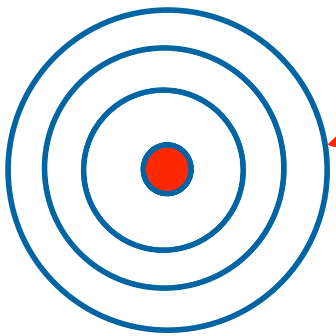
Electrons in an atom

- Analogy:
  - Satellite orbiting the Earth contains gravitational potential energy
  - Satellite can orbit the Earth at any height. Or, it can contain any amount of gravitation energy—its gravitational potential energy is continuous
- Similarly, electron orbiting nucleus possesses electric potential energy. But it can only stay in a finite number of discrete energy levels (or orbits)
- => **energy levels of atoms are 'quantized'**

Earth-satellite:



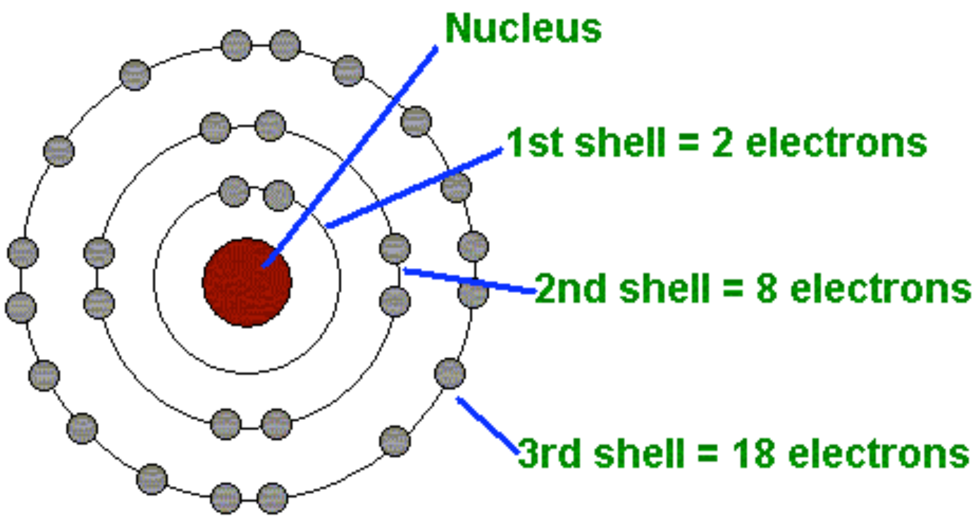
Nucleus-electrons



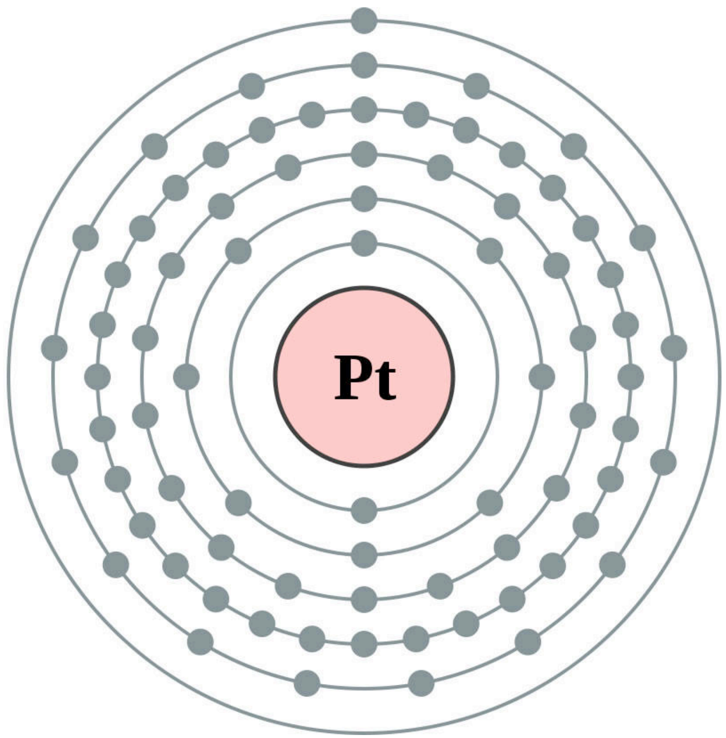
Allowed states

Electrons in an atom

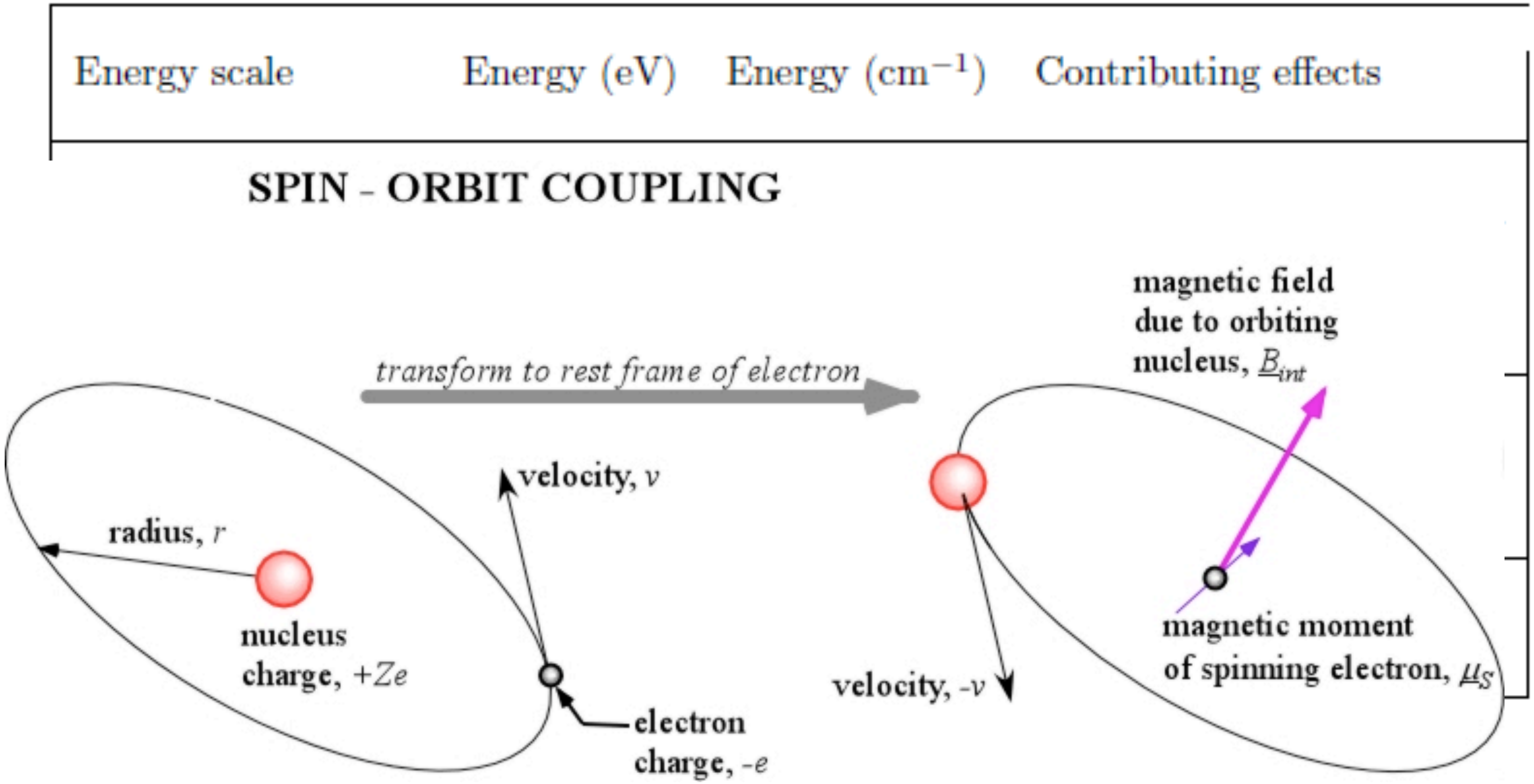
- Electrons orbit the atomic nucleus on orbits of fixed energy
- Energy of each electron level/orbit/shell is determined mostly by attraction of the nucleus and to a smaller degree by the repulsion of other electrons
- **Factors influencing electron energy: nucleus, el-el interaction, spin-orbit**
- Quantum mechanics is behind the existence of shells and the number of electrons on each shell



78: Platinum **2,8,18,32,17,1**



Atomic shell structure



Spin-orbit interaction: interaction between electron’s spin and orbital angular momentum (i.e. magnetic field generated by the electron's orbit around nucleus)
Hyperfine structure: nuclear spin experiences magnetic field due to current loop of electron and dipolar interaction of the electronic and nuclear spins

Electron quantum numbers

- n Principal Quantum Number (QN)
  - Specifies shell (radial dependence)
- l Azimuthal QN
  - s, p, d, f, … correspond to $l = 0, 1, 2, 3, \ldots n\text{-}1$
  - Gives orbital angular momentum $L^2 = \hbar^2 l(l+1)$
- m_l Magnetic QN
  - Projection of azimuthal QN along an axis ($-l < m_l < l$)
  - Projected angular momentum is $L_z = m_l \hbar$
- m_s Spin projection QN
  - Electron spin = (-1/2, 1/2)
- j total orbital angular momentum
  - Spin-orbit coupling: $j = 1/2, 3/2 \ldots n-1/2$, total: $J^2 = \hbar^2 j(j+1)$
- m_j orbital angular momentum
  - $m_j = -j\ ,-j+1 \ldots j$ and satisfies $m_j = m_l + m_s$

Quantum Numbers: describe the conserved quantities of the system: e.g. energy and angular momentum, spin

With spin-orbit interaction l, m, s no longer commute with Hamiltonian => change over time. Need new QN's

Electron quantum numbers

- In an electronic configuration, electrons can't have the same quantum number
  - Pauli exclusion principle
  - Applying this can be a bit complicated at times
- Some states may be indistinguishable
  - Have degeneracy rather than new configuration
- Example: Configuration: $2p^2$ ($n = 2$ with $2p$ electrons)
  - Important since this represents the electronic configuration of many of the most abundant ions

  - Total Spin: $S = 0$ (Singlet) or 1 (Triplet)
  - Orbital Angular Momentum: L = 0, 1, 2
  - Thus J ($= L + S$) could range from 0 to 3

Capital letters used for many-electron systems

When including interaction with nucleus of spin I:
Total angular momentum F; F quantum number F = |I-J|, … , I+J

Electron configuration

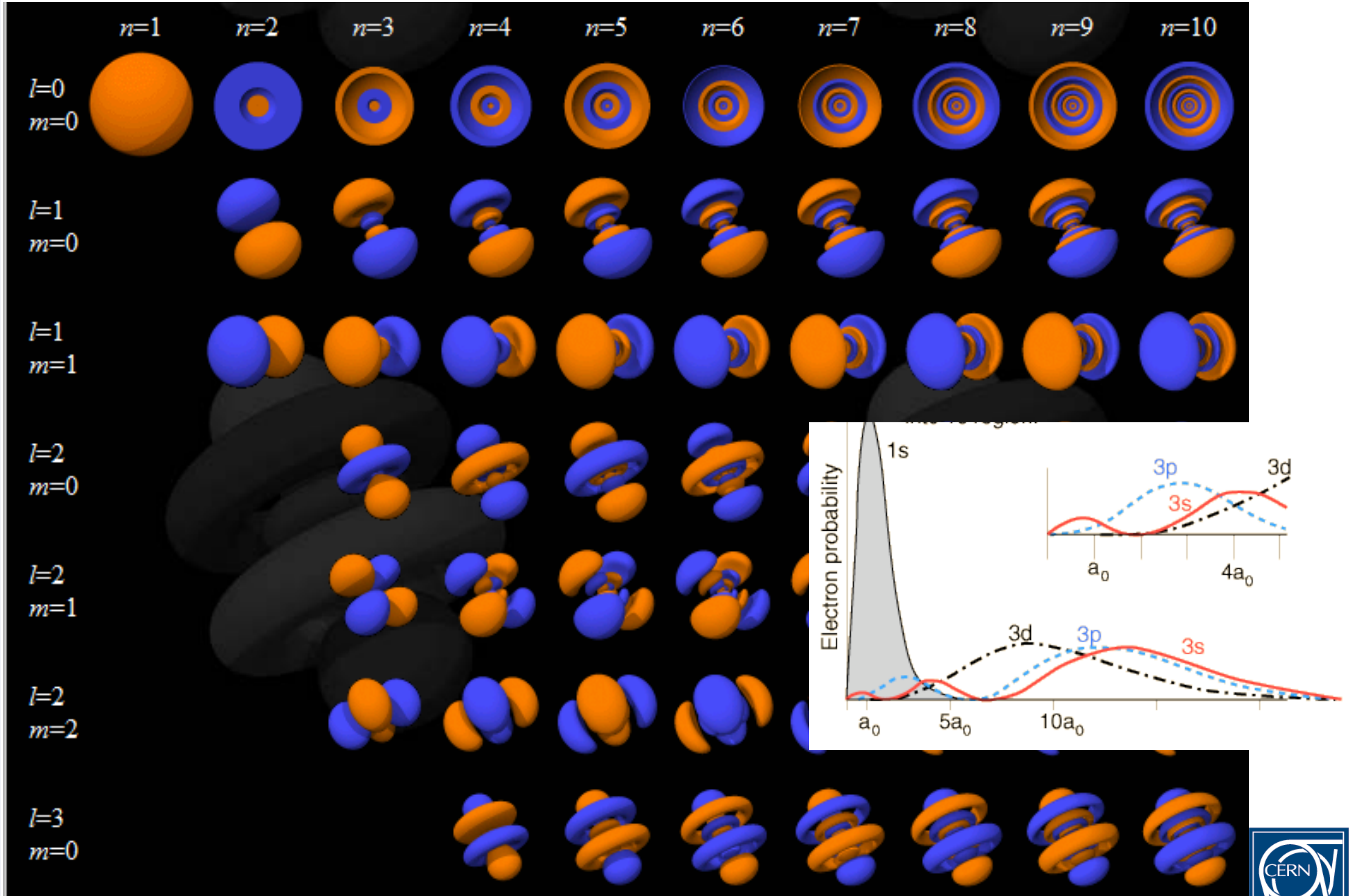
Quantum number	symbol	Value
principal	n	any integer > 0
orbital	l	integer up to $(n-1)$
magnetic	m_l	integer from $-l$ to $+l$
spin	m_s	$\pm 1/2$

$n = 1, 2, 3, ...$	$l = 0, 1, 2, ..., n-1$	$m = 0, \pm 1, \pm 2, ..., \pm l$	**Orbital**
1	**0**	**0**	$1s$
2	**0**	**0**	$2s$
2	**1**	**0**	$2p_z$
2	**1**	**+**	$2p_x$
2	**1**	**-**	$2p_y$

Orbital names: s, p, d, f, g, h ..:

sharp, principal, diffuse, fundamental, and then alphabetic

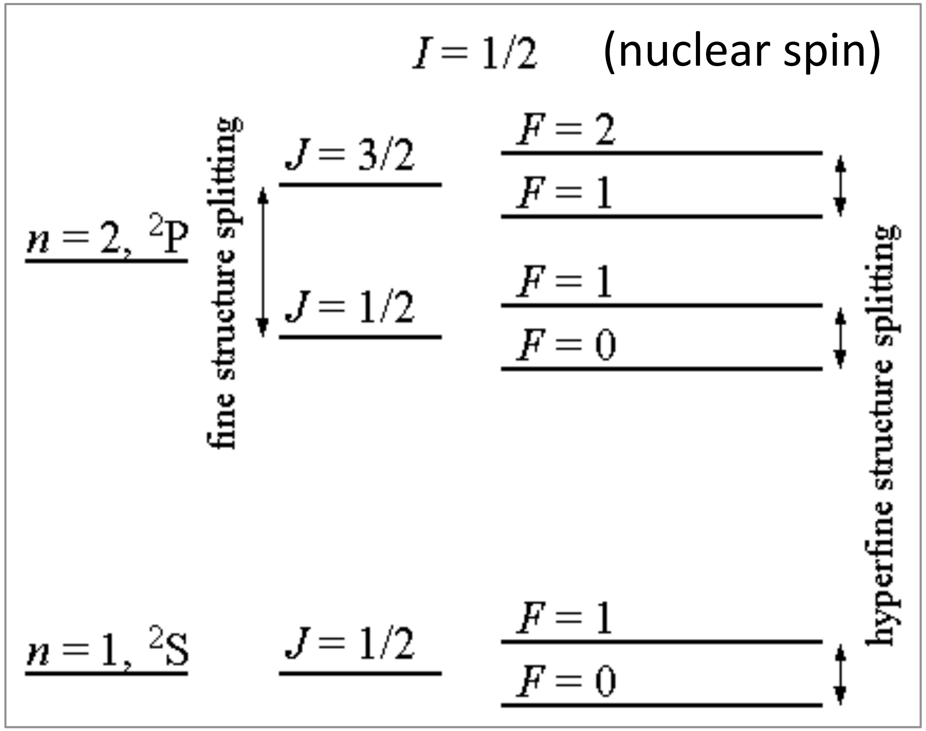
Electron orbitals



Electron terms

- Coming from valence electrons (those in outermost orbit)

Hydrogen terms



F=|J-I| to J+I

Term symbols contain 3 pieces of information:

$$^2\mathrm{P}_{3/2}$$

"Spin multiplicity" = 2*S*+1 (Where *S* is the total spin quantum number for the atom)

Gives *L*, the total orbital angular momentum quantum number for the atom:

S: *L = 0*

P: *L = 1*

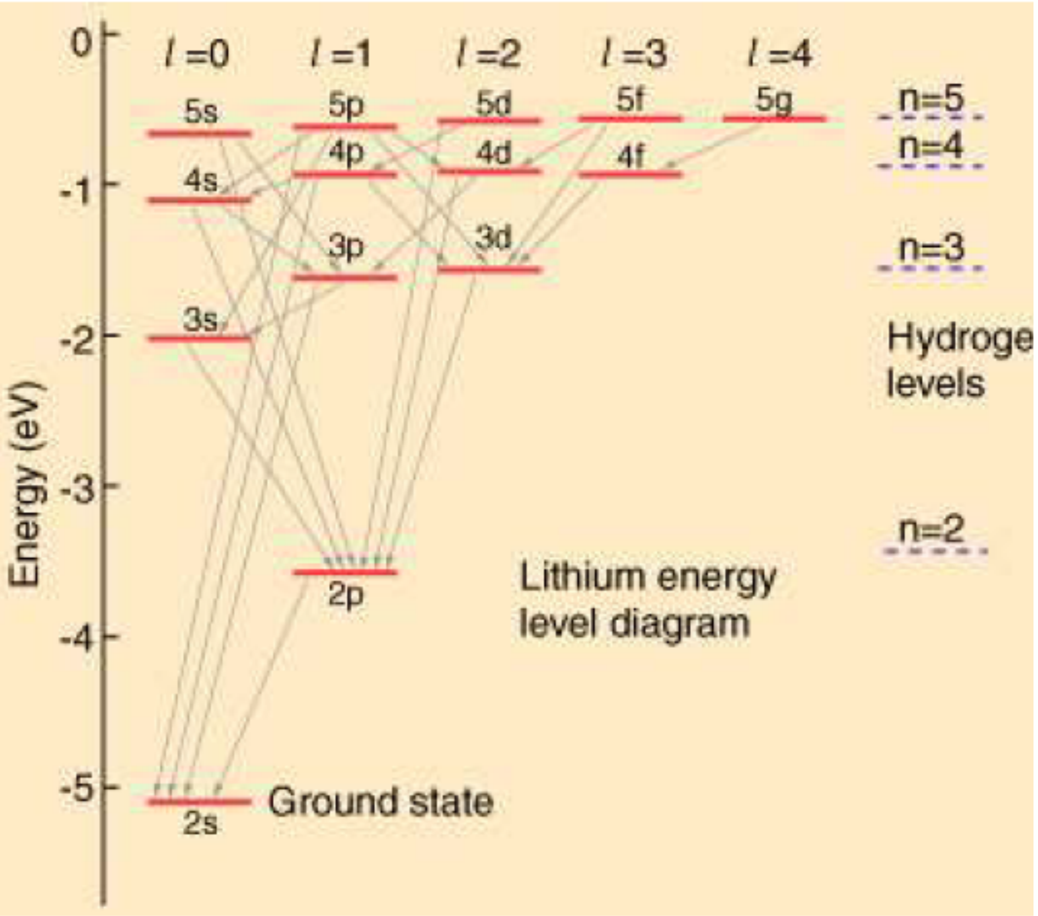
D: *L = 2*

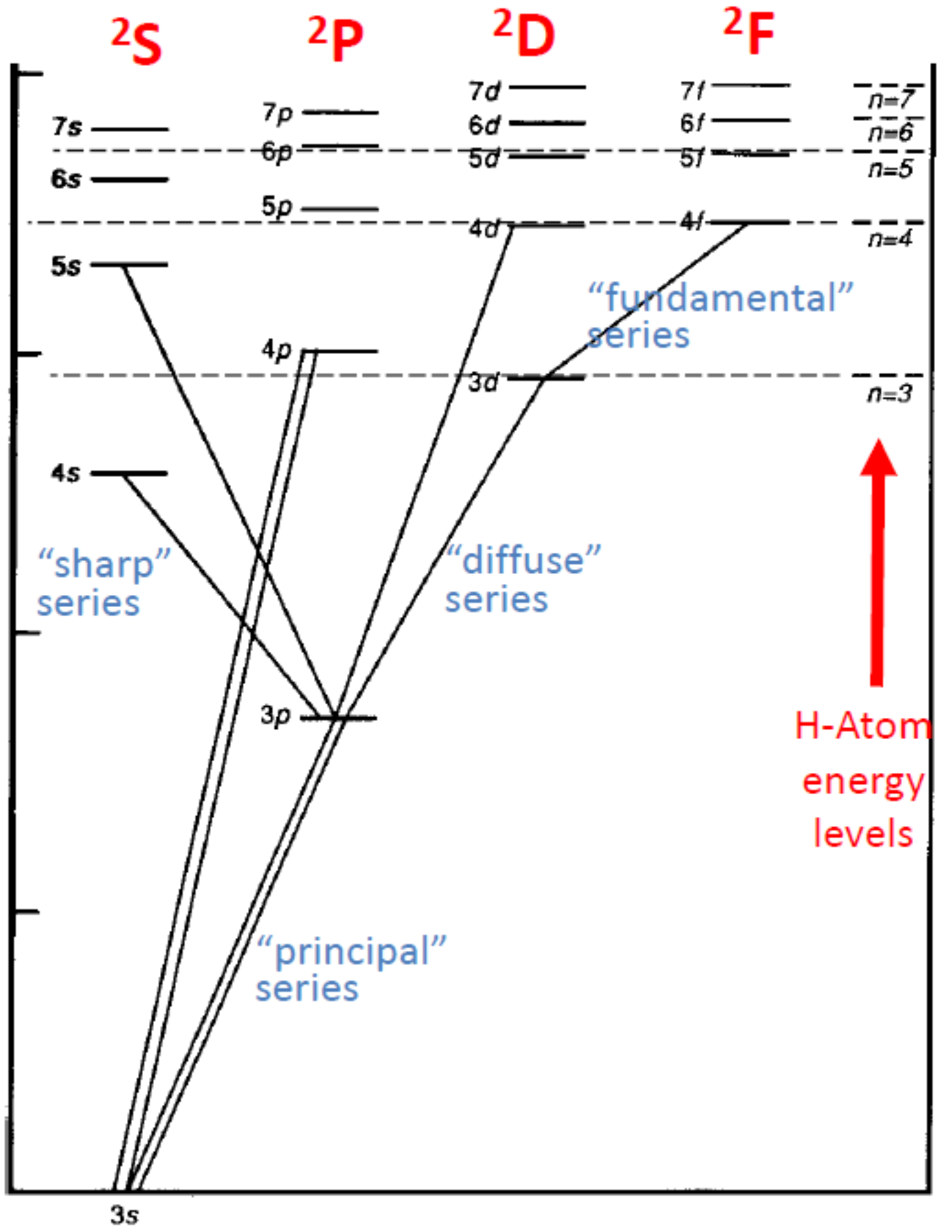
F: *L = 3, etc.*

J, the total angular momentum quantum number for the atom. *i.e.*, how *L* and *S* are coupled

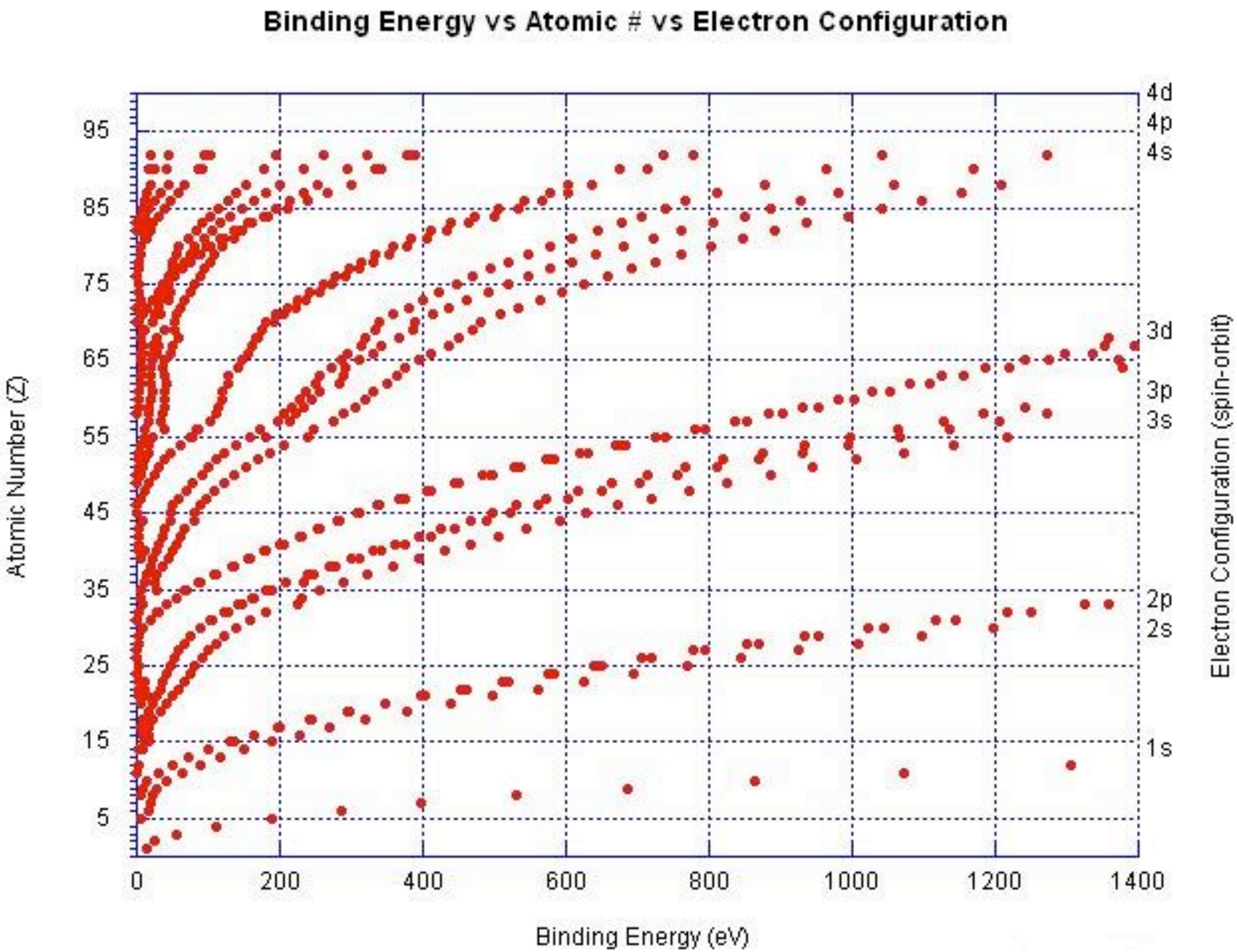
Electron configuration

- Examples:

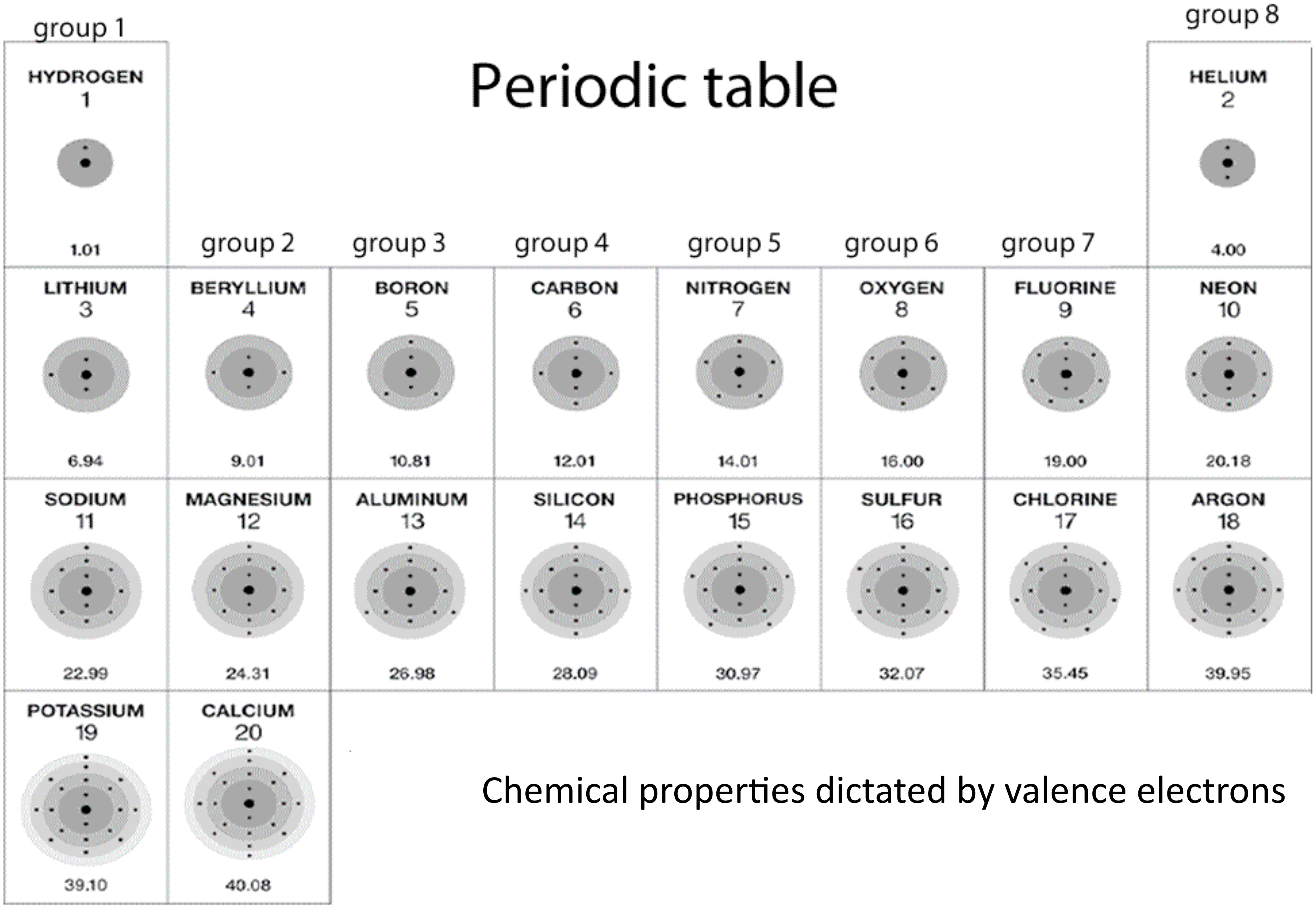




Electron binding energies



Periodic table of elements



Chemical properties dictated by valence electrons

Periodic table of elements

1 (1A) - alkali metals ($1s^1$-$7s^1$)
2 (2A) - alkaline earth metals ($1s^2$-$7s^2$)
17 (7A) - halogens ($2p^5$-$6p^5$)
18 (8A) - noble gases ($1s^2$,$2p^6$-$6p^6$)
14 (4A) - the Carbon family

New Designation / Original Designation

Atomic # / Symbol / Atomic Mass

s-block | d-block: *Transition Metals* | p-block: **Non-Metals** | **Metals**

Period	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 H 1.0094																	2 He 4.00260
2	3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
3	11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
4	19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 to 71	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.03	89 to 103	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)	110 Uun (267)								

(Mass Numbers in Parentheses are from the most stable of common isotopes.)

Phases: Solid, Liquid, Gas

Rare Earth Elements (d-block | f-block)

Series															
Lanthanide Series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide Series	89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

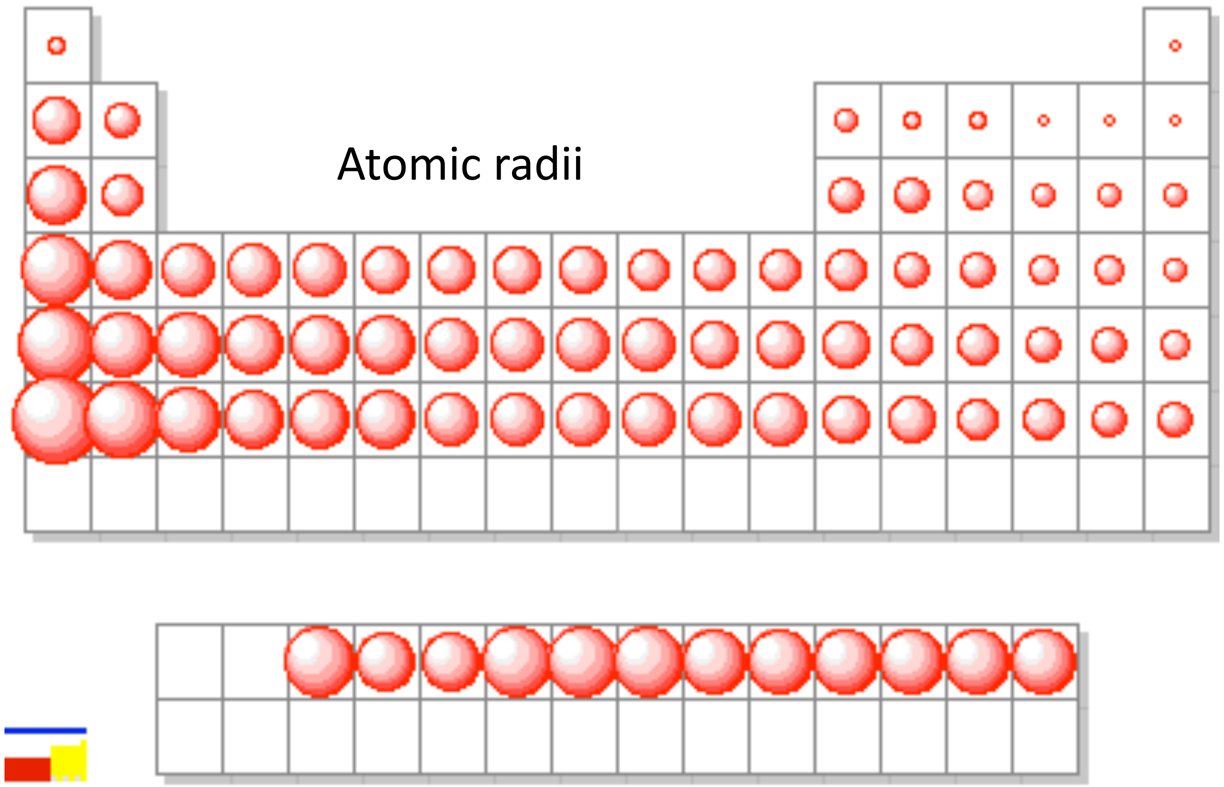
Ionization energy

- **Ionization energy (IE)**: **minimum energy required to remove an electron from gaseous atom** or ion (not solid or liquid)

- First ionization energy: minimum energy needed to remove an electron from the highest occupied sub-shell (outermost electron) of gaseous atom
- Second ionization energy: minimum energy needed to remove the second electron from the highest occupied sub-shell of gaseous atom
- Third, fourth, … ionization energy – analogous
- "Total" ionization energy: minimum energy required to remove all electrons from gaseous atom
- Naming: known also as ionization potential
- Units: eV or kJ/mol in chemistry
- It governs chemical properties of atoms

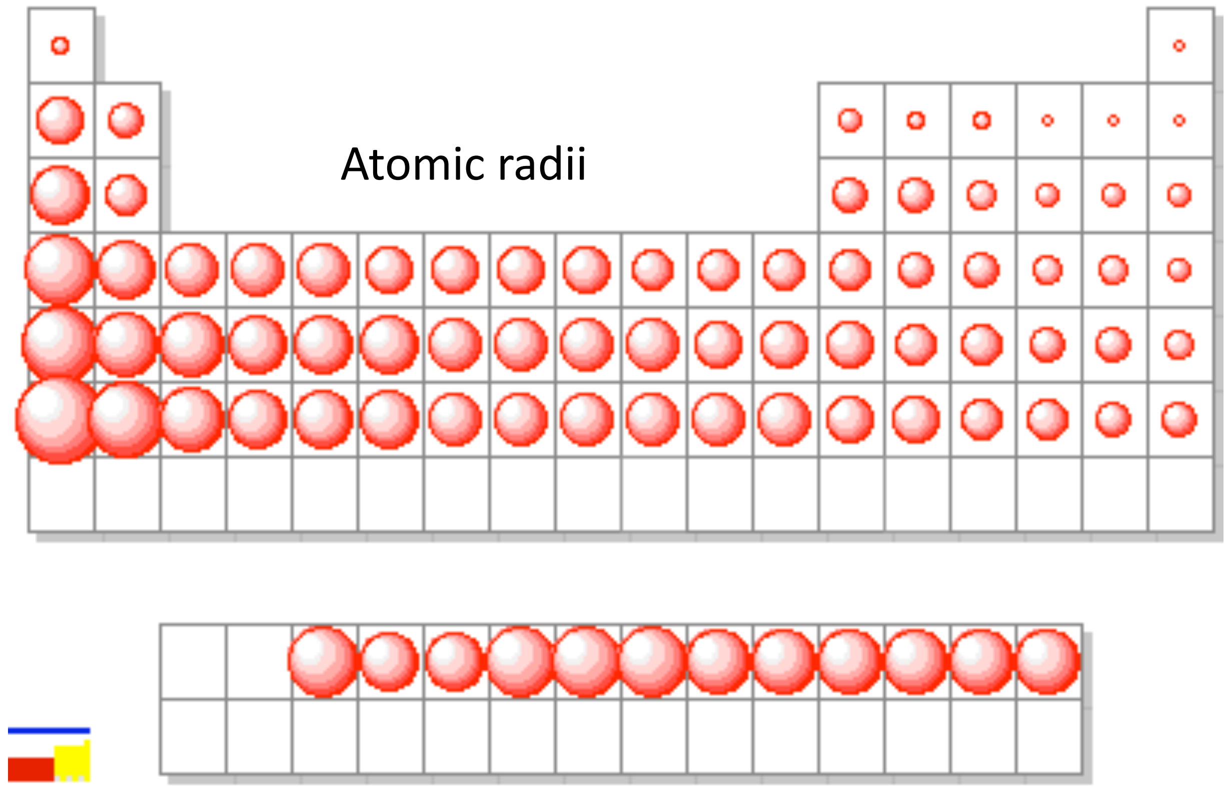
Ionization energy and shell structure

- **IE shows how easy it is to pull electron completely from atomic nucleus**
- IE is influenced by (in order of importance):
  - Nuclear charge – nucleus-electron attraction increases with nuclear charge
  - Number of shells – in presence of levels closer to nucleus outermost electrons are further from nucleus and are not so strongly attracted
  - Shielding – electrons on orbits closer to nucleus shield/protect outermost electron from attraction of nucleus
- Atomic radii and IE are connected
- What has lower 1st IE:
  - Mg or Ne
  - K or Ca
  - K or Rb
  - P or Ar
  - Etc …



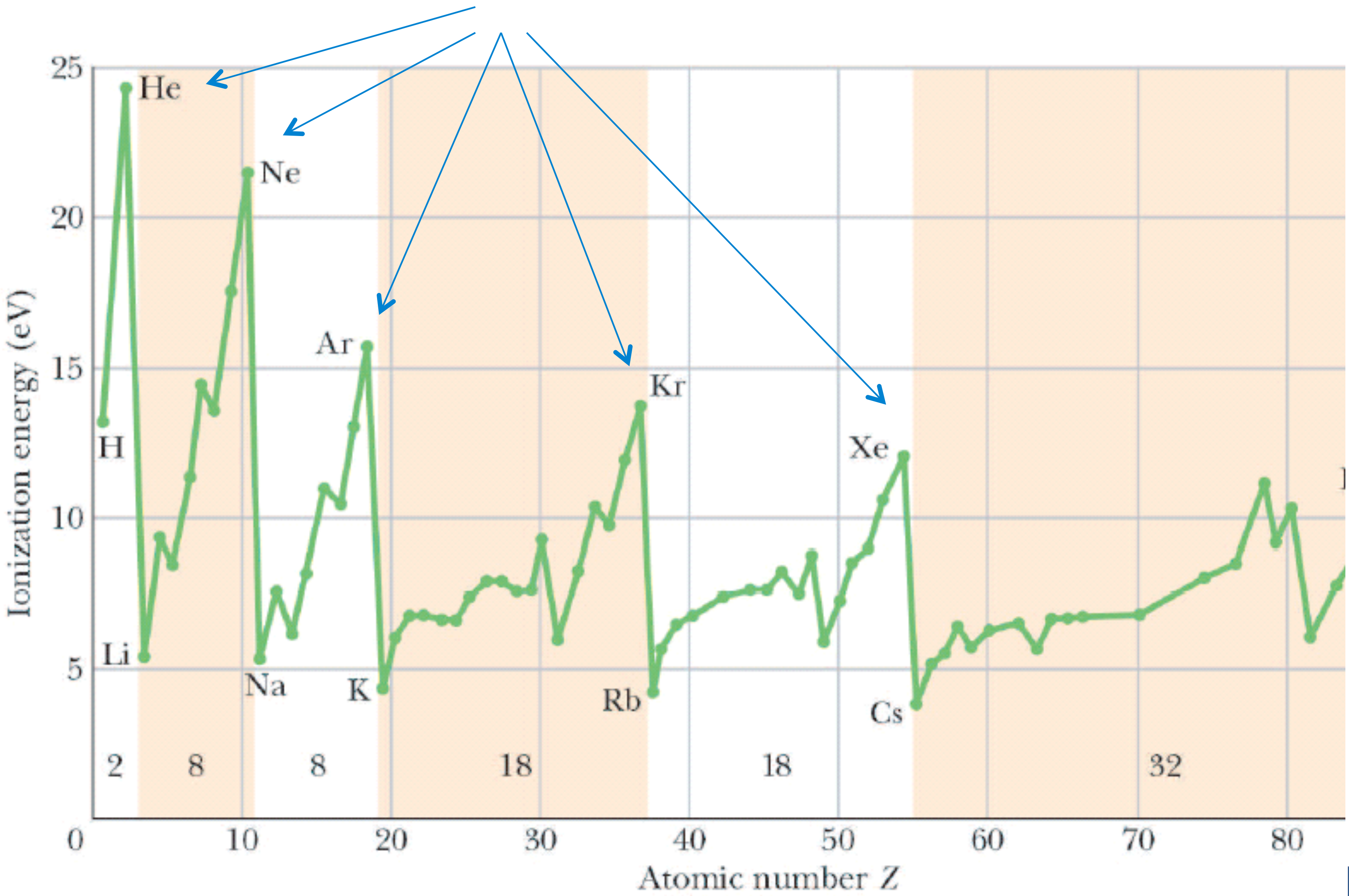
Ionization energy and shell structure

- Atomic size increases down a Periodic Table group while ionization energy decreases, as negative valence electron is further from positive nucleus
- 1st ionization energy generally increases across periods of Periodic Table due to increase in nuclear charge: additional electrons go into same shell, are about the same distance from nucleus, but positive nuclear charge increases
- 2nd ionization energy is larger than 1st, as electron is removed from positive ion
- As number of electrons in outermost shells increases across a period so too does the first ionization energy, therefore a high first ionization energy indicates shell or sub-shell that is almost full
- What has lower 1st IE:
  - Mg or Ne
  - K or Ca
  - K or Rb
  - P or Ar
  - Etc …



First ionization energy

- Closed-shell atoms



First ionization energy

CHEMIX - PERIODIC TABLE

Graphics | Close

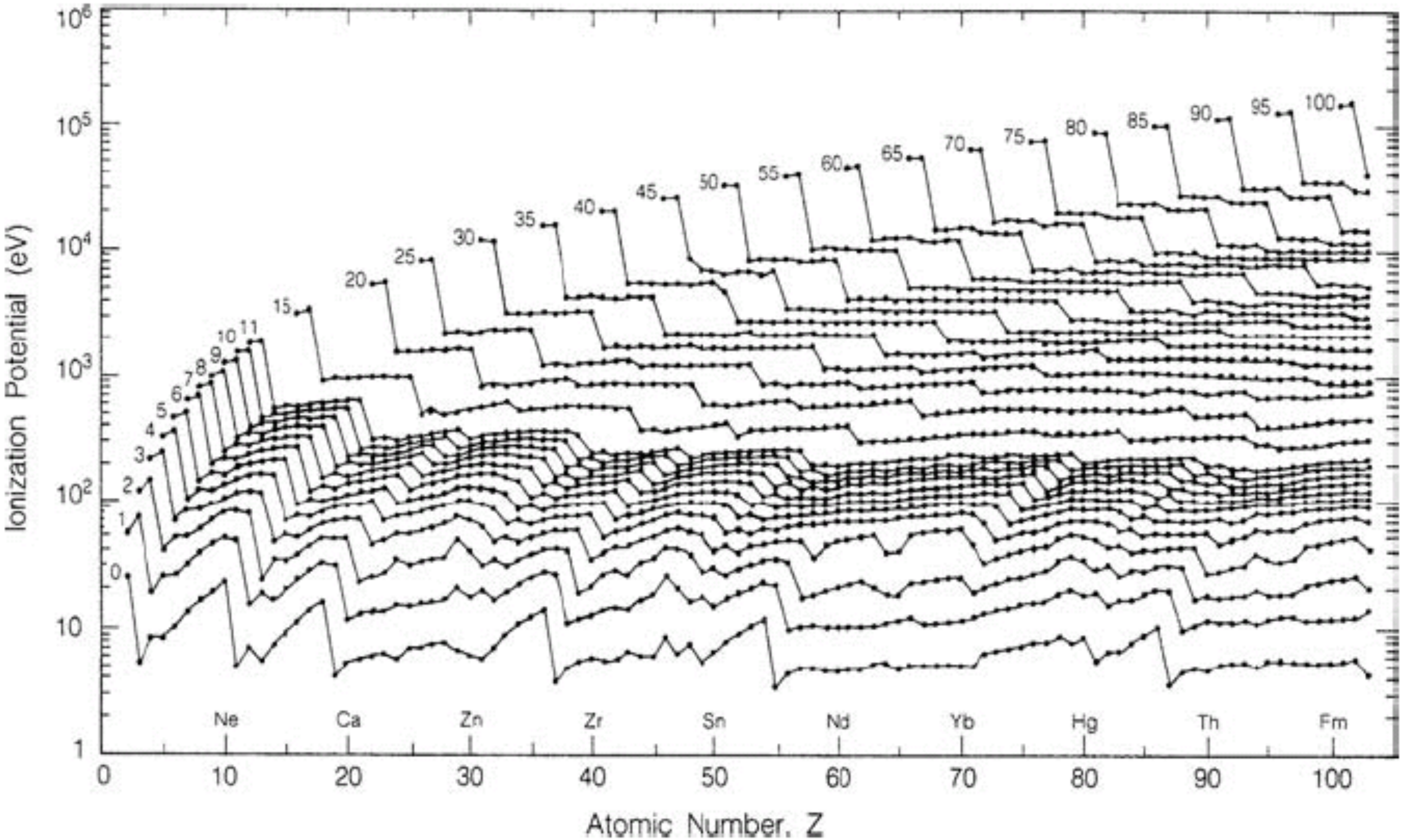
- Atomic number
- Name
- Relative atomic mass u
- Melting point °C
- Boiling point °C
- Density g/cm ^{3}
- Covalent radius $*10^{-10}$ m
- Atomic radius $*10^{-10}$ m
- Atomic volume cm ^{3} /mol
- (selected) First ionization potential V
- Specific heat capacity $Jg^{-1}K^{-1}$
- Electrical conductivity $*10^6 Ohm^{-1}cm^{-1}$
- Thermal conductivity $Wcm^{-1}K^{-1}$
- Electronegativity Pauling
- Heat of fusion kJ/mol
- Heat of vaporization kJ/mol
- Acid-base properties
- Number of stable isotopes
- Electron configuration
- Oxidation states
- Phase 20 °C
- Crystal structure

Group

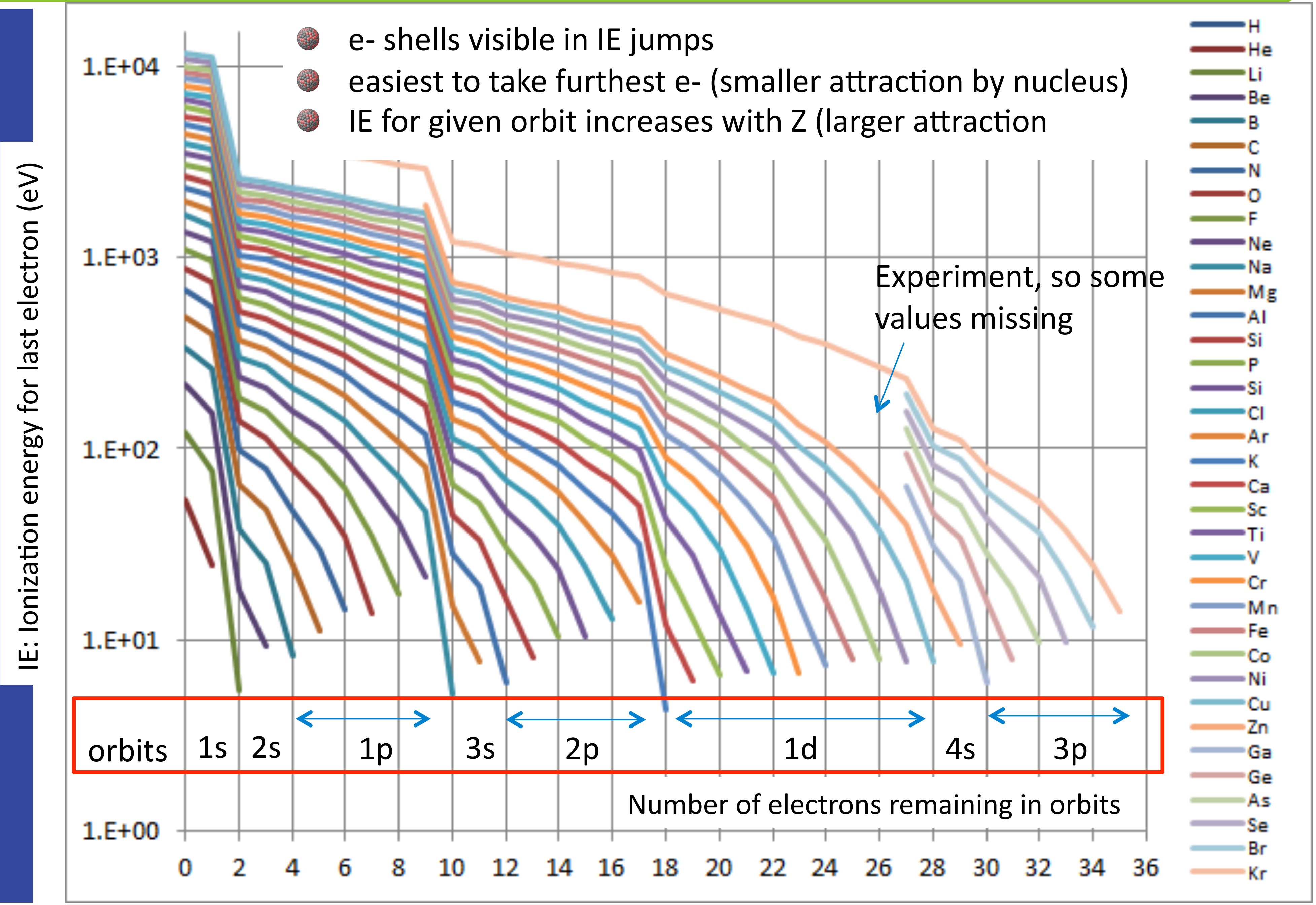
1/IA	2/IIA	3/IIIB	4/IVB	5/VB	6/VIB	7/VIIB	8/VIII	9/VIII	10/VIII	11/IB	12/IIB	13/IIIA	14/IVA	15/VA	16/VIA	17/VIIA	18/VIIIA
13.59																	24.58
H																	He
5.392	9.322											8.298	11.26	14.53	13.61	17.42	21.56
Li	Be											B	C	N	O	F	Ne
5.139	7.646											5.986	8.151	10.48	10.36	12.96	15.75
Na	Mg											Al	Si	P	S	Cl	Ar
4.341	6.113	6.540	6.820	6.740	6.766	7.435	7.870	7.860	7.635	7.726	9.394	5.999	7.899	9.810	9.752	11.81	13.99
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
4.177	5.695	6.380	6.840	6.880	7.099	7.280	7.370	7.460	8.340	7.576	8.993	5.786	7.344	8.641	9.009	10.45	12.13
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
3.894	5.212	5.580	6.650	7.890	7.980	7.880	8.700	9.100	9.000	9.225	10.43	6.108	7.416	7.289	8.420		10.74
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	5.279	5.170															
Fr	Ra	Ac															
				5.540	5.460	5.530	5.554	5.640	5.670	6.150	5.860	5.940	6.018	6.101	6.184	6.254	5.430
Lanthanides ->				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				6.080	5.890	6.050	6.190	6.060	5.993	6.020	6.230	6.300	6.420	6.500	6.580	6.650	
Actinides ->				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Ionization energy

- Ionization energy for multiply charged ions



Ionization energy

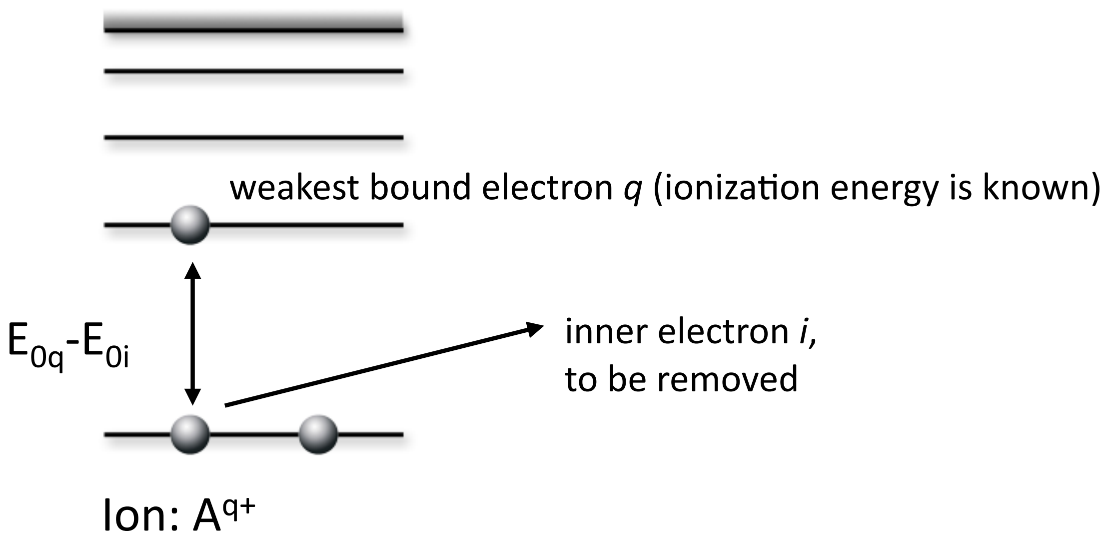


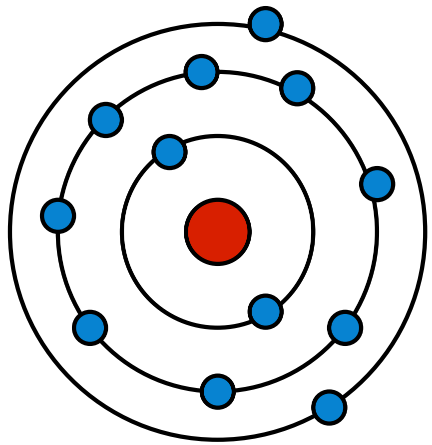
Ionization energy

- When ionization energies for more bound electrons are not known, **Carlson-correction** is used:
- Ionization energy $P_{q,i}$ is calculated from ionization energy $W_i(q)$ of ion with charge state *q* and the atomic binding energies of electrons (measured or calculated)

$$P_i = E_{0i} + W_i(q) - E_{0q}$$

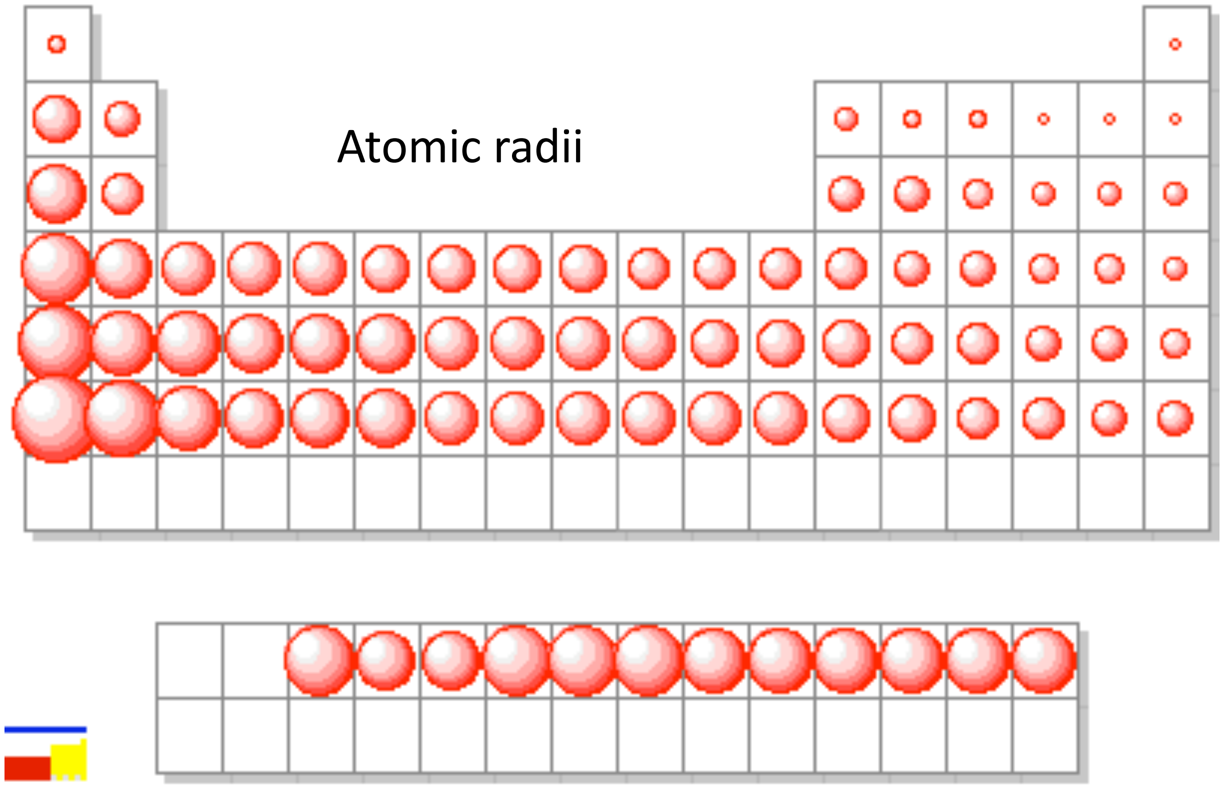
E_{0i} : binding energy of an electron in the i-th shell of an atom
E_{0q} : atomic binding energy of the electron, which is the weakest bound electron in the ion of the charge state q
$W_i(q)$: ionization energy of the ion (describes always the weakest bound electron)





Negative ions: electron affinity

- **Electron affinity (EA):** energy given off when neutral atom in gas phase gains extra electron to form *negatively charged ion*
- IE is influenced by the same effects as EI:
  - Nuclear charge
  - Number of shells
  - Shielding
- Atomic radii and IA are connected



Electron affinity

- Electron affinity <0 – negative ion is not stable

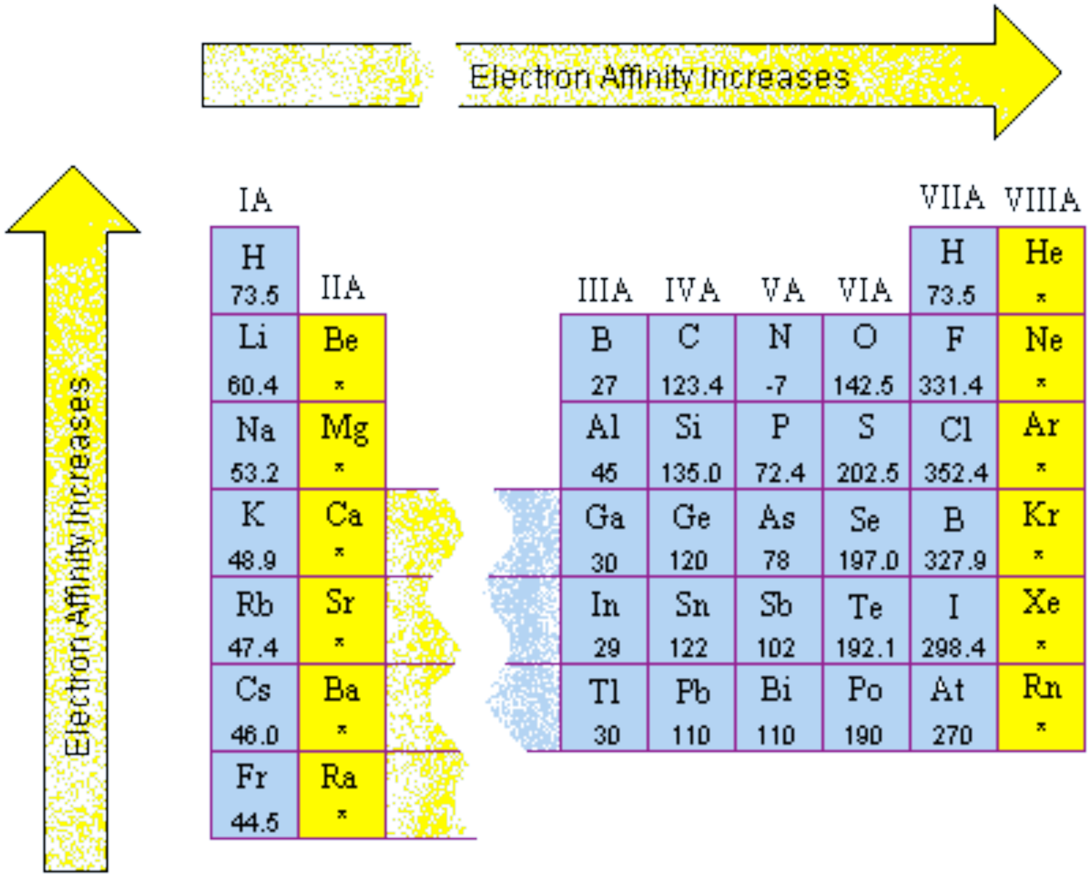
Electron affinities and ionization energies of elements

Ionization potential (eV)
– Electron affinity (eV)

Group I A	II A	III A	IV A	V A	VI A	VII A	VIII A
1 H 13.59 0.75							2 He 24.58 0.078
3 Li 3.39 0.62	4 Be 9.32 < 0	5 B 8.30 0.28	6 C 11.26 1.26	7 N 14.54 ≤ 0	8 O 13.61 1.46	9 F 17.42 3.39	10 Ne 21.56 < 0
11 Na 5.14 0.54	12 Mg 7.64 < 0	13 Al 5.98 0.46	14 Si 8.15 1.38	15 P 10.55 0.74	16 S 10.36 2.07	17 Cl 13.01 3.61	18 Ar 15.76 < 0
19 K 4.34 0.50	20 Ca 6.11 ≈ 0	31 Ga 6.00 0.3	32 Ge 7.88 1.2	33 As 9.81 0.80	34 Se 9.75 2.02	35 Br 11.84 3.36	36 Kr 14.00 < 0
37 Rb 4.18 0.48	38 Sr 5.69 < 0	49 In 5.78 0.3	50 Sn 7.34 1.25	51 Sb 8.64 1.05	52 Te 9.01 1.97	53 I 10.45 3.06	54 Xe 12.13 < 0
55 Cs 3.89 0.47	56 Ba 5.21 < 0	81 Tl 6.11 0.3	82 Pb 7.41 1.1	83 Bi 7.29 1.1	84 Po 8.43 1.9	85 Ar 9.5 2.8	86 Rn 10.74 < 0

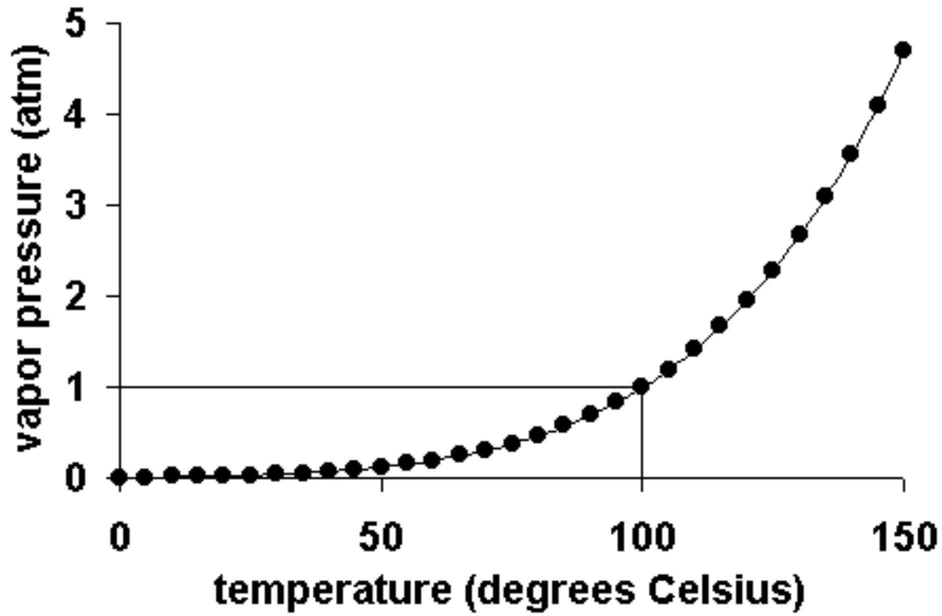
Electron affinity patterns

- Electron affinities get smaller when going down a column of periodic table:
  - ➢ electron added to atom is placed in larger orbitals, where it spends less time near nucleus
  - ➢ number of electrons on atom increases as we go down a column, so repulsion between electron being added and electrons already present on a neutral atom becomes larger
- Electron affinity data are complicated because repulsion between electron added to atom and electrons already present depends on atom's volume

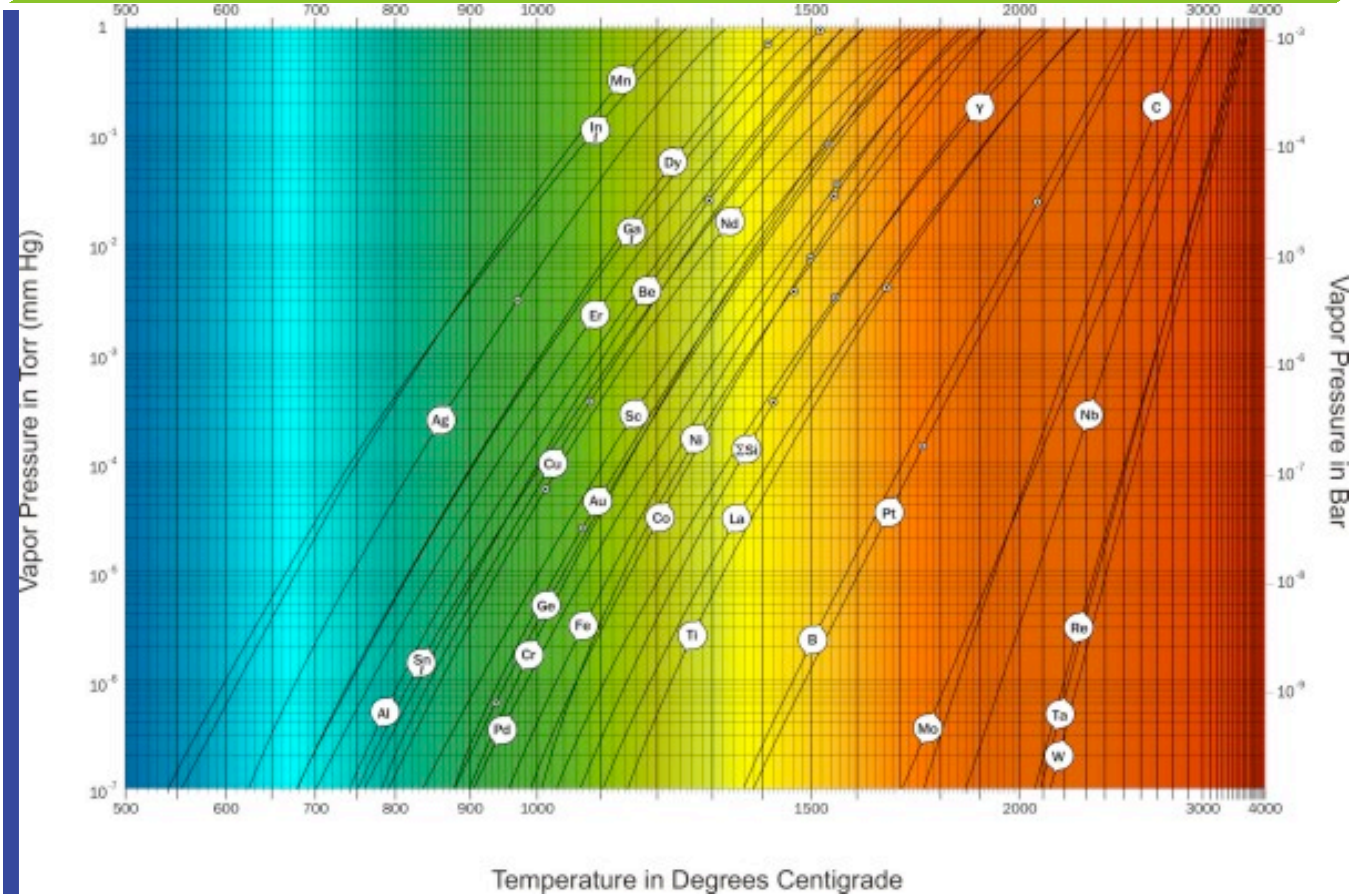


Vapour pressure

- vapor pressures: equilibrium pressure of vapour above its liquid (or solid); pressure of the vapour resulting from evaporation of a liquid (or solid) above a sample of the liquid (or solid) in a closed container
- vapor pressures at ambient temperatures increase with decreasing boiling points
- Important especially in surface ion sources



Vapour pressure



Atomic processes in ion sources

In most ion sources, ions are produced in a plasma.
The basic atomic processes (selection) in plasmas are:

collisions with electrons

Impact Ionization		Three-Body-Recombination (TBR)
$A^{Z+} + e$	$\leftrightarrow$	$A^{(Z+1)+} + e' + e''$

Impact excitation		Impact disexcitation	
$A^{Z+} + e$	$\leftrightarrow$	$\left(A^{Z+}\right)^* + e'$	⇨ Non-radiative transition

> A^{Z+}: Atom of species A with charge state Z
> e': electron changed energy

collisions with photons

Photo ionization		Radiative Recombination (RR)	
$A^{Z+} + h\upsilon$	$\leftrightarrow$	$A^{(Z+1)+} + e$	⇨ Line spectrum

Excitation		Spontaneous emission
$A^{Z+} + h\upsilon$	$\leftrightarrow$	$\left(A^{Z+}\right)^*$

Photo absorption		Bremsstrahlung	
$A^{Z+} + h\upsilon + e$	$\leftrightarrow$	$A^{Z+} + e'$	⇨ Continuous spectrum

The electron changes from one free state to another free state with lower energy.

Atomic processes in ion sources

From these multiple processes arise the dynamic balance quantities:

- Distribution of the abundance of all charge states Z (=0...Z_{max}), **Ionization equilibrium**
- Number of emitted and absorbed photons per time interval, **Radiative equilibrium**

The density of the particle species are determined from so-called **rate equations**:

$$\frac{dn}{dt} = \text{souces} - \text{sinks}$$

Example: impact ionization:

$$\frac{dn_{z+1}}{dt} = n_e \cdot n_z \cdot v_e \sigma_{z \to z+1} - n_e \cdot n_{z+1} \cdot \beta_{z+1,TBR}$$

$\beta_{z+1,\ TBR}$: rate coefficient for Three-Body-Recombination (TBR)

The **rate coefficients** often not be calculated with sufficient precision; experimental data are only available to a limited extent. Therefore one tries to obtain data from thermo dynamical equilibrium.

With decreasing electron density the TBR drops, so that the impact ionization is not in equilibrium with the TBR anymore. The RR rate also decreases but not as strong. With decreasing n_e also the photo ionization becomes unlikely. As result the impact ionization and the RR-process dominate. The photons leave the plasma without being re-absorbed.

Atomic processes in ion sources

$$q^{n+} \rightarrow q^{(n+1)+}$$

$$q^{n+} \rightarrow q^{(n-1)+}$$

- **Ionization**
  - single-ionization
  - double-ionization

  The production of higher charge states is a successive process

  The ionization has energy threshold → higher charge states need higher projectile energies (electron energies)

- **Charge exchange**
  (for low charge states)

- **Recombination**
  - radiative recombination
    The cross section is larger for lower electron temperatures
  - dielectronic recombination
    (resonant process)

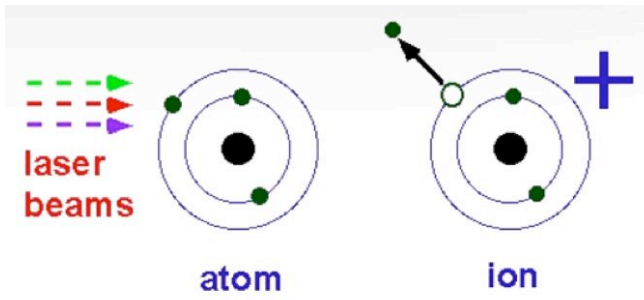
- **Charge exchange**
  (for high charge states)

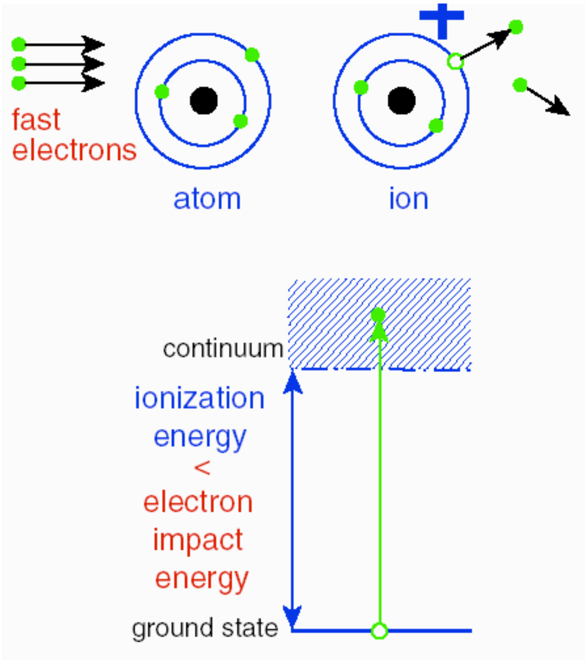
  depending on the neutral particle density residual gas)

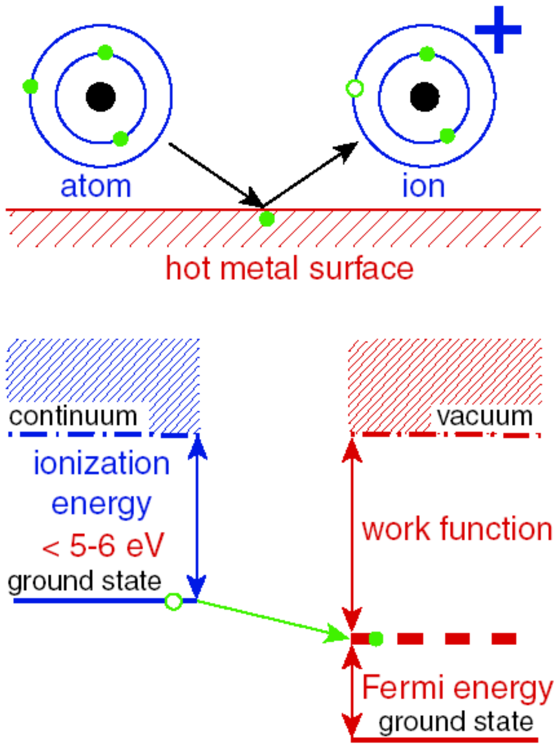
  cross section are larger for higher charge states

Ways to ionize atoms

- Positive ions:
  - Electron impact
  - Photons
  - Hot surfaces
- Negative ions:
  - Electron attachment
  - Charge exchange of a positive ion on a hot surface or in metal vapour
  - (Molecule dissociation)
  - (Molecule excitation)

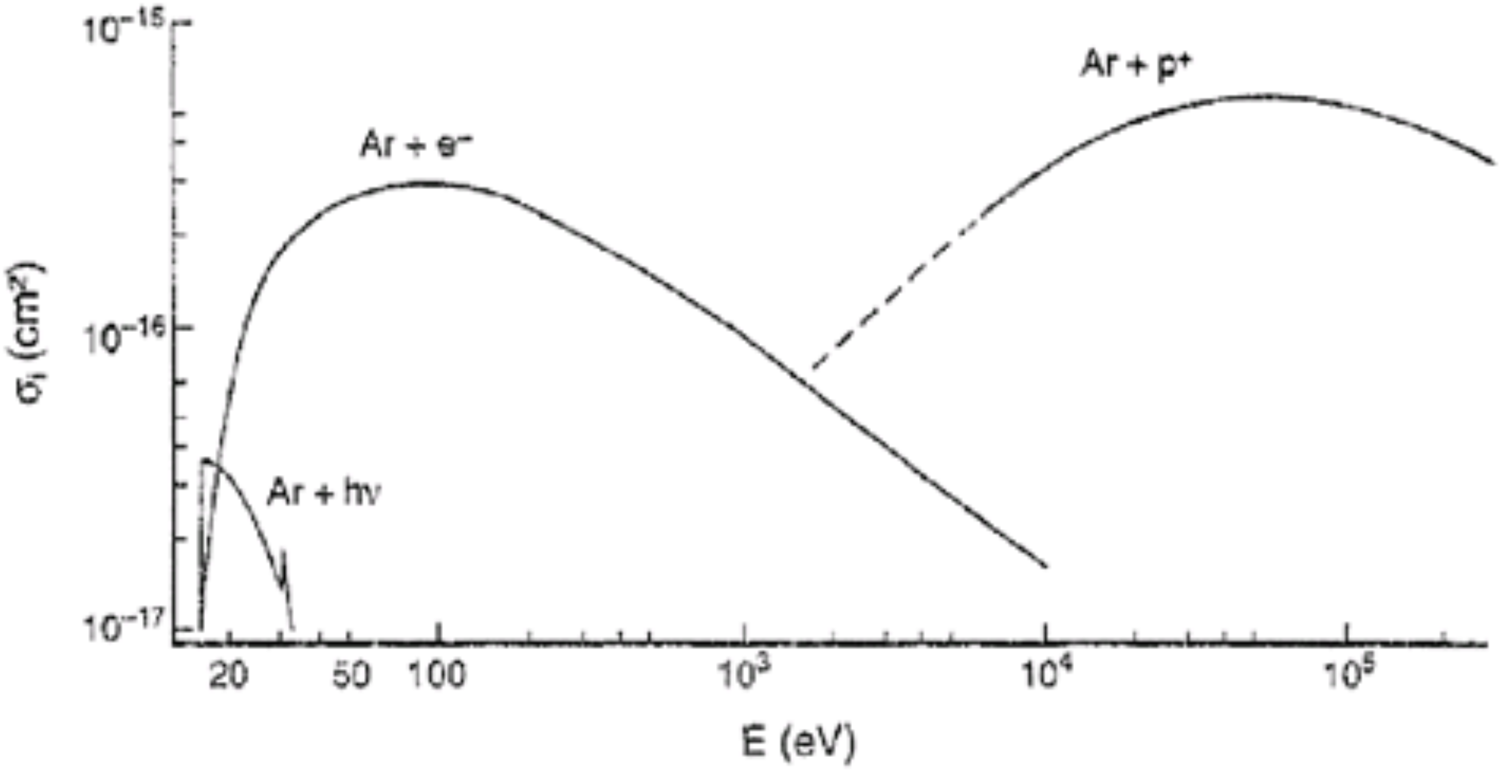






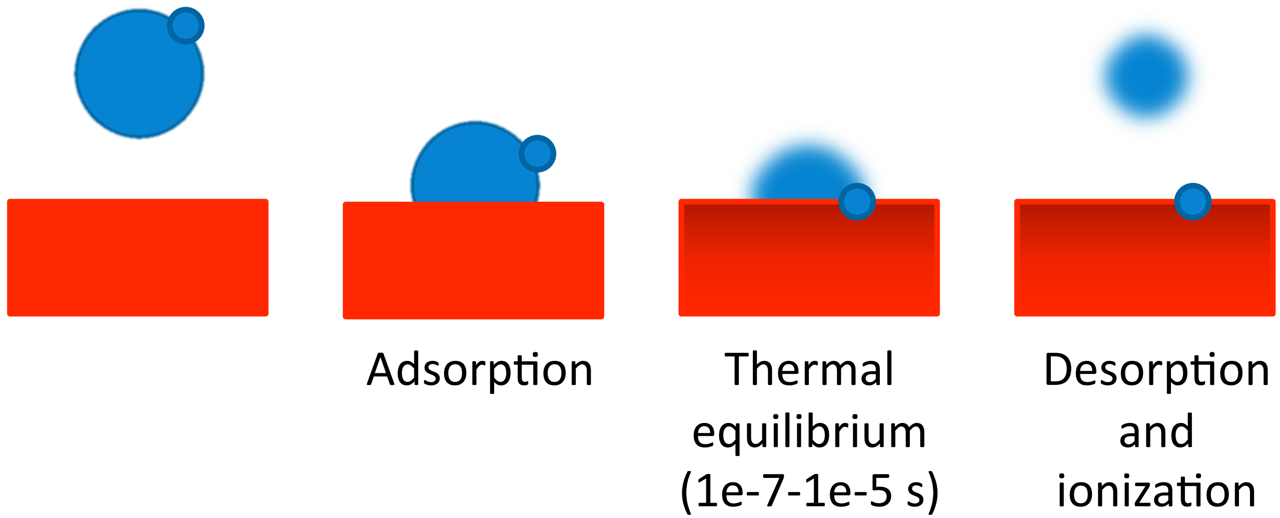
Ways to ionize atoms

- Ionization cross sections for Ar vs energy of ionizing collisions with:
  - Photons
  - Electrons
  - protons



Surface ionization

- **Surface ionization: ionization by contact with a (metal) surface**
- Requirements:
  - Atom sticks (is adsorbed) to the surface long enough to reach thermodynamic equilibrium => atom valence electron is "broadened" and can move between atom and surface
  - Surface is hot enough to desorb particles: some are neutral atoms, or positive/negative ions
- Material work function (W) = minimal energy required for an electron to escape the material surface
- Work function for elements follows a trend similar to ionization energy



Surface ionization

- Degree of positive surface ionization: **Saha-Langmuir equation**

Constant describing atom properties

Material **work function**

Atom **ionization energy**

$$Pi = \frac{ions}{atoms} = G\ \exp\left(\frac{W - Ei}{kT}\right)$$

Boltzman's constant

Material **temperature**

- Not important: Charge state before adsorbing on the surface (due to equilibrium)
- Important: material work function and state of particles before desorption (but after adsorption), i.e. atom ionization energy

$$G = \frac{g_i}{g_A}\frac{1-r}{1-r_0} = \frac{2J_i+1}{2J_A+1}\frac{1-r}{1-r_0}$$

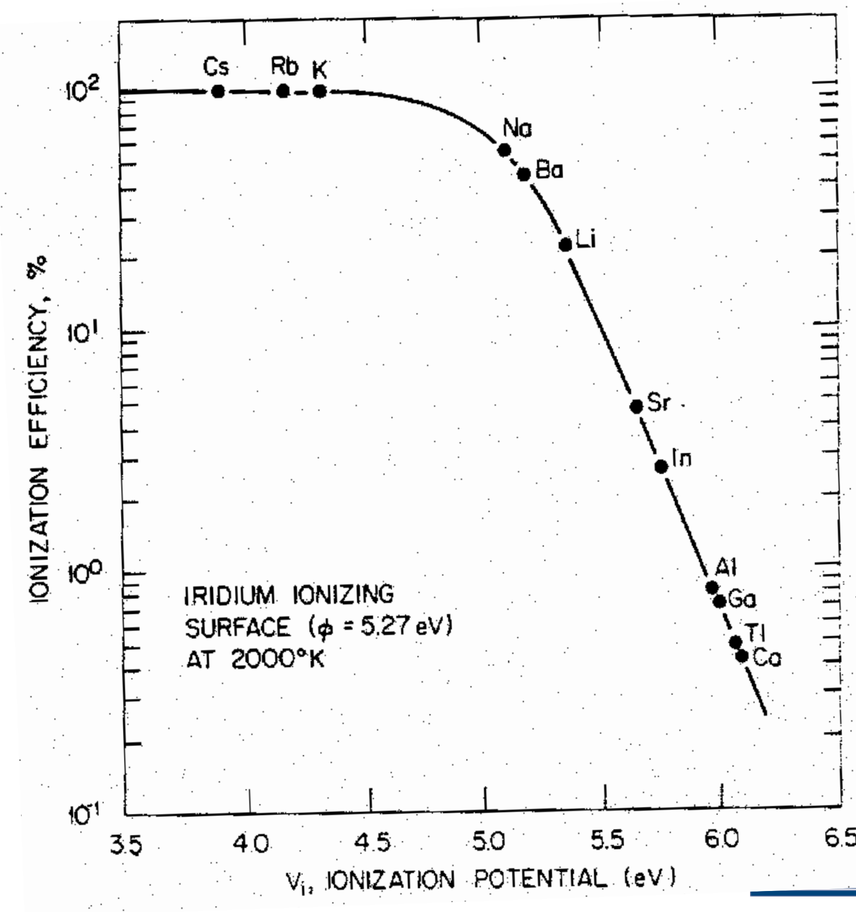
gi/gA=1/2 for group I and 2 for group II

J = 0, 1, … = quantum number (electron total angular momentum)
r = 0 to 1, reflection coefficient

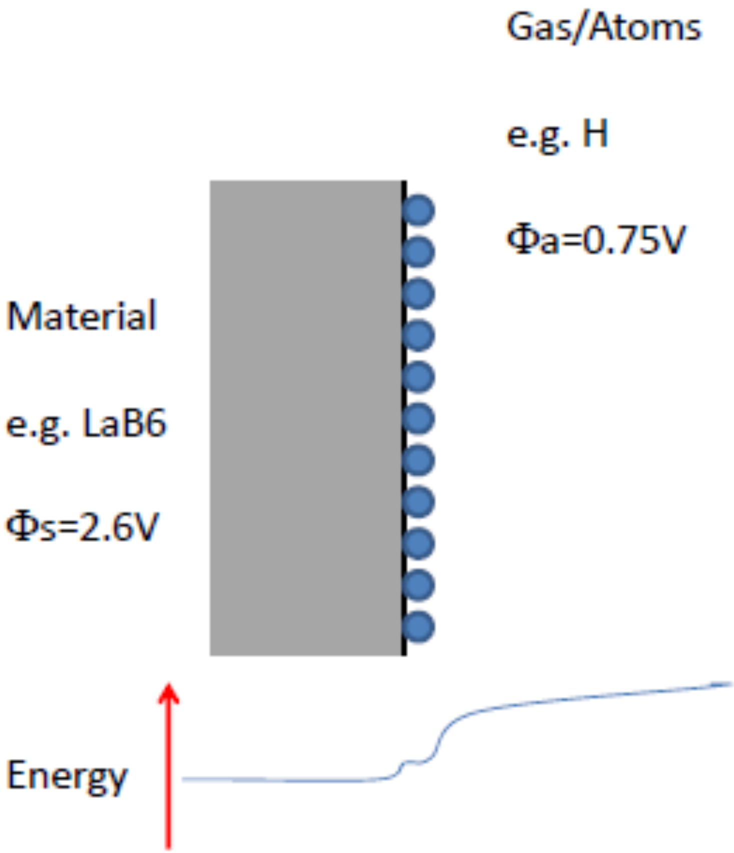
Surface ionization

particle	Ei (eV)	W-Ei (eV)	Pi(1000 K)	Pi(1500 K)	Pi(2000 K)	Pi(2000 K)
Cs	3.88	0.64	790	72	20	10
K	4.32	0.20	6.3	2.2	1.6	1.3
Na	5.12	-0.60	5e-4	5e-3	1.6e-2	3e-2
Li	5.40	-0.88	2e-5	6e-4	3e-3	8e-3

- Pi decreases with increasing T if *W-Ei* > 0
- Surface ionization possible also for W-Ei<0
- T must be sufficiently high to evaporate given element (e.g. Li, Na).
- On the contrary, the diffusion of surface material must be low enough (< 10% of a mono-layer), to keep the ionization conditions as constant as possible
- **=> trade-off required**



Surface negative ionization



- If the base material has a low work-function, and the atoms a high electron affinity-
- The electrons have a finite probability of being present on the electron.
- Use plasma bombardment to liberate the atoms from the surface.
- Use a alkali metal coating deposited on the surfaces inside a plasma discharge source, to produce the ions.

See 1st lecture

Resonant ionization by photons

RILIS (Resonant ionization laser ion source)

absorption

$h\nu + E_l \rightarrow E_u$

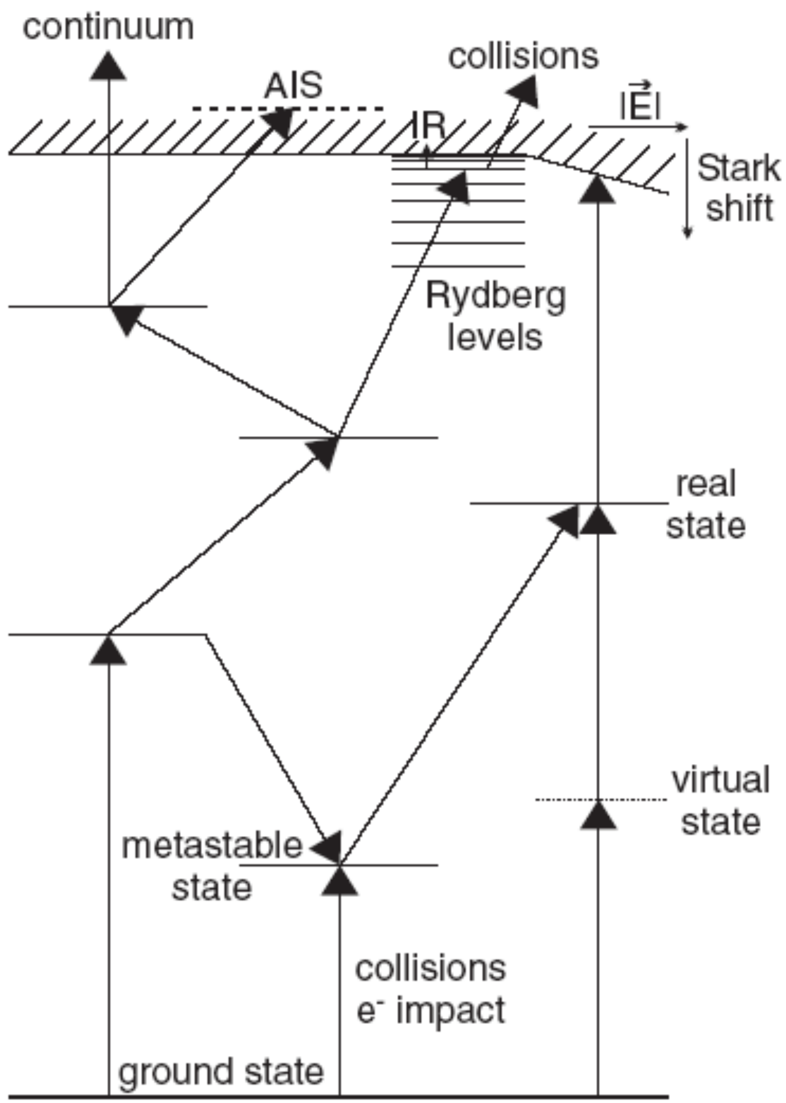
emission

spontaneous (isotropic) $E_u \rightarrow E_l + h\nu$

stimulated (direction of incoming photon) $h\nu + E_u \rightarrow E_l + 2h\nu$

<u>Orders of magnitudes for the cross sections:</u>

- non-resonant (direct ionization): $\sigma = 10^{-19} - 10^{-17}$ cm^2
- resonant: $\sigma = 10^{-10}$ cm^2
- AIS (auto-ionizing states): $\sigma = 1.6 \times 10^{-14}$ cm^2
- Rydberg states: $\sigma \sim 10^{-14}$ cm^2

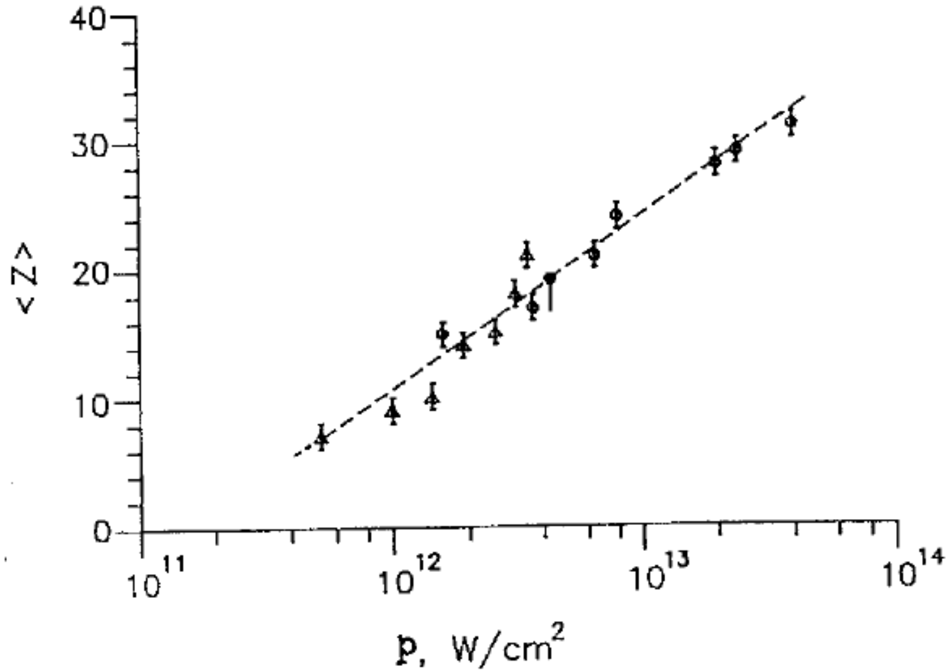


Excitation schemes used for resonant laser ionization

Non-resonant photo-ionization

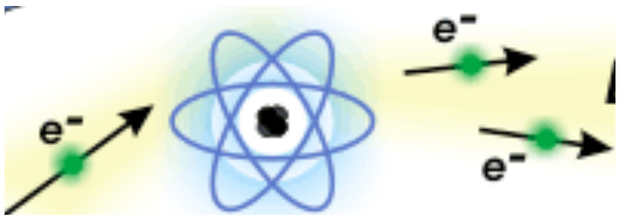
- In contrast to resonant ionization, ions/ plasma within this source is generated via energy deposition
- Laser frequency couples to free electron plasma frequency (either in material, or formed plasma)
- The laser beam penetrates material
- Local heating of electrons by inverse Bremsstrahlung + excitation of atoms
- Material is ablated and an expanding plasma-plume develops
- If plasma density is lowered and cut-off frequency drops below laser-frequency, laser light can re-enter plasma.
- => Electrons inside plasma are accelerated up to 100 keV

Charge state vs laser power



Ionization by particle impact

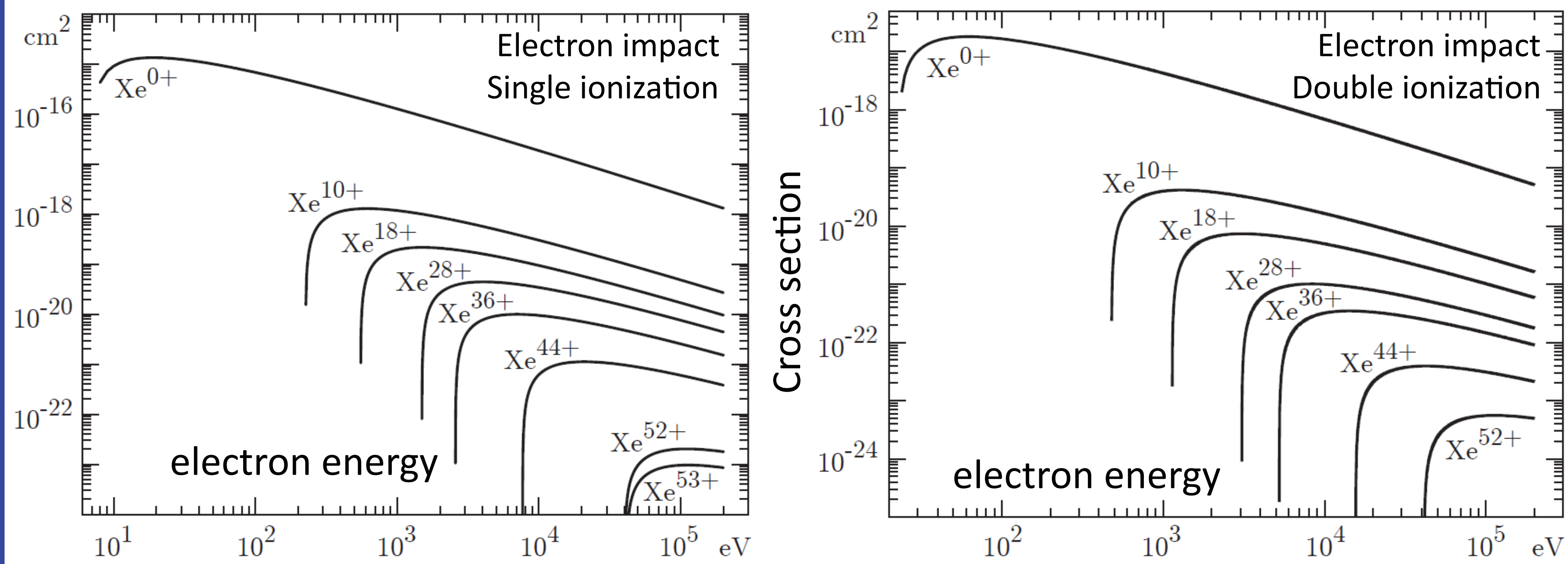
- Impact ionization is by orders of magnitudes higher than cross section for photo ionization
- Cross section depends on mass of colliding particle: energy transfer of a heavy particle is lower, proton needs for an identical ionization probability an ionization energy three orders of magnitudes higher than electron
- Thus, electrons are most common ionizing particles



- Processes involved:
  - Direct knockout ionization
  - Indirect processes (based on inner-shell excitation and subsequent autoionization); more important for heavier atoms

Ionization by electron impact

- Ionization cross section: electron energy has to be > ionization energy



- For energetic reasons most probable process is ionization releasing only one electron from atomic shell
- To produce highly charged ions, kinetic energy of projectile electrons has to be at least equivalent to *n*-th ionization potential

Ionization by electron impact

- Approximation of cross section and ionization time for production of bare ions from H-like ions using Mosley's law, for X-ray frequencies emitted in transitions from continuum to K-shell:

σ – single ionization cross-section cm²
j_e – electron current density A/cm²

$$E_{i\to k}(Z) = 13.6\cdot Z^2\ [eV] \Rightarrow$$

$$\sigma_{z-1\to z} = 4.5\cdot 10^{-14}\cdot \frac{\ln e}{e\cdot 13.6^2 Z^4} = \frac{9\cdot 10^{-17}}{Z^4}$$

with $E = e\cdot E_{i\to k}(Z)$

$$\nu_{z-1\to z} = \frac{j_e}{e}\sigma_{z-1\to z} = \frac{1}{\tau_{z-1\to z}}$$

$$\Rightarrow\quad j_e\tau_{z-1\to z} = \frac{e}{\sigma_{z-1\to z}} \approx \frac{eZ^4}{9\cdot 10^{-17}} \approx \left(\frac{Z}{5}\right)^4$$

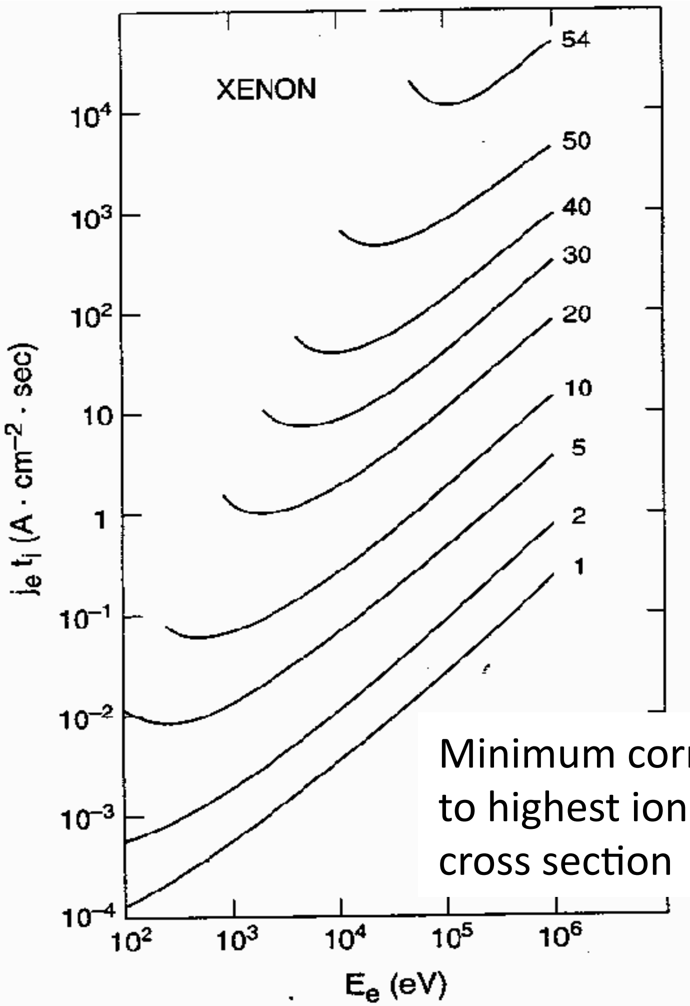
Ionization by electron impact

- Lotz formula: semi-empirical formula for cross-section of multiple ionization

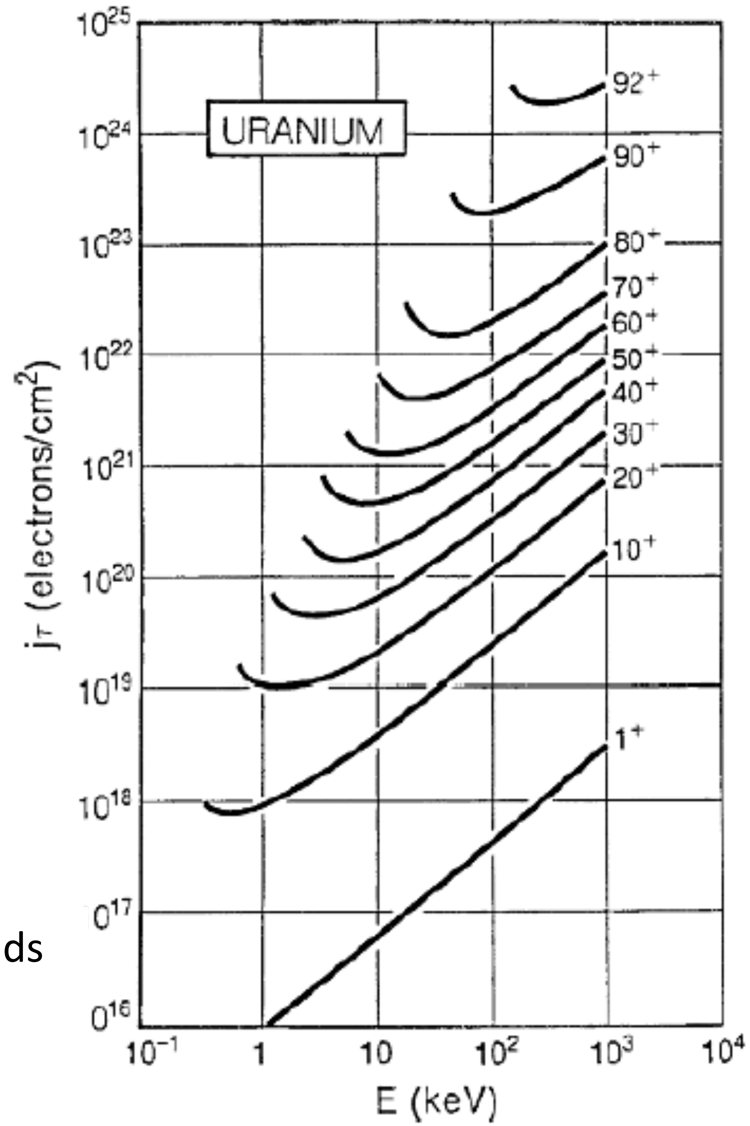
$$\sigma_{q\rightarrow q+1} = 4.5\cdot 10^{-14}\cdot \sum_{nl} \frac{\ln\left(E_{kin}/P_i\right)}{E_{kin}\cdot P_i} \quad [\mathrm{cm}^2]$$

Higher E

Ionization factor $j_e{}^*\tau$ for different charge states of Xe depending on electron energy



Minimum corresponds to highest ionization cross section



W. Lotz, Zeitschrift fuer Physik 206, 205 (1967)

Ionization by electron impact

- Lotz formula in detail:
  - 3 parameters to represent cross sections for single ionization from ground-state
  - Approximates almost all data within 10% and within exp. errors for up to 10keV-electrons
  - Empirical formula, but with proper theory basis: follows earlier theoretical work on e-e scattering, uses approximation of starting and final wave functions, gets parameters from fits

Total ionization cross-section; # of subshell; # of electrons in subshell

$$\sigma = \sum_{i=1}^{N} a_i q_i \frac{\ln(E/P_i)}{E P_i} \{1 - b_i \exp[-c_i(E/P_i - 1)]\};$$

E<E(max cross section):

$$\sigma = \sum_{i=1}^{N} a_i q_i \frac{\ln(E/P_i)}{E P_i} \{1 - b_i \exp[-c_i(E/P_i - 1)]\};$$

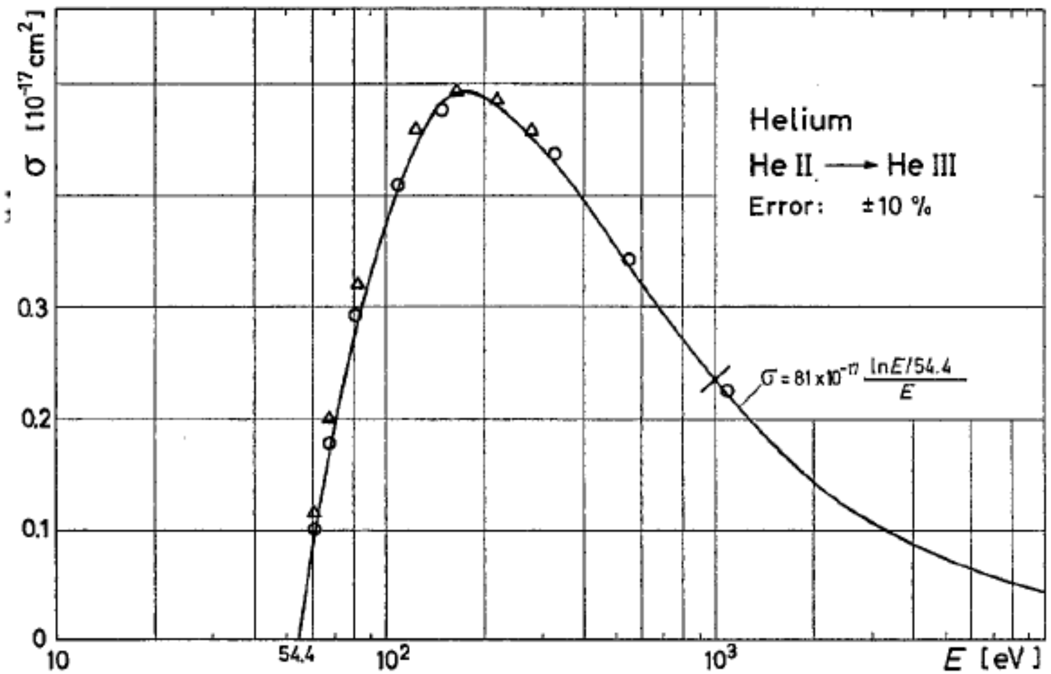
E close to Pi

$$U = E/P_1.$$

$$\sigma \approx a_1 q_1 \frac{(E/P_1 - 1)}{P_1^2}(1 - b_1) \propto U - 1$$

E >>Pi $\sigma_i = a_i q_i \frac{\ln(E/P_i)}{E P_i} \propto \frac{\ln E}{E}.$

a_i= 2.6 – 4.5 e-14 cm2 (empirically)



W. Lotz, Zeitschrift ftir Physik 206, 205 (1967)

Optimal electron energy

- Where $\sigma(E)$ has maximum, ionization factor $j_e * \tau$ has minimum there
- Cross section for the last electron, which is removed, determines ionization time

$$\frac{d\sigma_{z\to z+1}}{dE} = 4.5\cdot 10^{-14}\cdot \sum_{i=1}^{N} \frac{d}{dE}\left(\frac{\ln\left(E_{kin}/P_i\right)}{E_{kin}\cdot P_i}\right) = 0$$

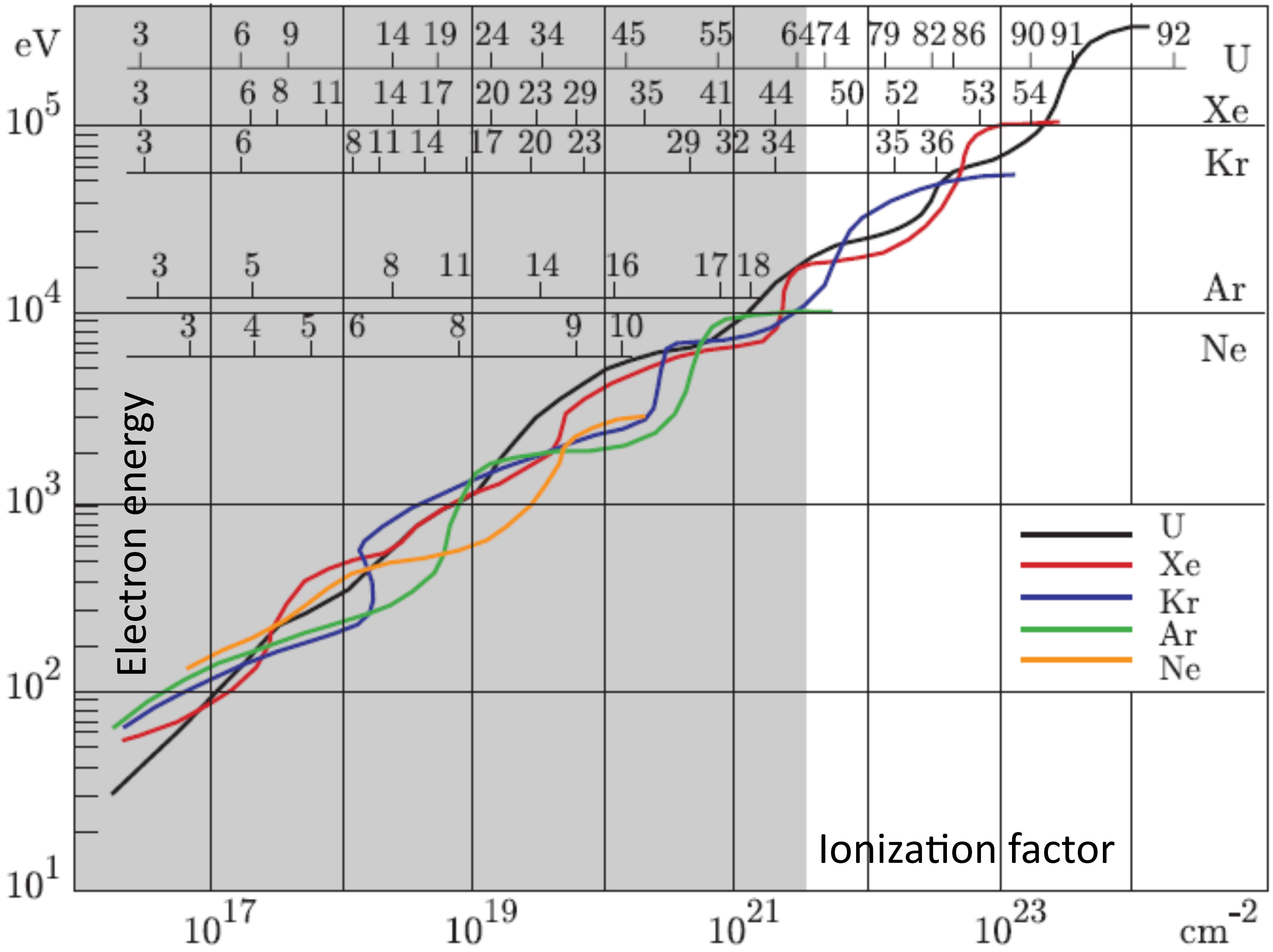
$$\sum_{i=1}^{N} \frac{1}{P_i E^2}\left(1-\ln\left(\frac{E}{P_i}\right)\right) = 0 \quad \Rightarrow \quad E_{\max} = \exp\left(\frac{\sum_{i=1}^{N}\frac{1+\ln P_i}{P_i}}{\sum_{i=1}^{N} 1/P_i}\right) = e\cdot\exp\left(\frac{\sum_{i=1}^{N}\frac{\ln P_i}{P_i}}{\sum_{i=1}^{N} 1/P_i}\right)$$

- Optimal energy of last electron, which is removed:

$$E_{\max} \approx e\cdot\exp\left(\frac{\frac{\ln P_z}{P_z}}{1/P_z}\right) = e\cdot P_z$$

- => Optimal energy is nearly e-times ionization energy of last electron removed from ion with charge state z

Ion. factor and optimal electron energy



Summary

- Atomic physics governs many aspects of ion sources
- Electron shell structure determines energy required to excite electrons and even to eject them from atoms (ionization)
- These energies dictate chemical properties of elements
- There are different paths to atom ionization (surface, particle, photon impact)
- Their details depend on electron structure of ionized atoms and involve many atomic physics processes

Literature

- B. Wolf, *Handbook of ion sources, CRC Press 1995*
- G. Brown, *The physics and technology of ion sources, 2004, Wiley VCH Verlag GmbH, ISBN 3-527-40410-4*
- F.J. Currell, *The Physics of Multiply and Highly Charged Ions Volume 1: Sources, Applications and Fundamental Processes , 2004, Kluwer*
- O. Kester, *Lectures on Ion Sources:* *http://acc.physik.uni-frankfurt.de/vorlesung/vorlesung.html*
- Ch. Foot*, Atomic Physics, Oxford University Press 2005*

Additional slides

Ionization by particle impact

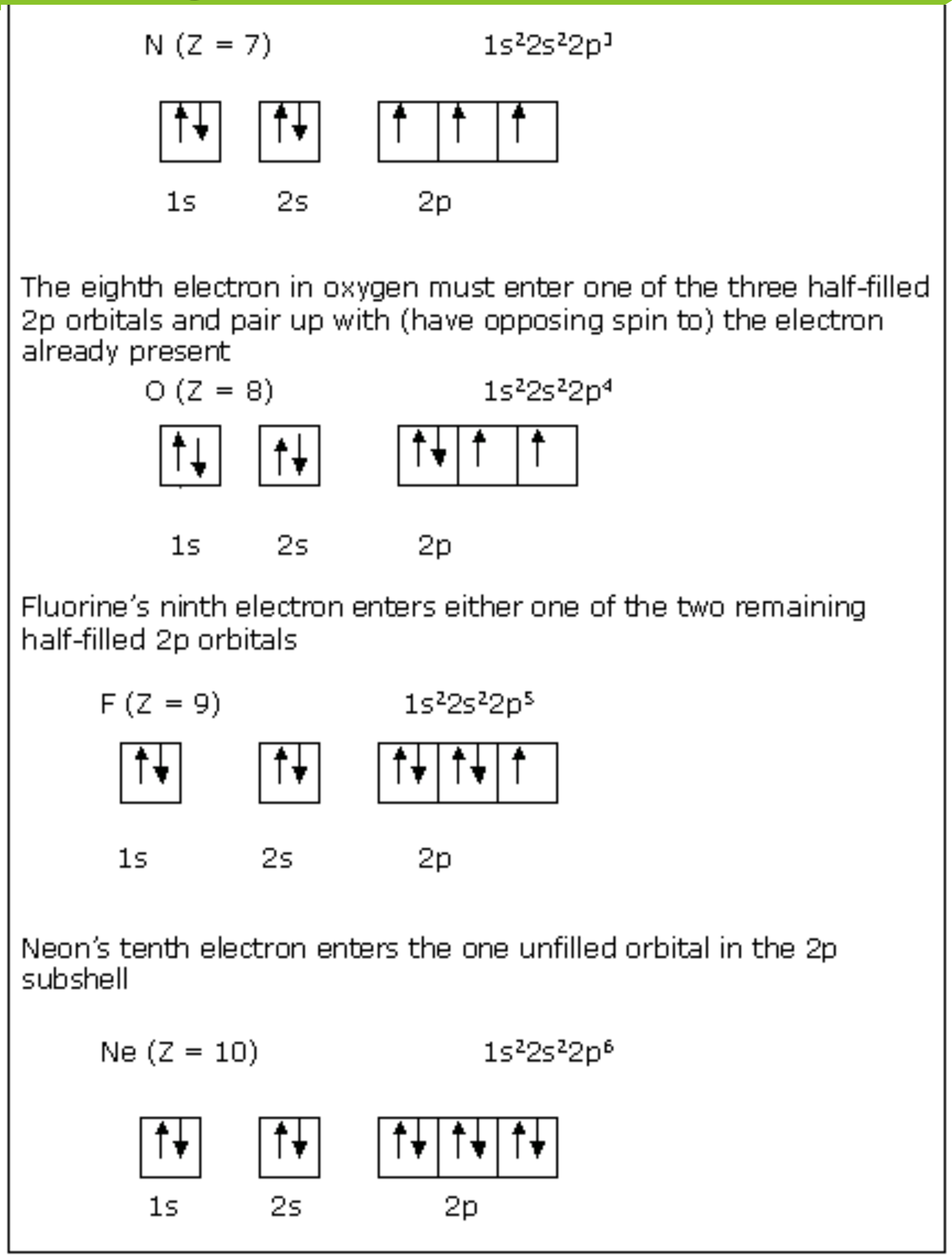
Approximate Ionization Energies, Ionization Cross Sections, and Required jτ Values for Bare Ions

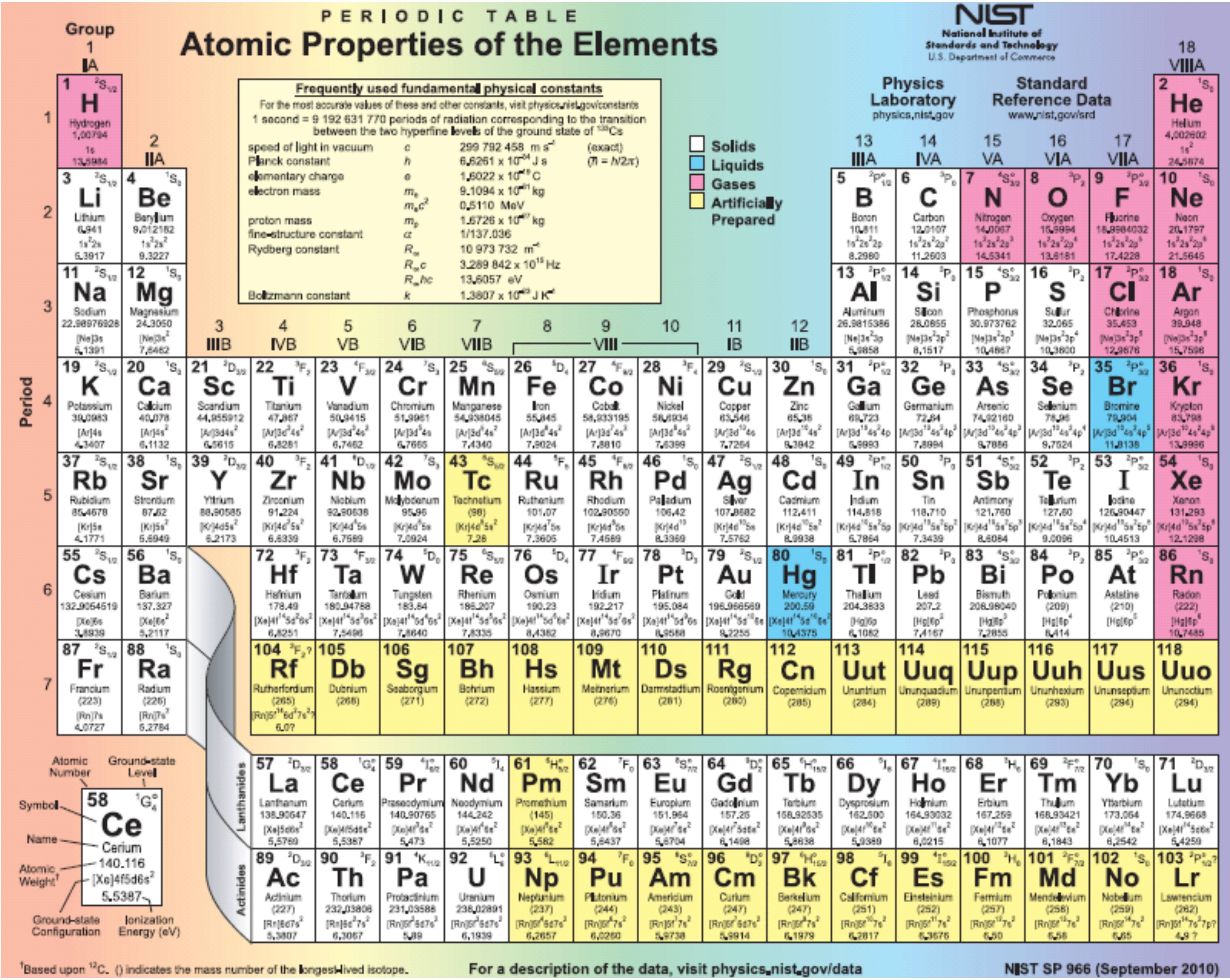
Ion	E_i(eV)	σ(cm²)	jτ(Cb/cm²)
C^{6+}	490	7.7×10^{-20}	2.1
N^{7+}	666	4.2×10^{-20}	3.8
O^{8+}	870	2.4×10^{-20}	6.5
Ne^{10+}	1360	1×10^{-20}	16
Ar^{18+}	4,400	9.5×10^{-22}	170
Kr^{36+}	17,600	6×10^{-23}	2,700
Xe^{54+}	39,700	1.2×10^{-23}	13,600
Pb^{82+}	91,400	2.2×10^{-24}	72,300
U^{92+}	115,000	1.4×10^{-24}	115,000

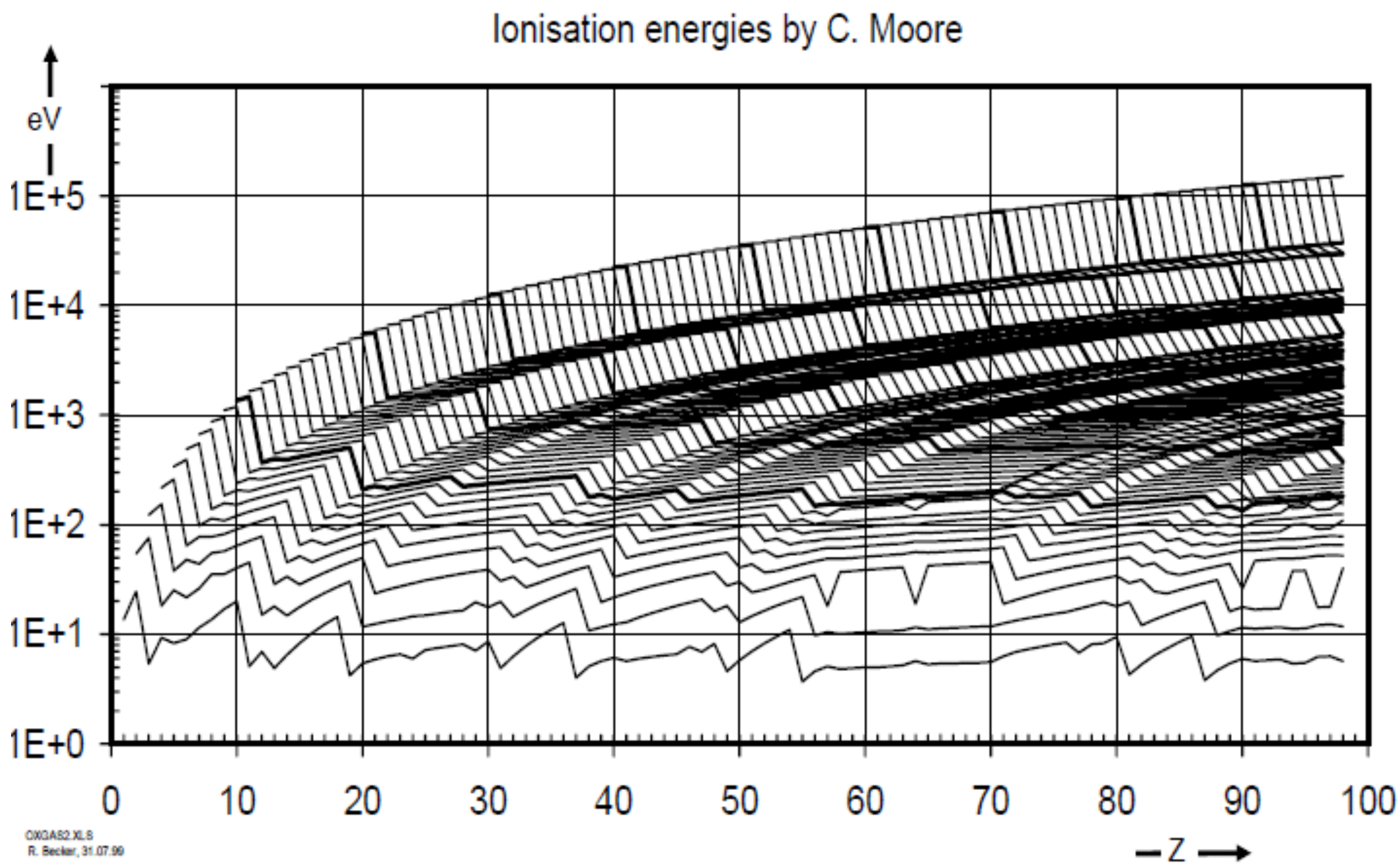
Examples: Argon can be ionized by 10 keV electrons, ions of the heavy elements by up to 100 keV electrons and Uranium by 150 keV electrons. The resulting values for the ionization energy, cross section and ionization factor are summarized in the table on the left side.

Electron configurations

- Hund's rule of Maximum Multiplicity




PERIODIC TABLE
Atomic Properties of the Elements
NIST National Institute of Standards and Technology U.S. Department of Commerce
Physics Laboratory physics.nist.gov
Standard Reference Data www.nist.gov/srd
Frequently used fundamental physical constants
For the most accurate values of these and other constants, visit physics.nist.gov/constants
1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of 133Cs
speed of light in vacuum c 299 792 458 m s-1 (exact)
Planck constant h 6.6261 x 10-34 J s (ħ = h/2π)
elementary charge e 1.6022 x 10-19 C
electron mass me 9.1094 x 10-31 kg
mec2 0.5110 MeV
proton mass mp 1.6726 x 10-27 kg
fine-structure constant α 1/137.036
Rydberg constant R∞ 10 973 732 m-1
R∞c 3.289 842 x 1015 Hz
R∞hc 13.6057 eV
Boltzmann constant k 1.3807 x 10-23 J K-1
Solids
Liquids
Gases
Artificially Prepared
Group
Period
Lanthanides
Actinides
Atomic Number
Ground-state Level
Symbol
Name
Atomic Weight†
Ground-state Configuration
Ionization Energy (eV)
58 Ce Cerium 140.116 [Xe]4f5d6s2 5.5387
†Based upon 12C. () indicates the mass number of the longest-lived isotope.
For a description of the data, visit physics.nist.gov/data
NIST SP 966 (September 2010)



Ionisation energies by C. Moore
eV
1E+5
1E+4
1E+3
1E+2
1E+1
1E+0
0
10
20
30
40
50
60
70
80
90
100
OXGAS2.XLS
R. Becker, 31.07.99
Z

Charge exchange

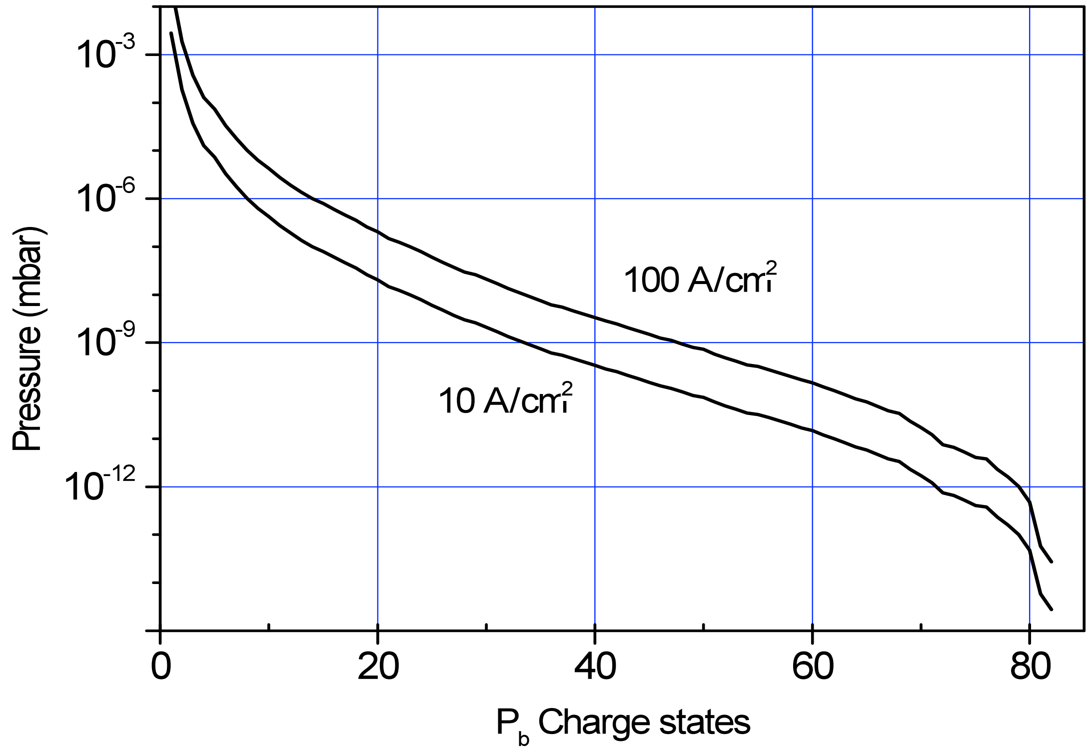
Charge exchange:

For the approximation of the charge exchange cross section, commonly the equation by **Müller and Salzborn** is used:

$$\sigma^{ex}_{i\to i-1} \approx 1.43\times 10^{-12}\ i^{\,1.17} E^{-2.76}_{ion,gas}\ [cm^2]$$

Therein i describes the charge state of the highly charged ion and $E_{ion,\,gas}$ is the ionization potential of the gas atoms interacting with the ion.

Example: Reachable charge states depending on the current density and the pressure



Radiative recombination

For the approximation of the RR cross sections the semi-classical expression by Kim und Pratt is used. Their formula bases on the first theoretical description of the Radiative Recombination by Kramers (1923):

$$\sigma(E) = \frac{8\pi}{3\sqrt{3}}\,\alpha\,(\lambda_e)_r^2\,\chi\,\ln\left(1+\frac{\chi}{2(n_0)_{\text{eff}}^2}\right)$$

with $\chi = 2\, Z_{\text{eff}}{}^2 Ry/E$

with:

- the effective nuclear charge $Z_{\text{eff}} = \frac{1}{2}(Z+q)$ to take into account the shielding of the nuclear potential by the bound electrons
- the effective main quantum number

$$(n_0)_{\text{eff}} = n + (1-w_0) - 0.3$$

to include the capture into states with different angular momentums

Ry: Rydberg energy 13,6 eV

α: fine structure constant

ω_0 ratio between the numbers of occupied and unoccupied states

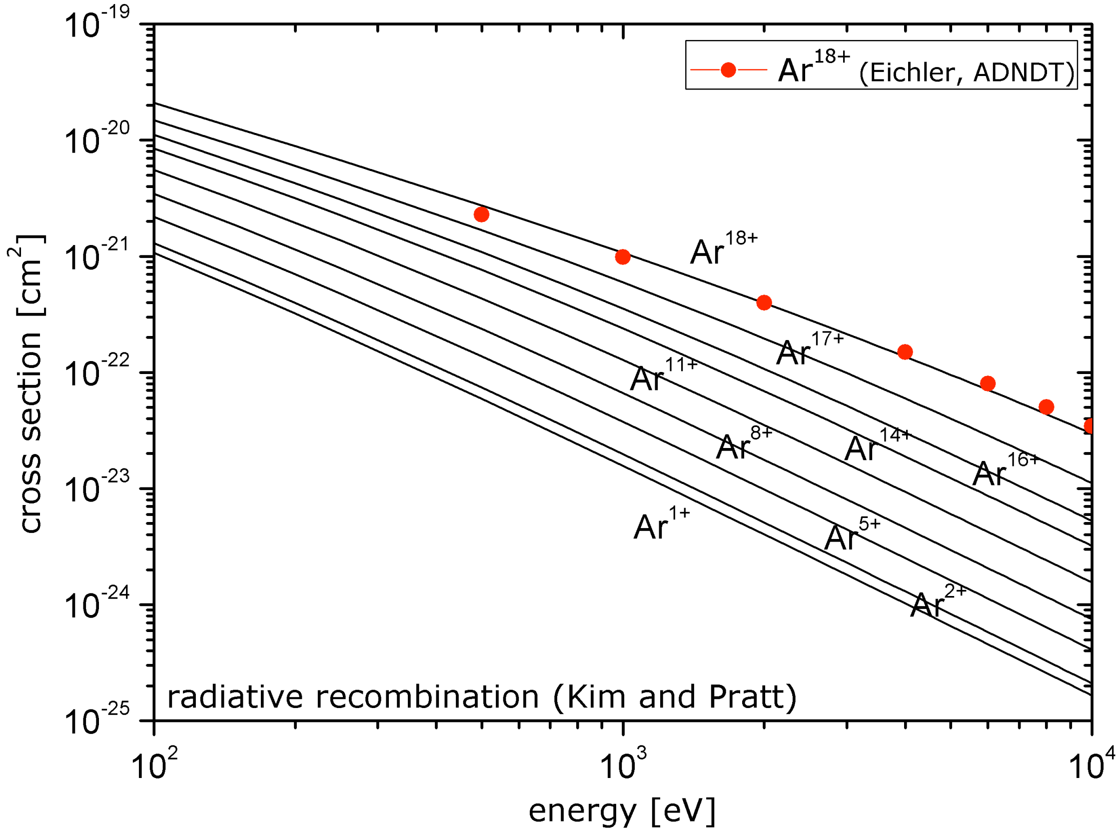
Z: nuclear charge

q: charge state

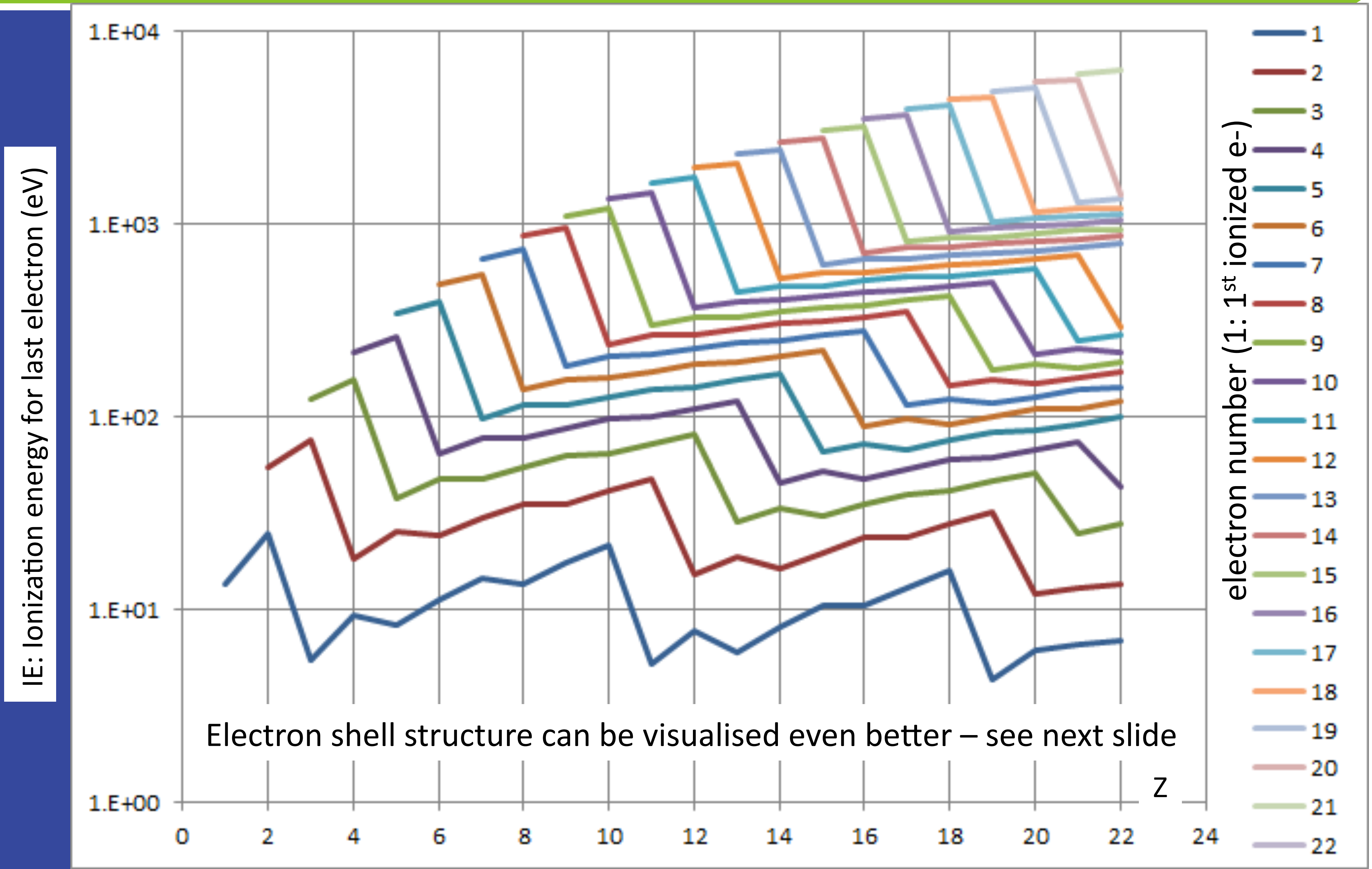
n: main quantum number

$(\lambda_e)_r$: reduced Compton-wavelength

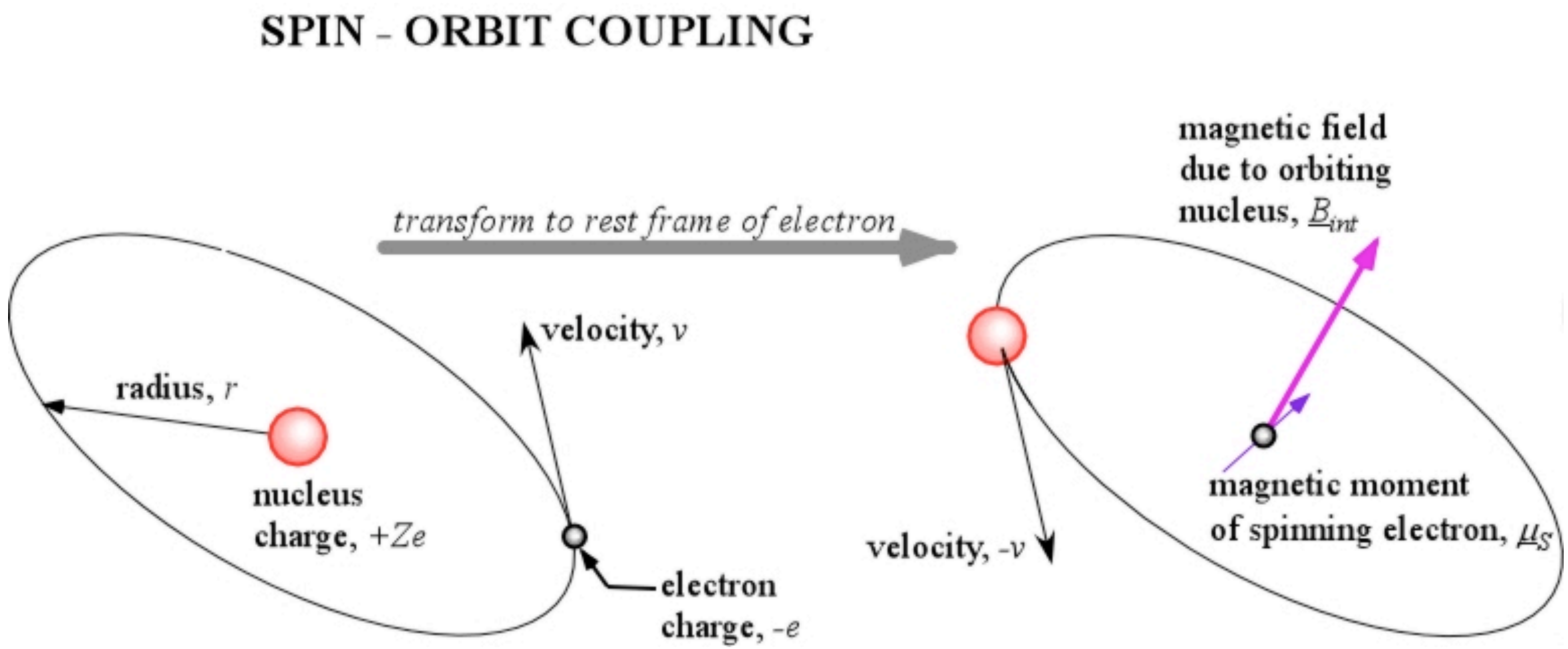
E: electron energy



Ionization energies



Spin-orbit coupling



Ionization by photons

The reaction is: $A + h\nu = A^{+} + e^{-}$

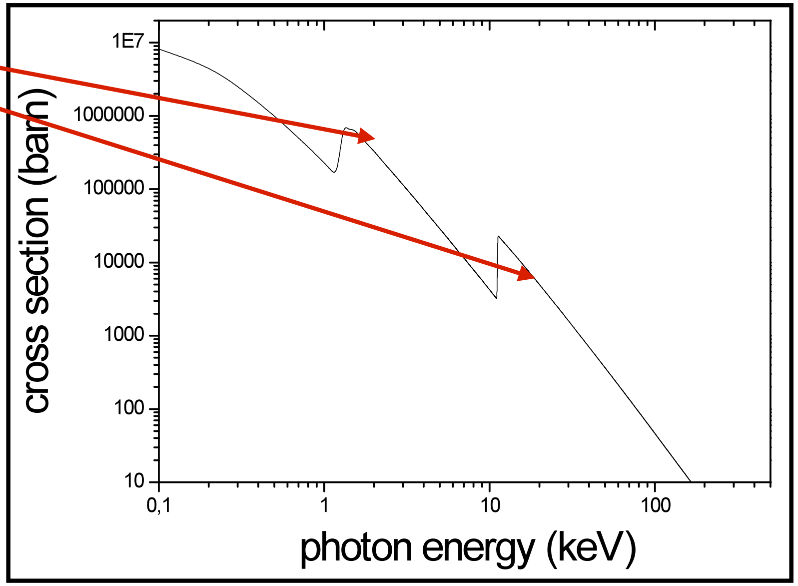
Atoms of a gas can be ionized by an intensive beam of photons with the adequate energy **(photo ionization)**. Therefore the photon energy has to be $h \cdot \nu > e \cdot \varphi_{q,i}$

The energy of a photo electron is: $\frac{1}{2} m v_{max}^2 = h\nu - e \cdot \varphi_{q,i}$

Cross section σ_p:

- σ_p has a strong dependence on the photon energy and the nuclear charge Z: $\sigma_p \propto \frac{Z^{4-5}}{(\hbar \cdot \omega)^{7/2}}$
- For a given atomic shell the cross section σ_p is the largest close to threshold, meaning where the photon energy reaches the ionization energy I (resonance/ threshold behavior):

$$\sigma_{max} : \hbar \cdot \omega \approx I_K, I_L, I_M$$



- For high photon energies $\hbar \cdot \omega \gg I_K$ the ionization of the s-orbital is most probable and the K-shell ionization delivers the dominant contribution:

$$\sigma_{p_n} = \frac{1}{n^3} \cdot \sigma_K \quad \rightarrow \quad \sigma_p = \sigma_{p_K} \cdot \sum_{n=1}^{\infty} \frac{1}{n^3} = 1.2021 \cdot \sigma_{p_K}$$

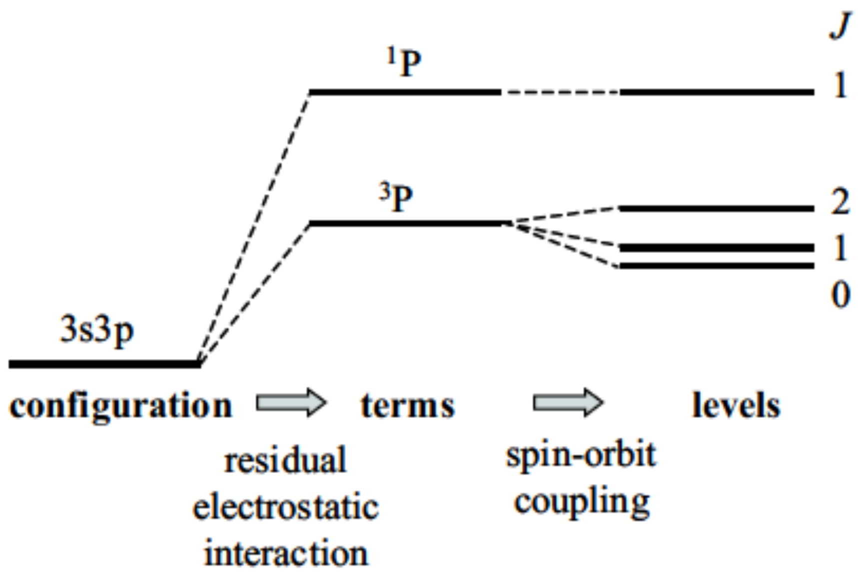
σ_{pn} : *cross section for RR into the K-shell*

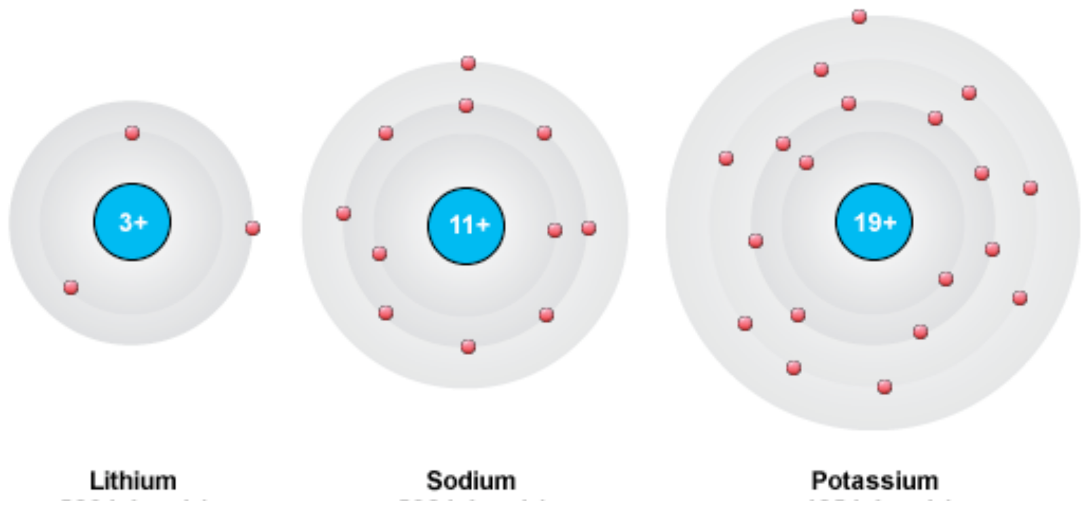
n: main quantum number

- Description of σ_p as time-inverse effect to the radiative recombination by the Milne-formula:

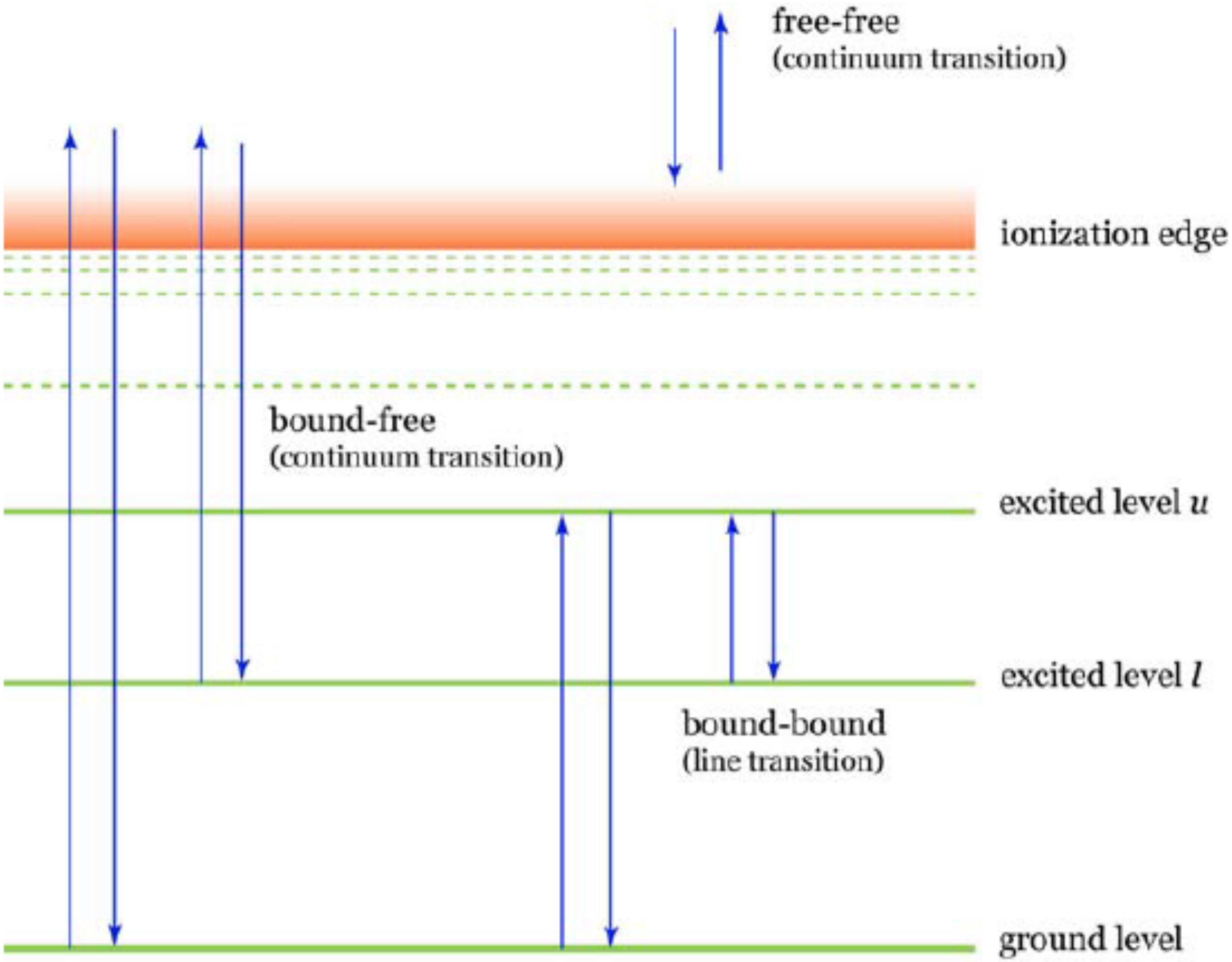
$$g_{q+1} \cdot \sigma_{RR} = \frac{(\hbar\omega)^2}{2 m_e c^2 E} g_q \cdot \sigma_P$$ with *g: statistical weights*

Atomic shell structure

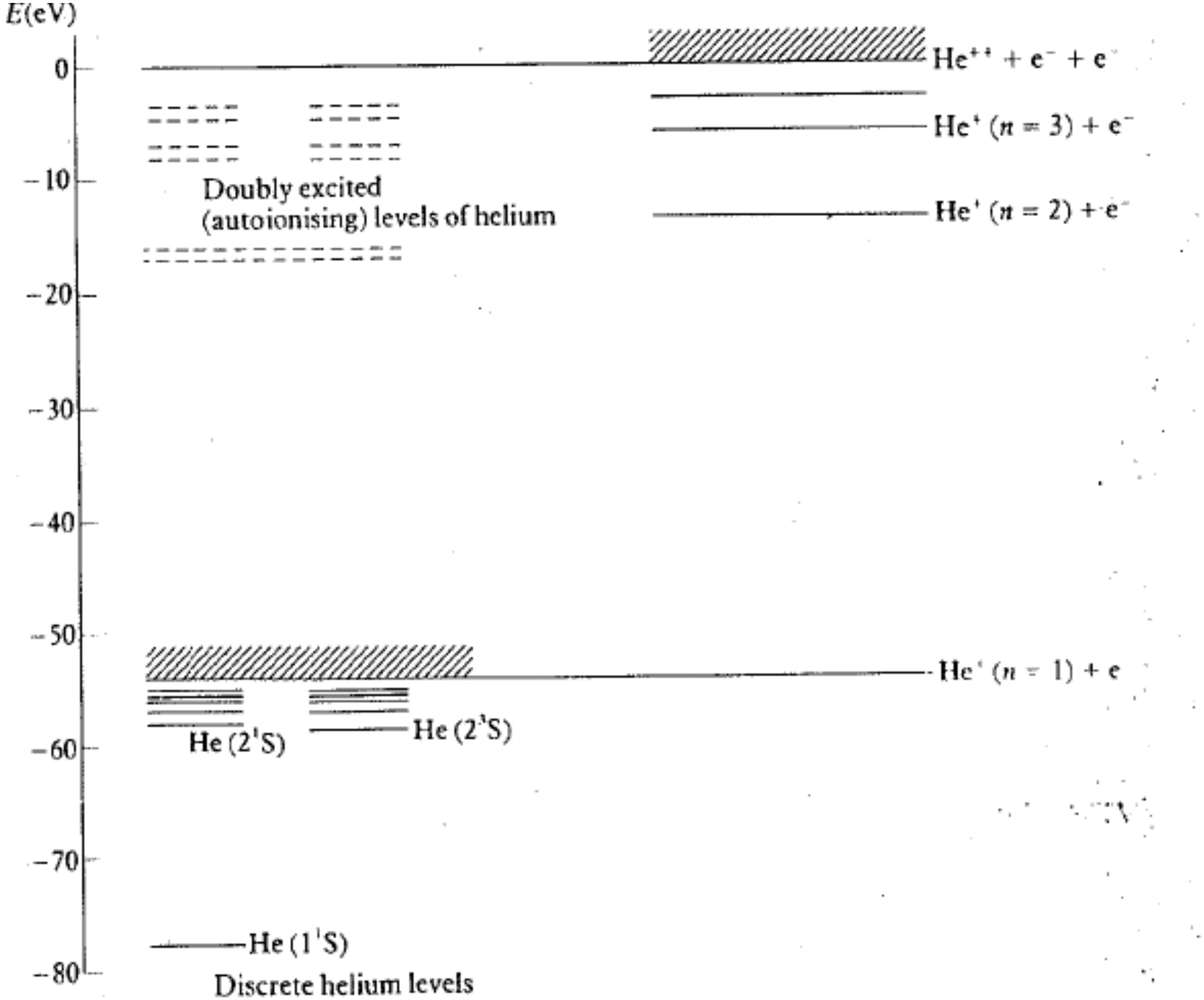




Atomic shell structure



Energy spectrum: He example



6.3 The 'complete' energy level spectrum of helium. The energy scale is relative to the threshold for the ionisation of both electrons and the zero of energy is 54 eV (the ground state energy of He^+), above the zero energy of the scale of Fig. 6.2.

Ionization energy