PERIODIC TRENDS

General Chemistry I, Lecture Series 8

Pengxin Liu

Reading:

OGB8 §3.2, §§3.4–3.6, §5.5

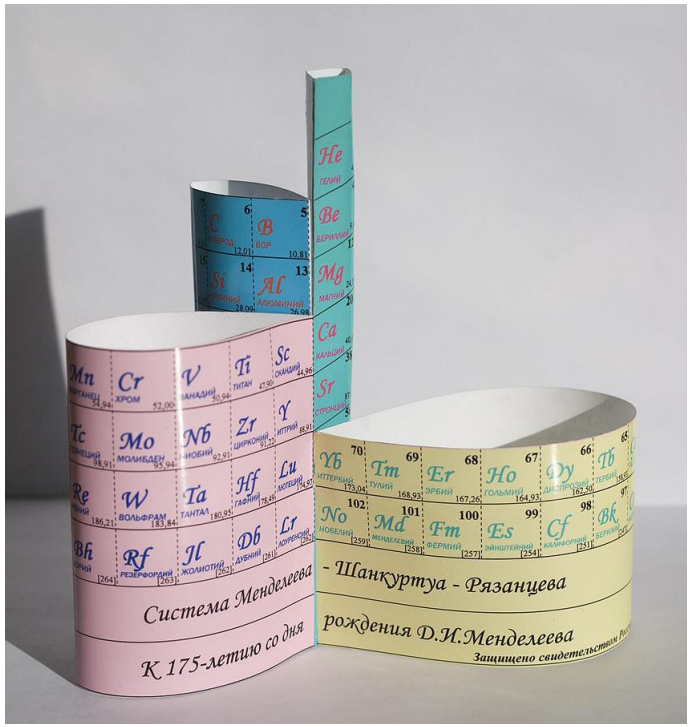
Alternative Periodic Tables

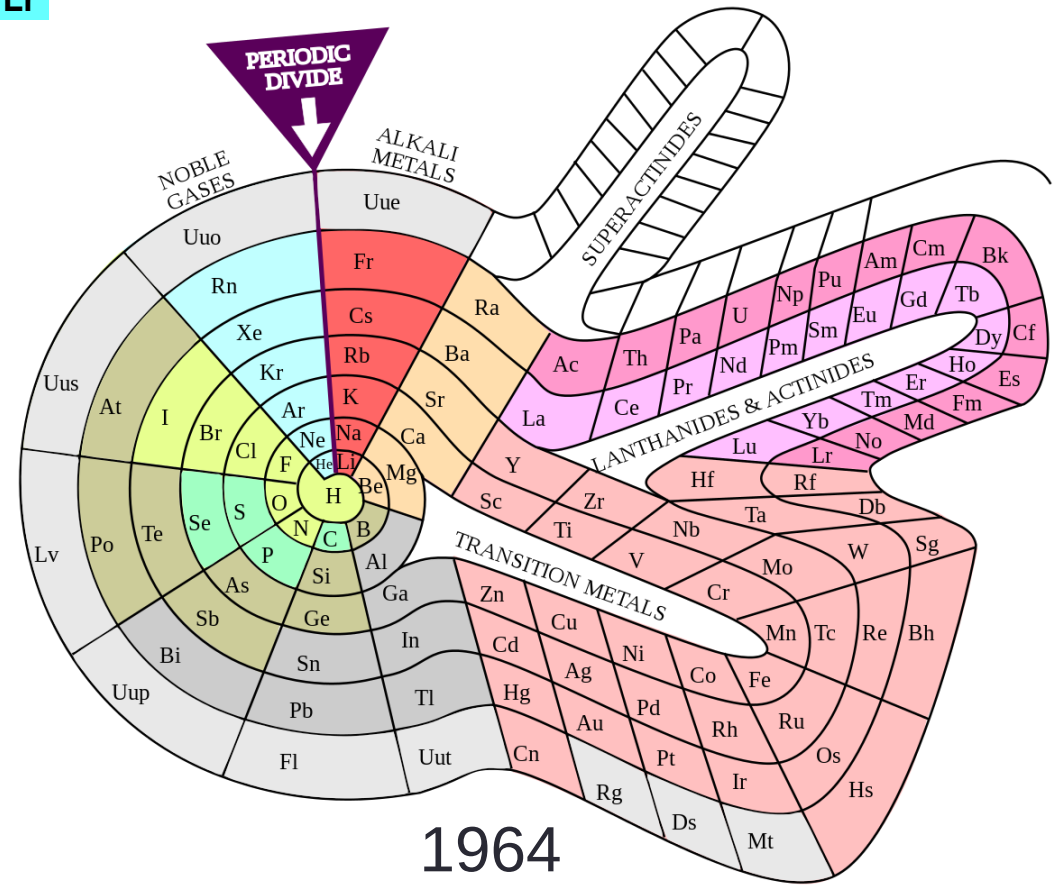
1928

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	

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn					
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd					
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg					
Lr														

												H		He
												Li	Be	
								B	C	N	O	F	Ne	Na	Mg
								Al	Si	P	S	Cl	Ar	K	Ca
Ga	Ge	As	Se	Br	Kr	Rb	Sr								
In	Sn	Sb	Te	I	Xe	Cs	Ba								
Tl	Pb	Bi	Po	At	Rn	Fr	Ra								





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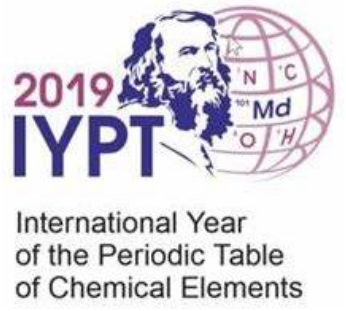


The Periodic Table

IUPAC #

Group 族 ⟶

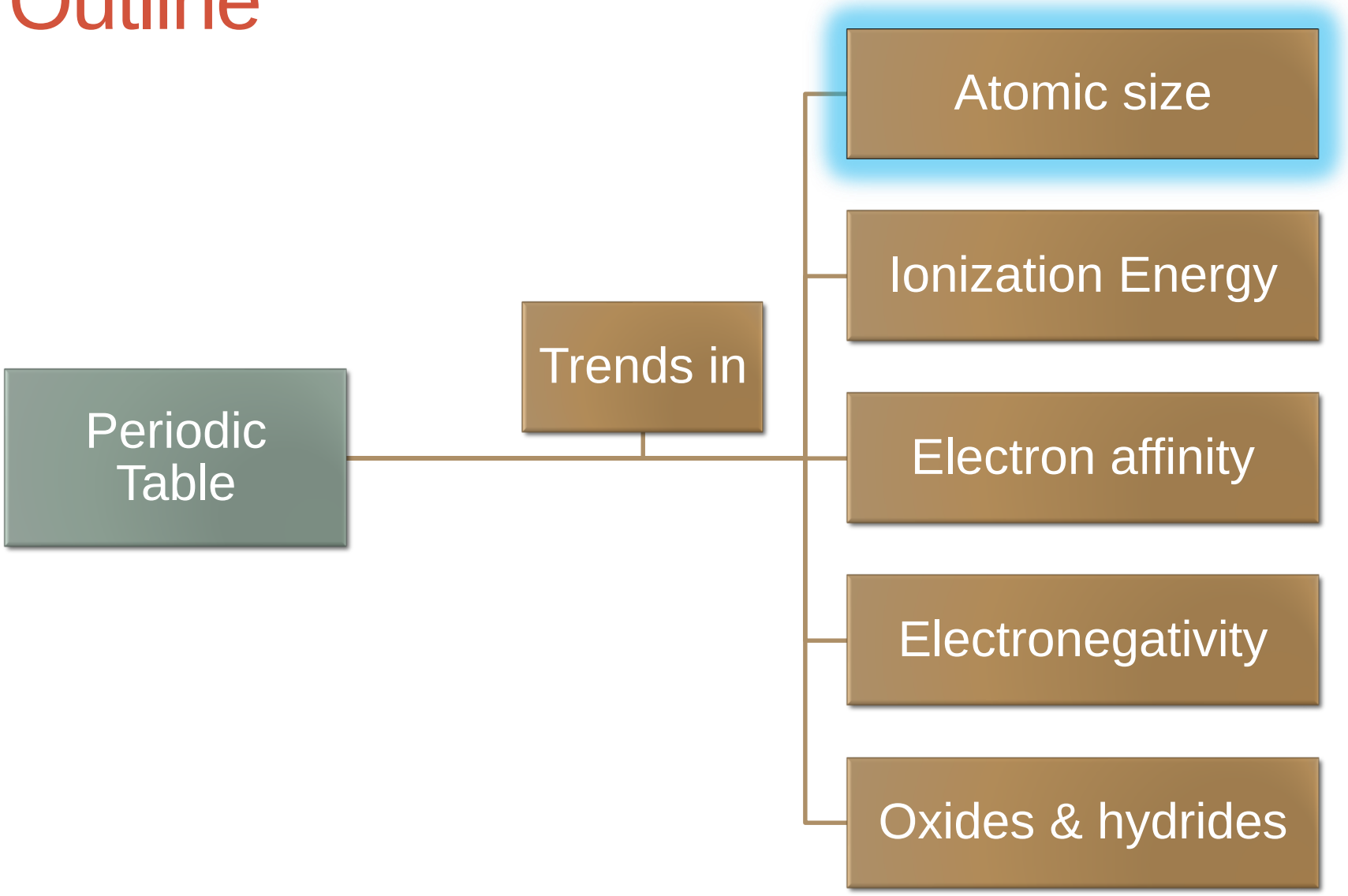
Period 周期	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	**															

s block *p* block
d block *f* block

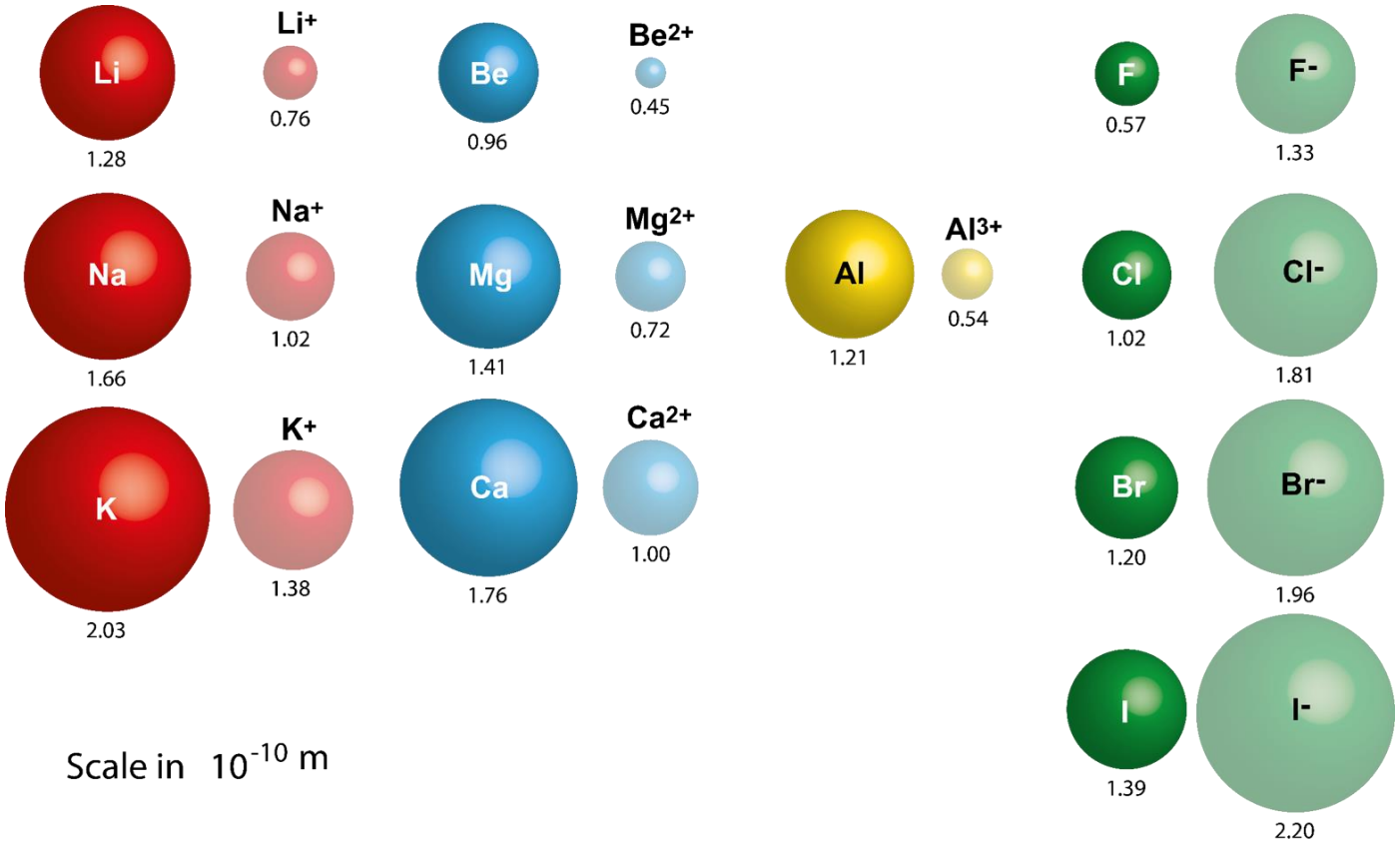
CAS #

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Outline

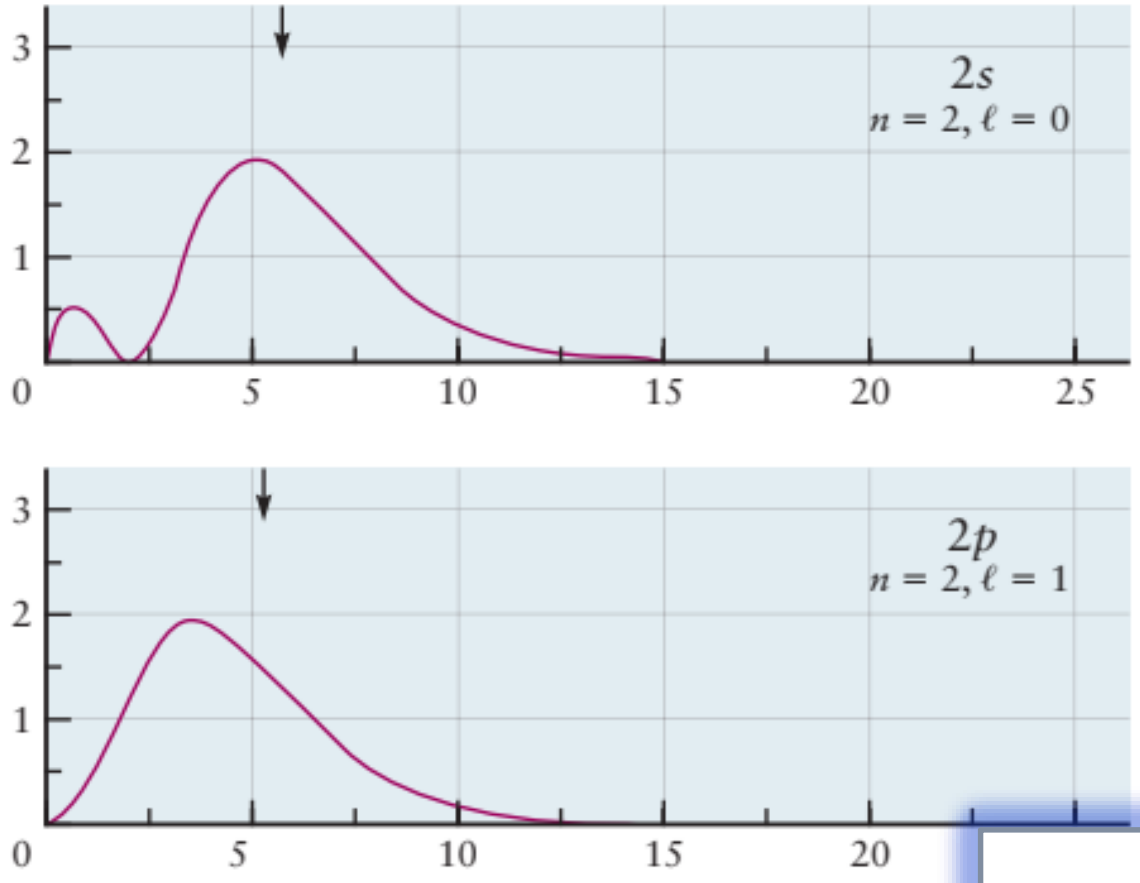

Periodic Table
Trends in
Atomic size
Ionization Energy
Electron affinity
Electronegativity
Oxides & hydrides

Atomic size



- No precise definition
- Atomic/ionic radius = radius of outermost orbital

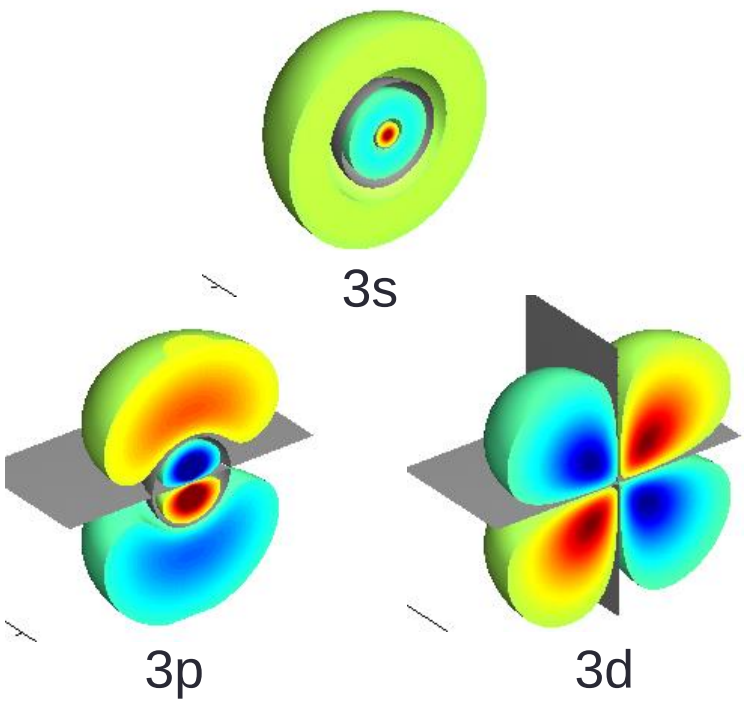
Radial Distribution

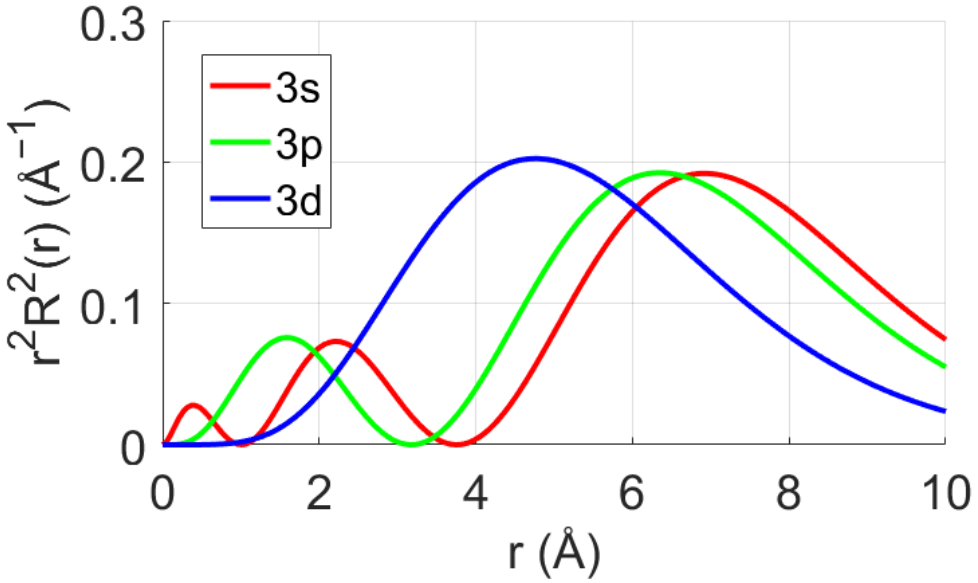


For H atom,
$r(2s) > r(2p)$

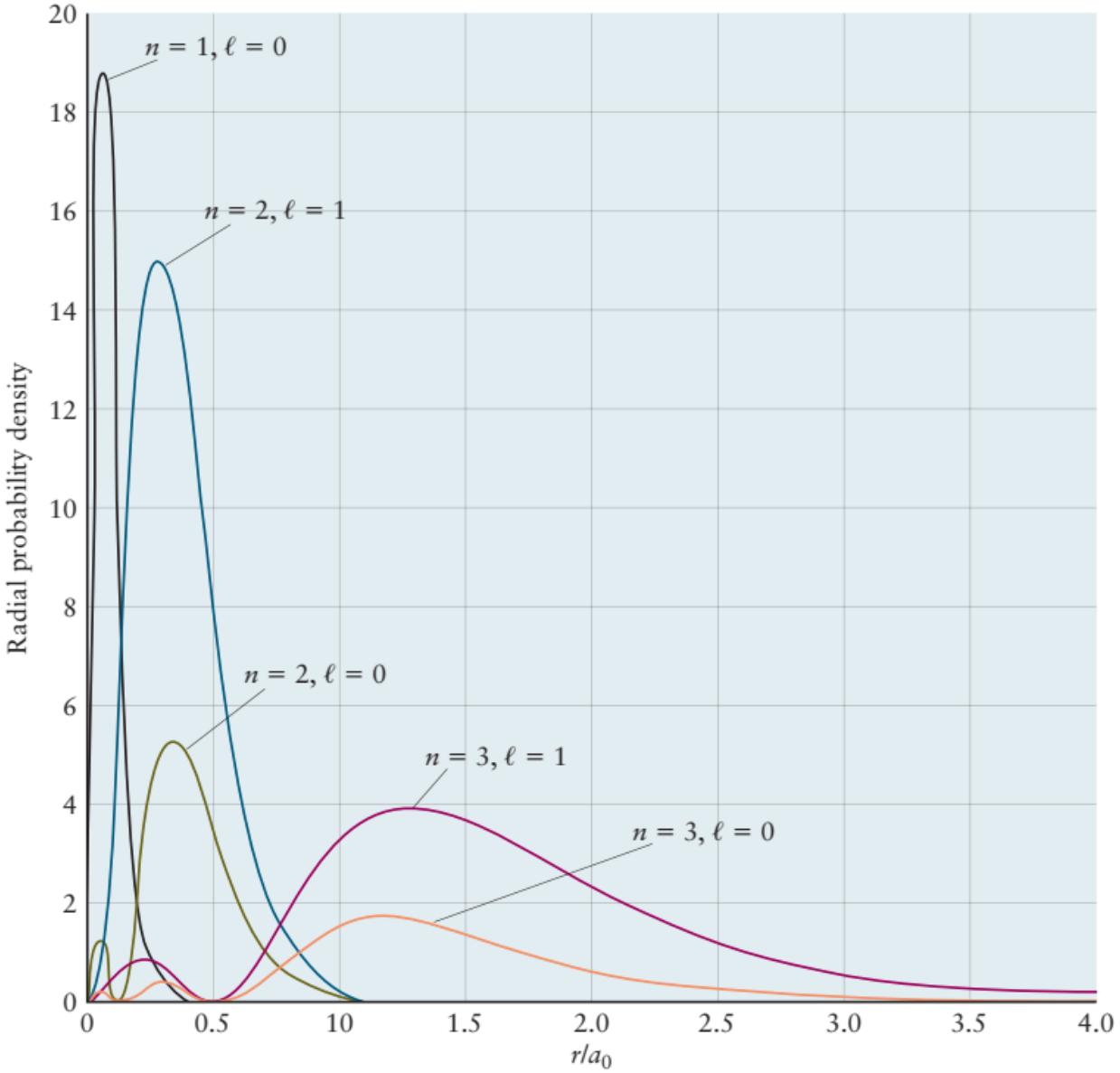
Radial Distribution

For H atom,
$r(3s) > r(3p) > r(3d)$

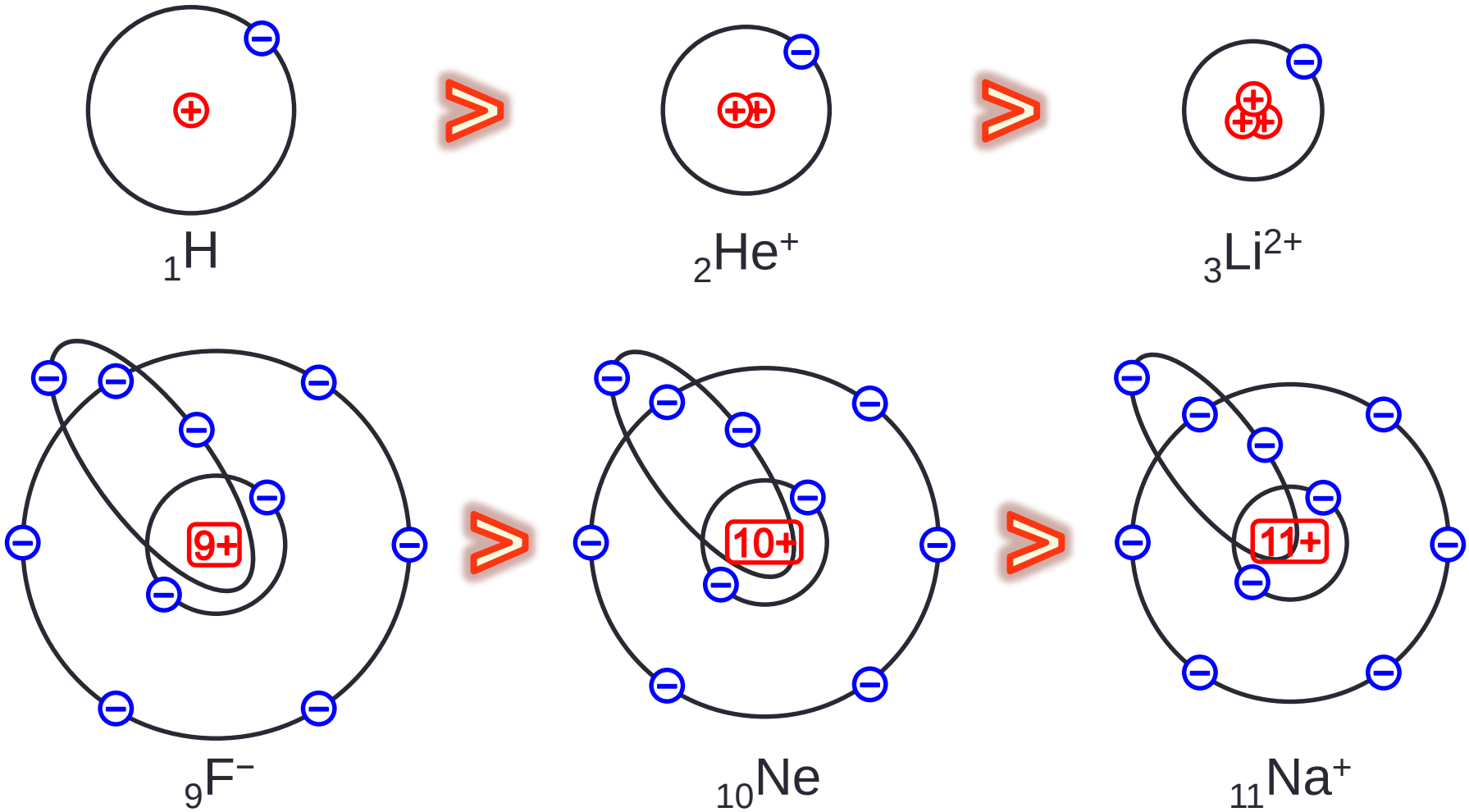




Radial Distribution



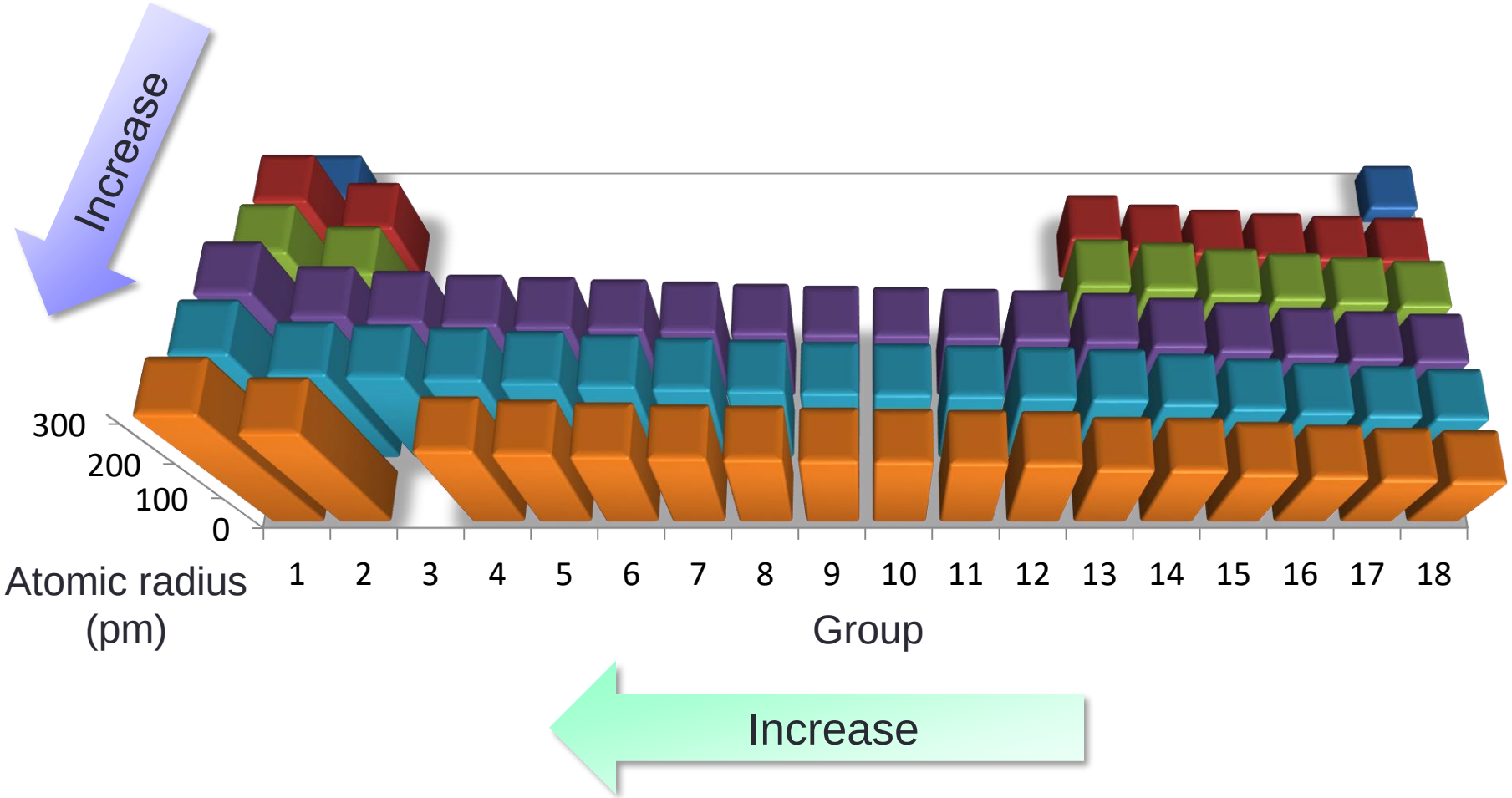
Radii of Isoelectronic (等电子的) Ions



$_{1}H$ > $_{2}He^{+}$ > $_{3}Li^{2+}$

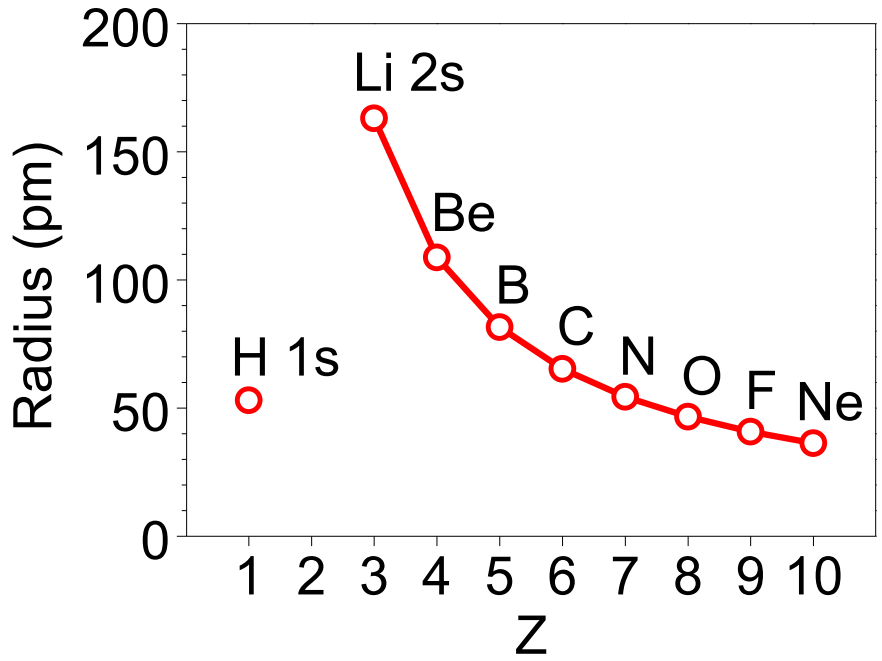
$_{9}F^{-}$ > $_{10}Ne$ > $_{11}Na^{+}$

Periodic Trends in Atomic Radii



Radii of Atoms with Same *n*

Atom	*Z*	$Z_{eff}(2s)$	Valence shell
Li	3	~1.30	$2s^1$
Be	4	~1.95	$2s^2$
B	5	~2.60	$2s^2 2p^1$
C	6	~3.25	$2s^2 2p^2$



For *s* and *p* subshells,

$\Delta Z_{eff}(ns) \approx 0.65\,\Delta Z$

For 2*s* and 2*p*,

$Z_{eff} \approx 0.65(Z - 1)$,

so $r(Z) = \frac{n^2}{Z_{eff}} a_0$

$\approx \frac{4a_0}{0.65} \cdot \frac{1}{Z - 1}$

Radii of Atoms with Same *n* (2)

For *d* subshells, $\Delta Z_{eff}(ns) \approx 0.15\,\Delta Z$;

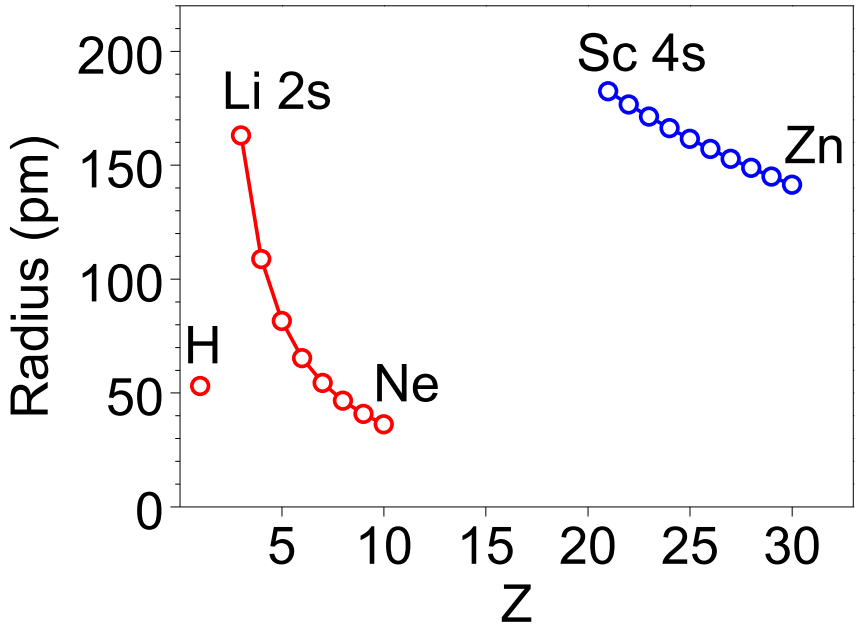
For *f* subshells, $\Delta Z_{eff}(ns) \approx 0$.

For 4*s*,

$Z_{eff} \approx 0.15Z + 1.53$,

so $r(Z) = \frac{n^2}{Z_{eff}} a_0$

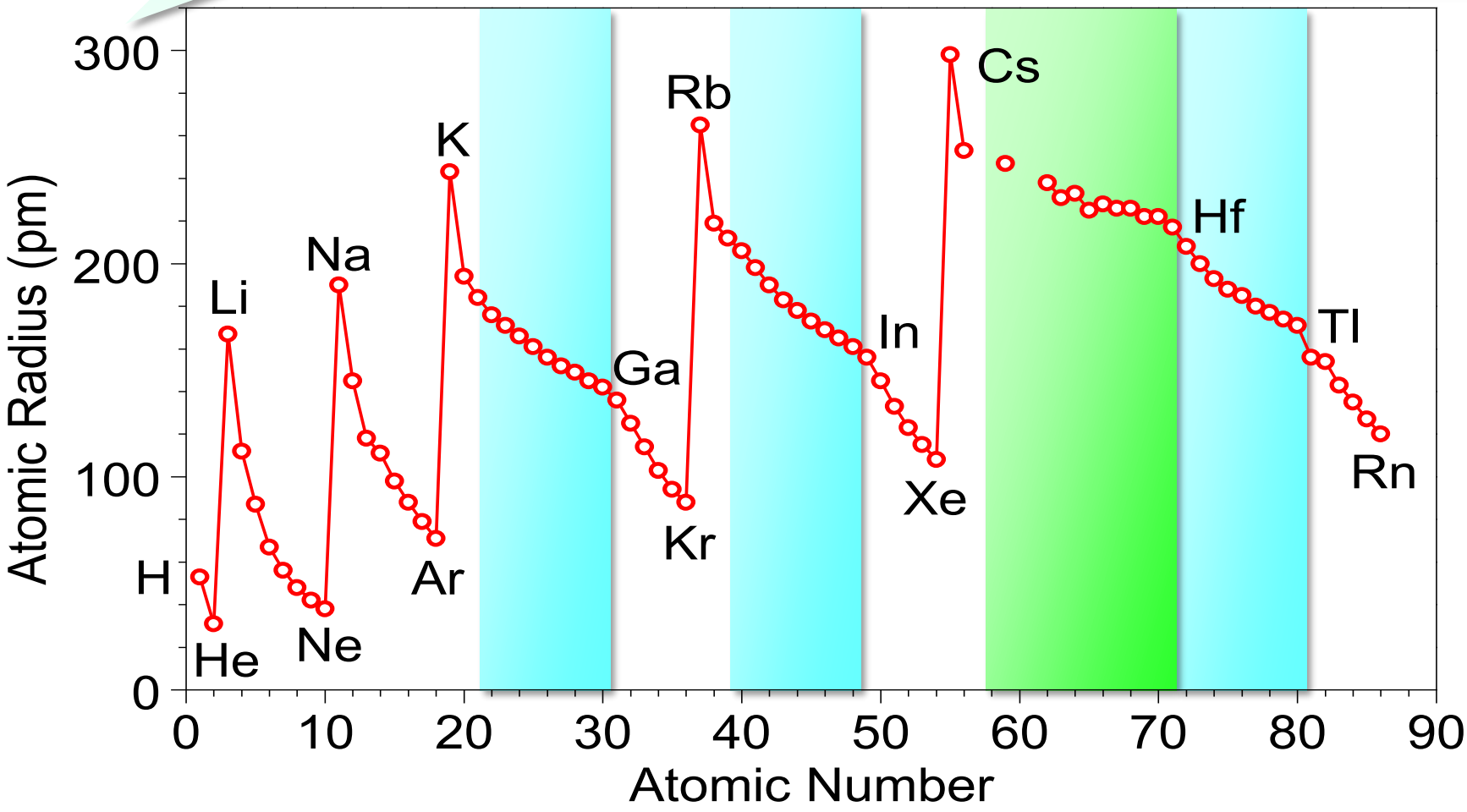
$\approx \frac{16a_0}{0.15} \cdot \frac{1}{Z + 10}$



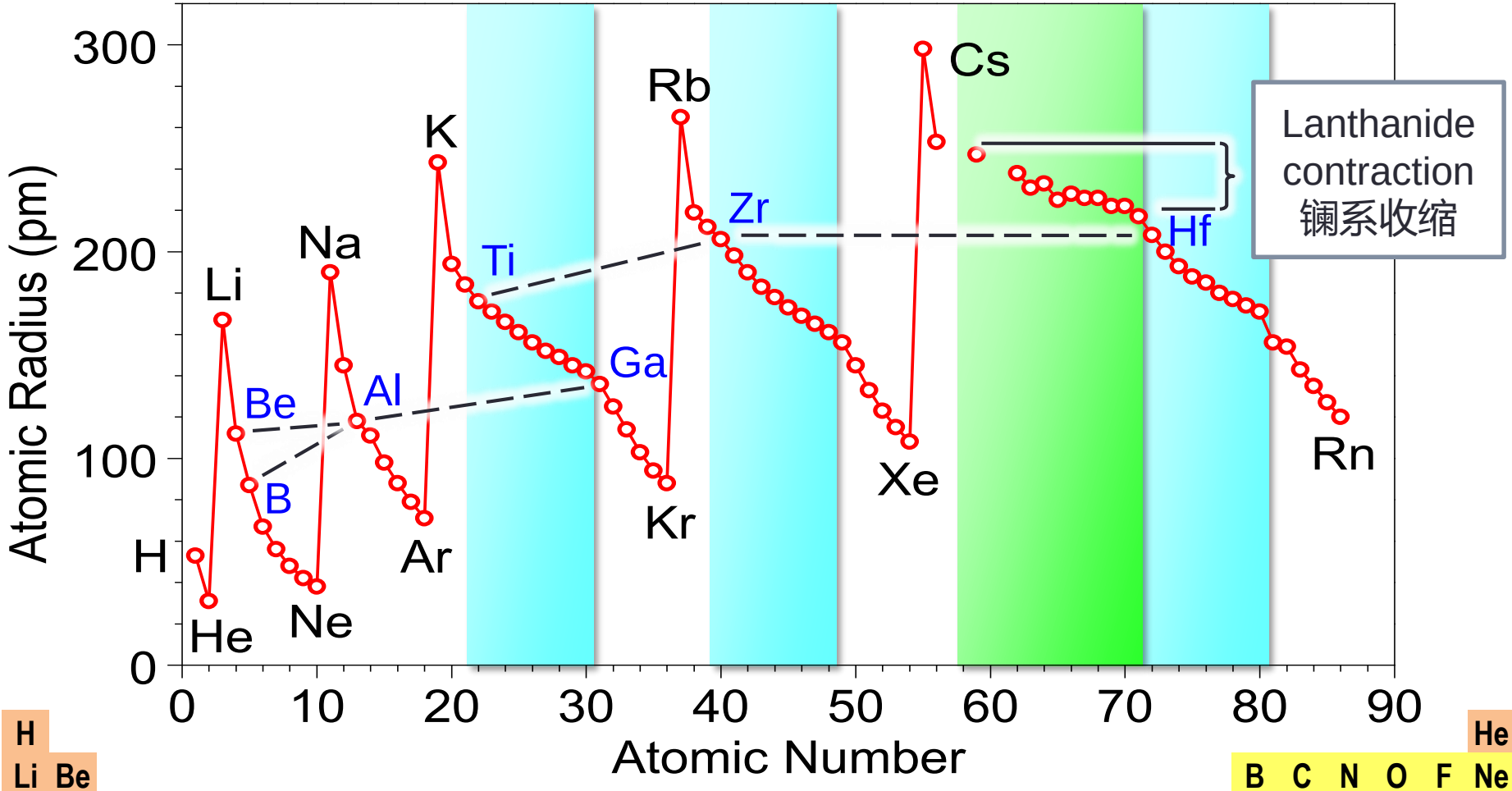
Atom	*Z*	Z_{eff}(4*s*)	Valence shell
Mn	25	5.28	$3d^5 4s^2$
Fe	26	5.43	$3d^6 4s^2$
Co	27	5.58	$3d^7 4s^2$
Ni	28	5.71	$3d^8 4s^2$

Trends in Atomic Radii (1)

$$r_{n,Z} \approx \frac{n^2}{Z_{\text{eff}}} a_0$$



Trends in Atomic Radii (2)



1	H																He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

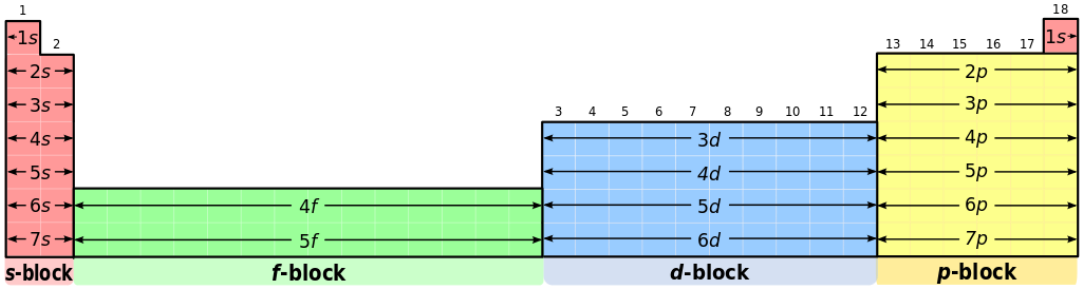
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb

Summary

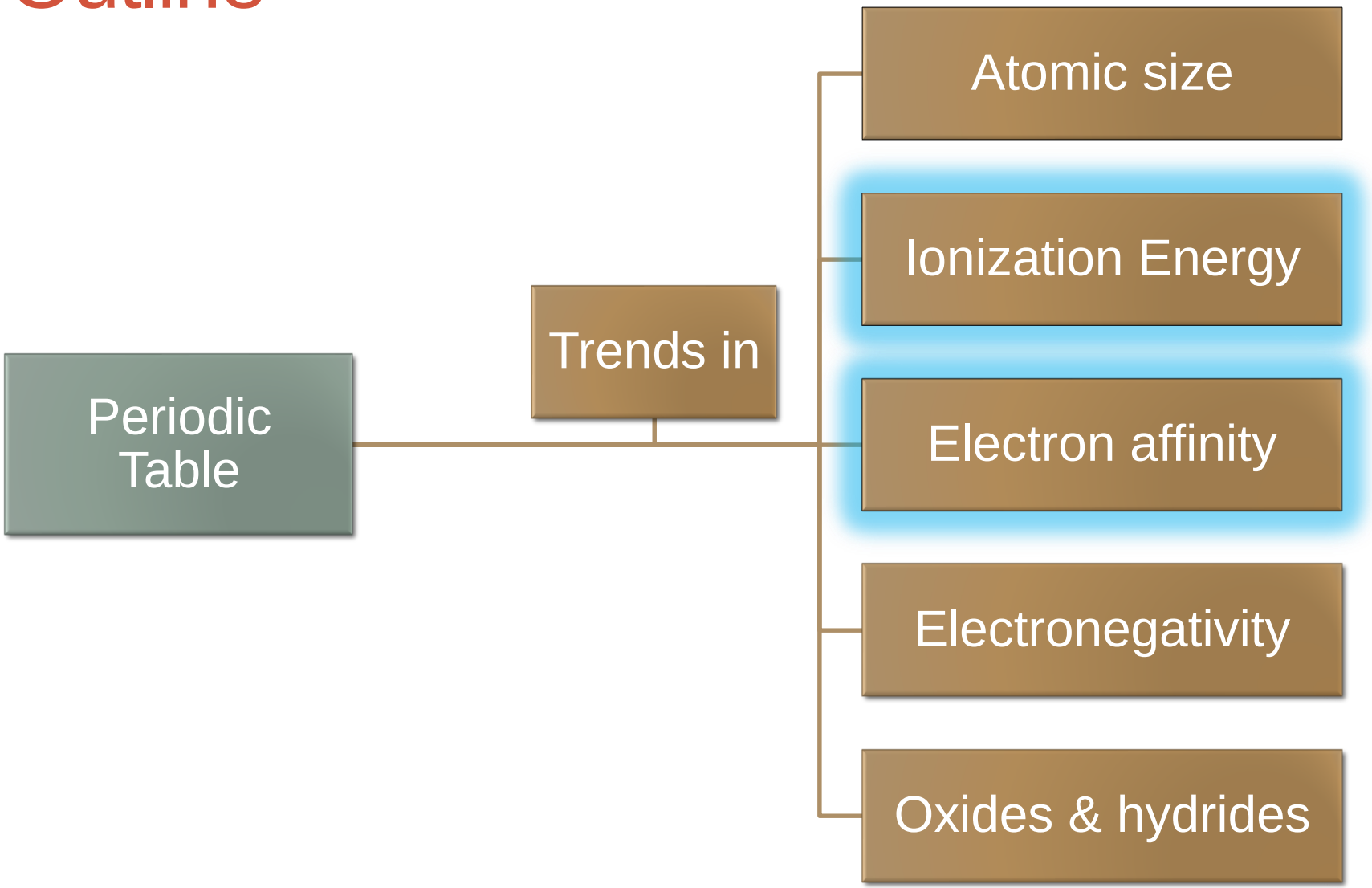
- Atomic radius is determined by the valence *s* subshell
- When estimating Z_{eff} for *ns*:
  - *np* electrons only partly screens *ns*;
  - (*n*−1)*d* electrons efficiently screens *ns*;
  - (*n*−2)*f* electrons completely screens *ns*.

- The trends in atomic radius $r_{n,Z}$
  - Periods according to *n*
  - $r_{n,Z}$ decreases within the same period
  - *s*-, *p*-, and *d*-blocks

- The Periodic Table



Outline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Electron affinity
Electronegativity
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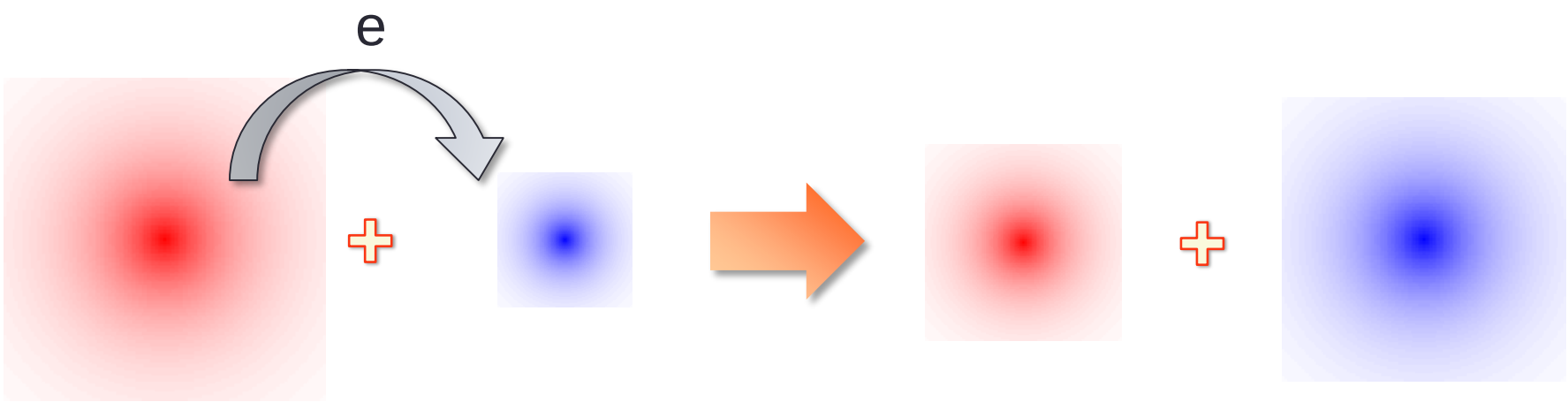
Gaining and Losing an Electron



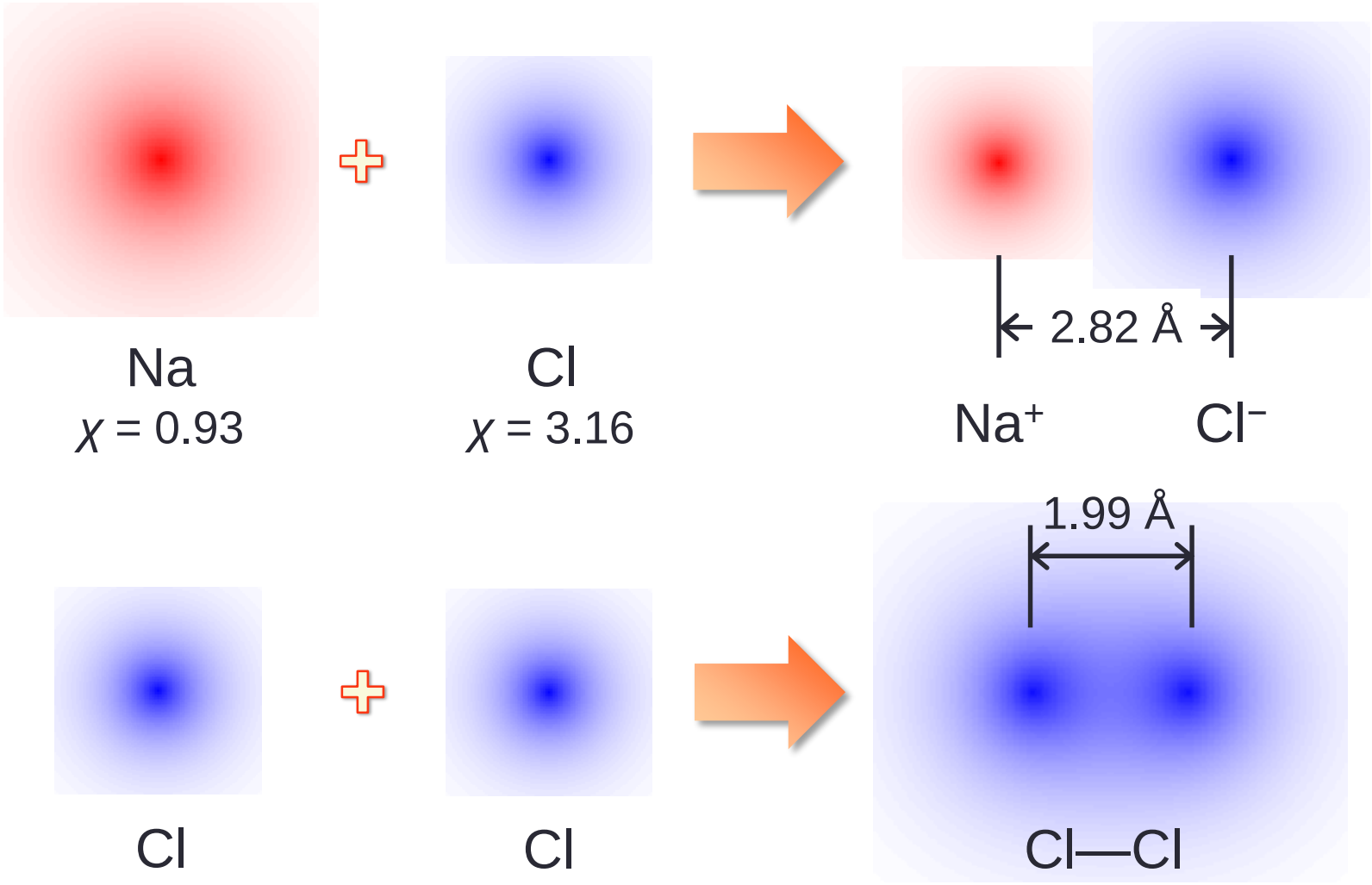
Na
r = 190 pm

Cl
r = 79 pm

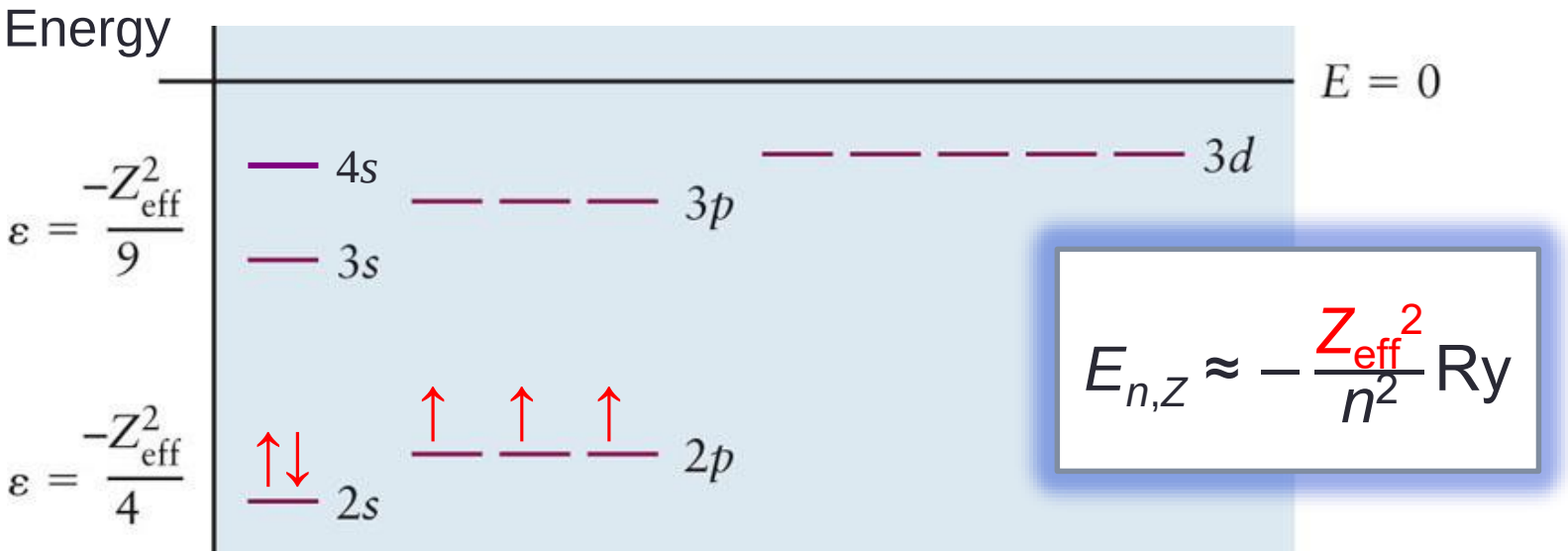
Na^+
r = 116 pm

Cl^-
r = 167 pm

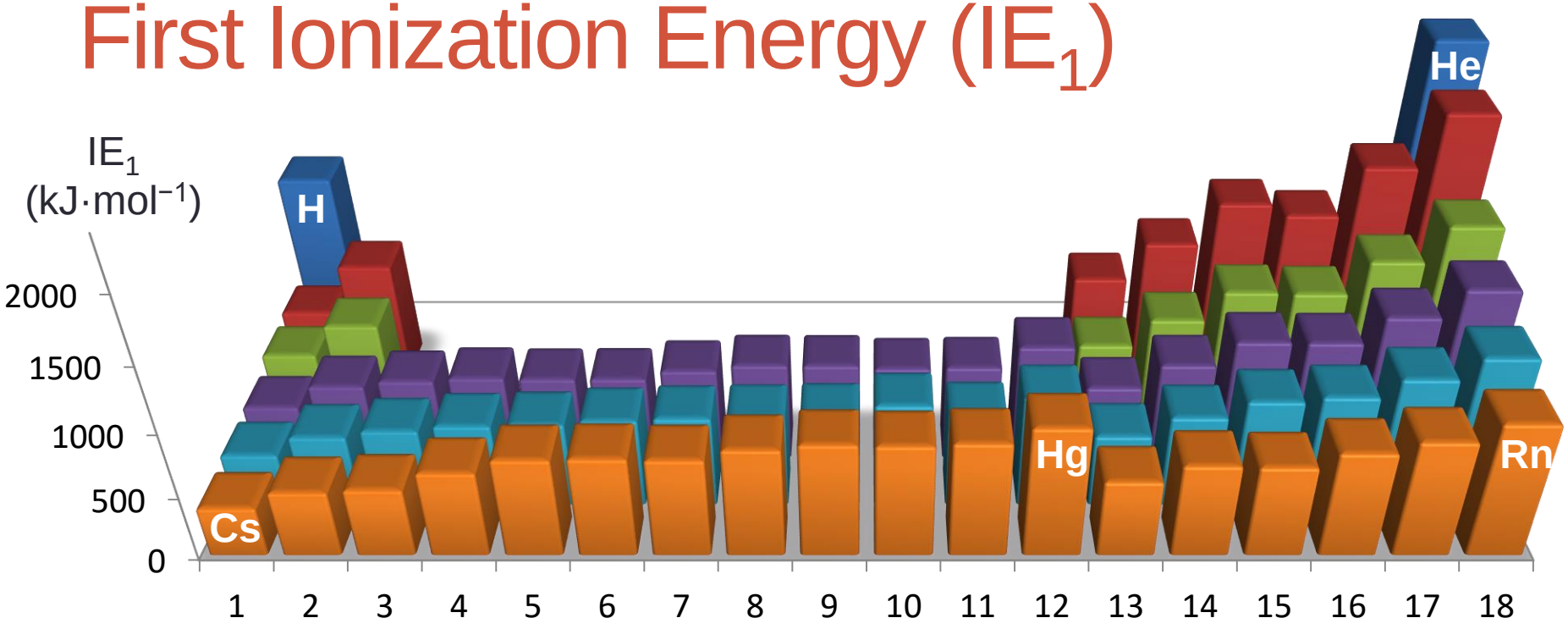
Ionic Bonds



First Ionization Energy (IE_1)



First Ionization Energy (IE_1)

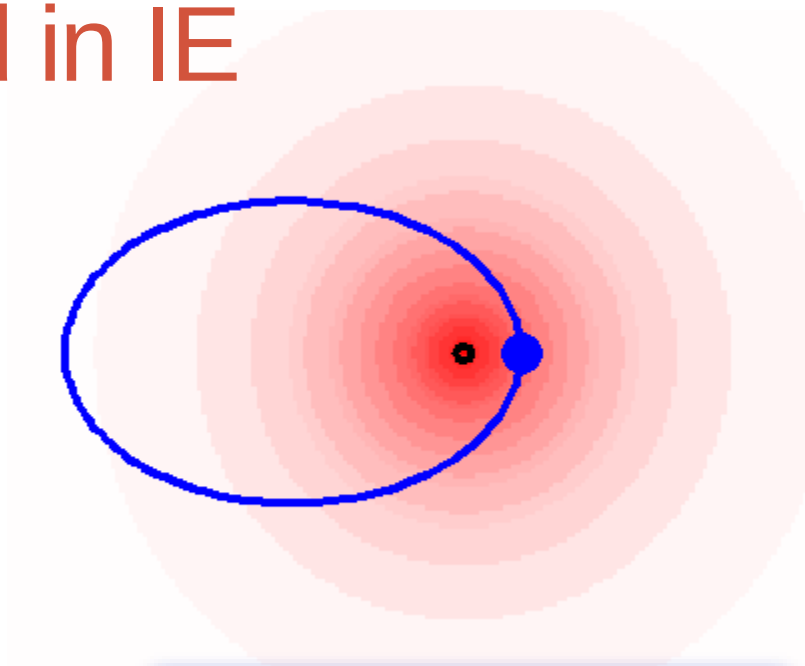


1. General Trend: generally increase moving across a period, then fall abruptly for the alkali atom at the beginning of the next period.
2. d-block contraction, Lanthanide contraction.
3. Zigzag: empty, half full of p orbitals.

Anomaly of the Trend in IE

Electron configurations

- Hg: [Xe] $4f^{14}\ 5d^{10}\ 6s^2$
- Hg^+: [Xe] $4f^{14}\ 5d^{10}\ 6s^1$
- Tl: [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$



Relativistic effect of 6*s* electrons

$$v \rightarrow c \Rightarrow m_e' = \frac{m_e}{\sqrt{1 - v^2/c^2}} \uparrow$$

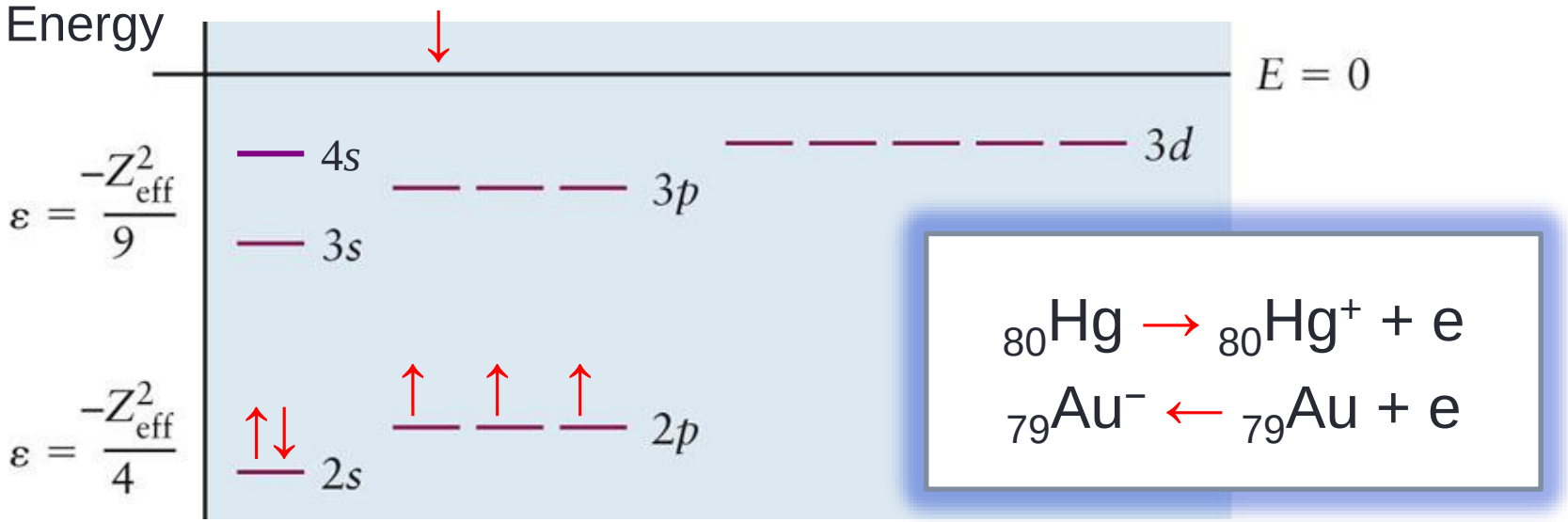
$$\Rightarrow \mathrm{Ry} = \frac{e^4 m_e}{8\varepsilon_0{}^2 h^2} \uparrow \Rightarrow E_{n,Z} \approx -\frac{Z_{\mathrm{eff}}{}^2}{n^2}\mathrm{Ry} \downarrow$$

For $_{80}$Hg $6s^2$,

$v/c \approx 80/137 \approx 0.58$

$m_e' = 1.23 m_e$

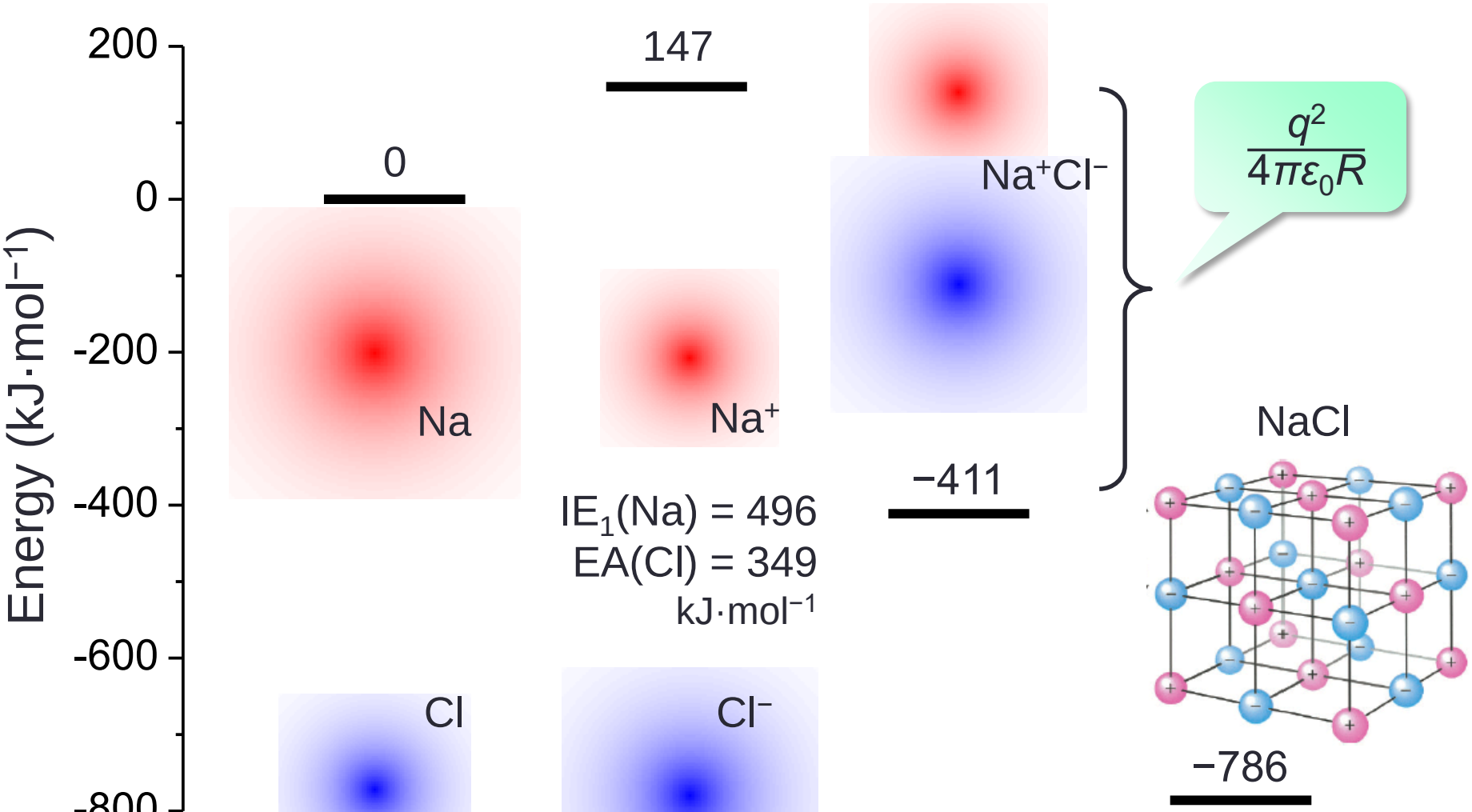
Electron Affinity 电子亲和能



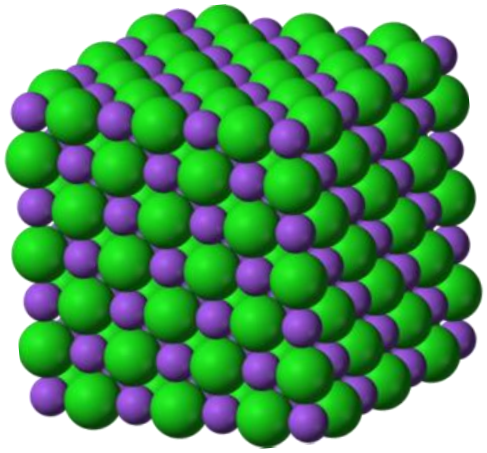
$_{80}Hg \rightarrow {}_{80}Hg^{+} + e$

$_{79}Au^{-} \leftarrow {}_{79}Au + e$

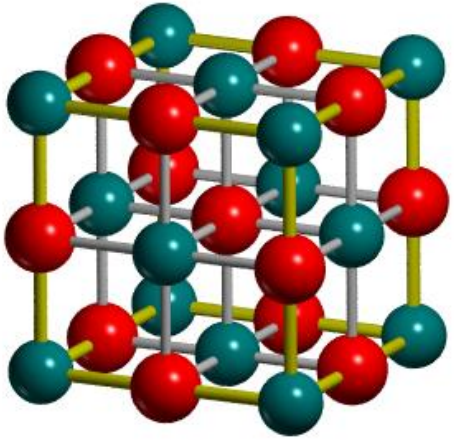
Ionic Bonding: Energetics



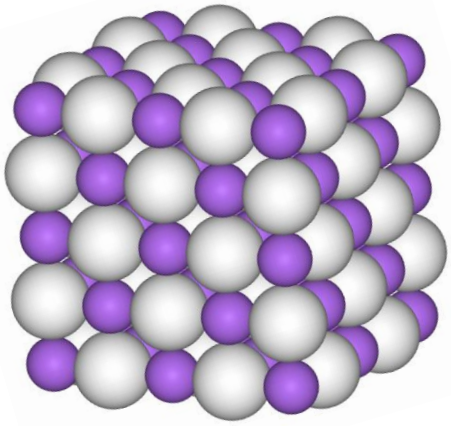
Ionic Bonding: Geometry



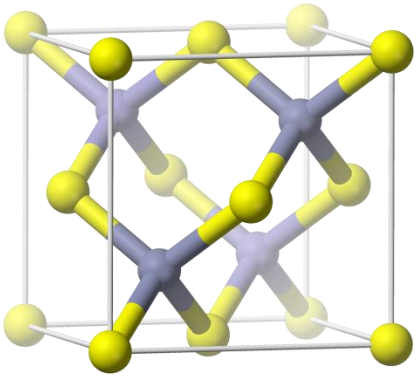
NaCl



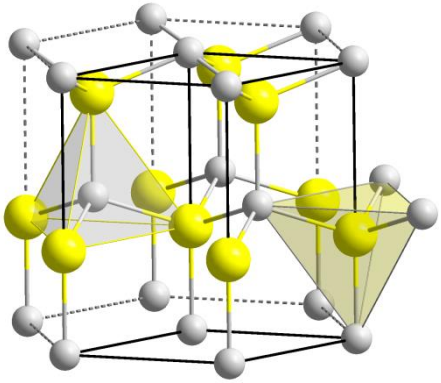
MgO



NaH

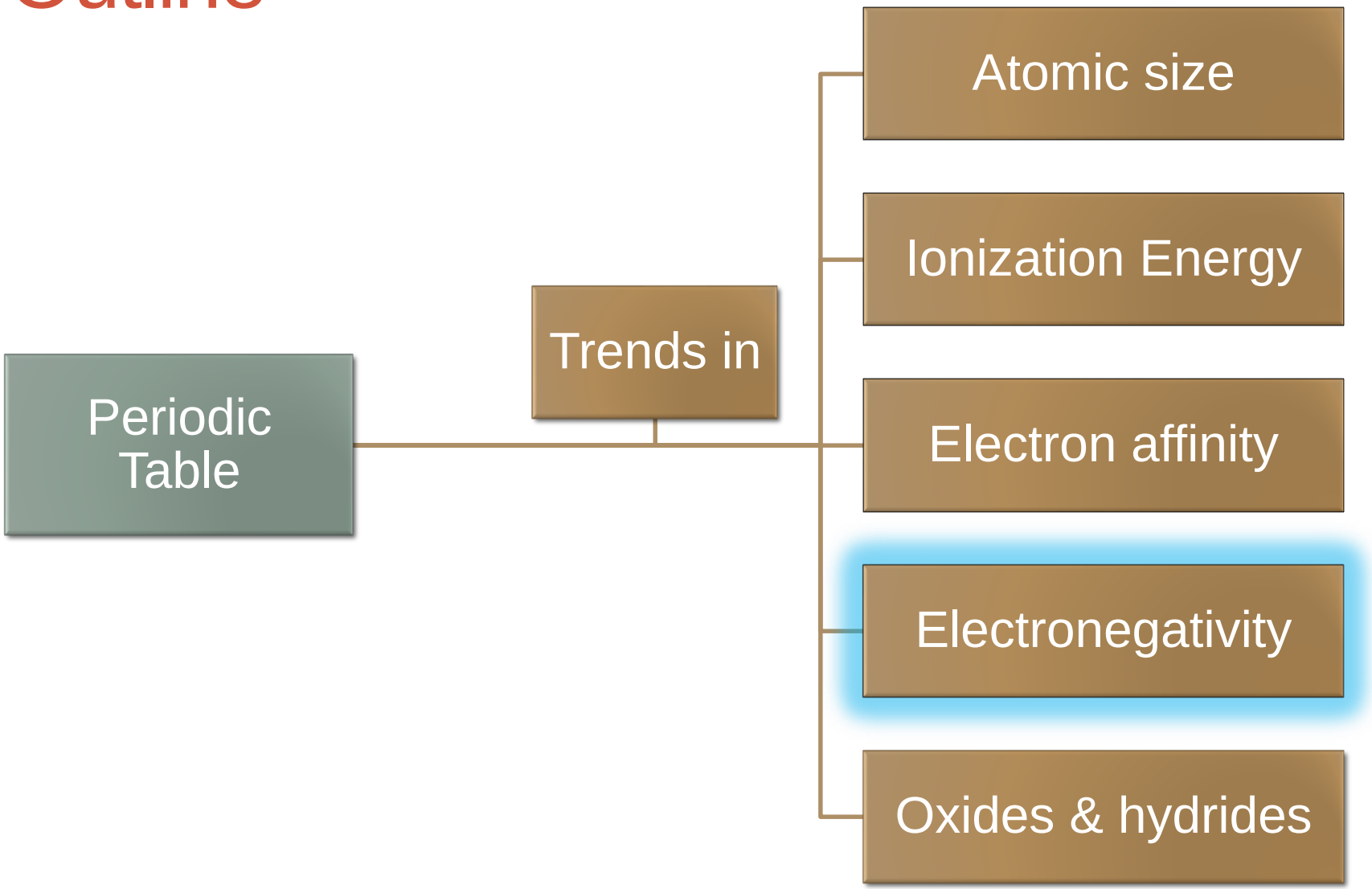


ZnO



ZnO

Outline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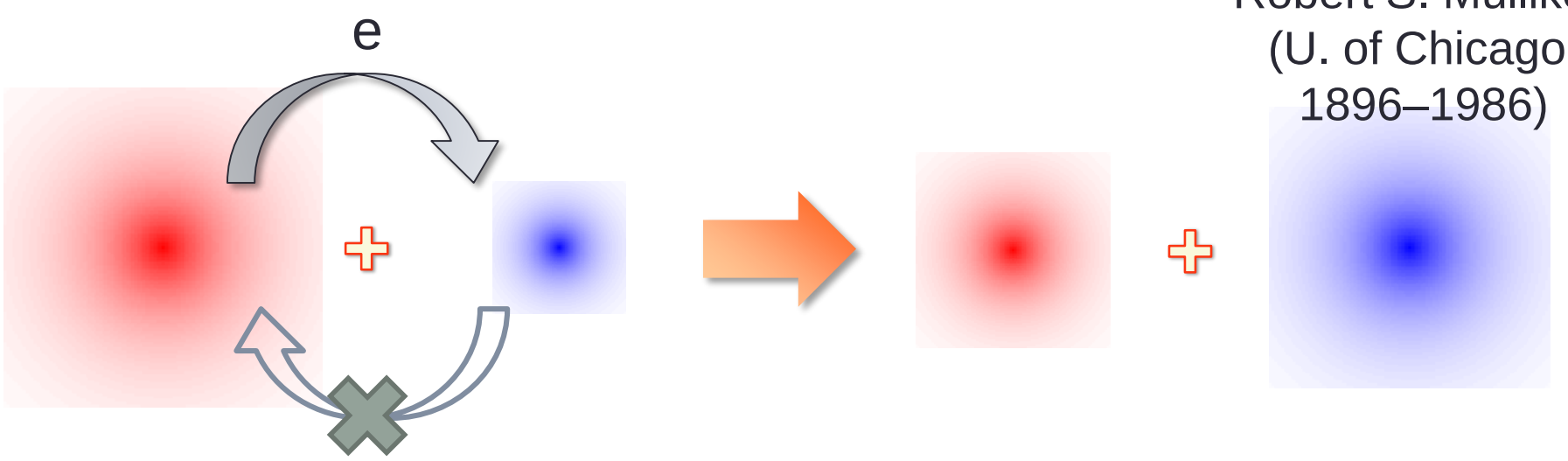
Mulliken's Electronegativity (1934)
电负性

Tendency to attract electrons from a nearby atom.

$$\chi \propto \frac{1}{2}(IE_1 + EA)$$

Robert S. Mulliken
(U. of Chicago,
1896–1986)



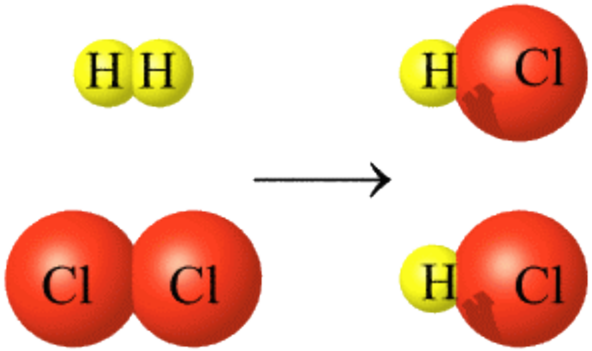
Na
r = 190 pm

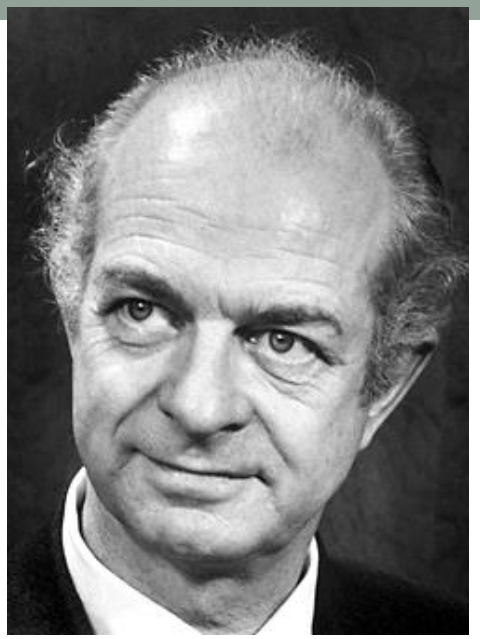
Cl
r = 79 pm

Na^+
r = 116 pm

Cl^-
r = 167 pm

Pauling's Electronegativity (1932)





Linus Pauling
(Caltech, 1901–1994)

$H_2 + Cl_2 \rightarrow 2\ HCl$

ΔE = −95 kJ/mol = −0.98 eV/molecule

$|\chi_{Cl} - \chi_H| \approx \sqrt{0.98} = 0.99$

$H_2 + Br_2 \rightarrow 2\ HBr$

ΔE = −53 kJ/mol = −0.55 eV/molecule

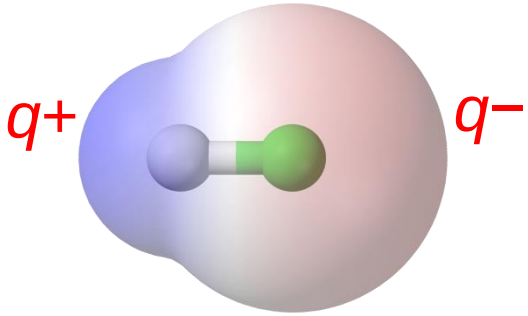
$|\chi_{Br} - \chi_H| \approx \sqrt{0.55} = 0.74$

$Br_2 + Cl_2 \overset{?}{\rightarrow} 2\ BrCl$

ΔE = −1.0 kJ/mol = −0.01 eV/molecule

$|\chi_{Cl} - \chi_{Br}| \approx \sqrt{0.01} = 0.1$

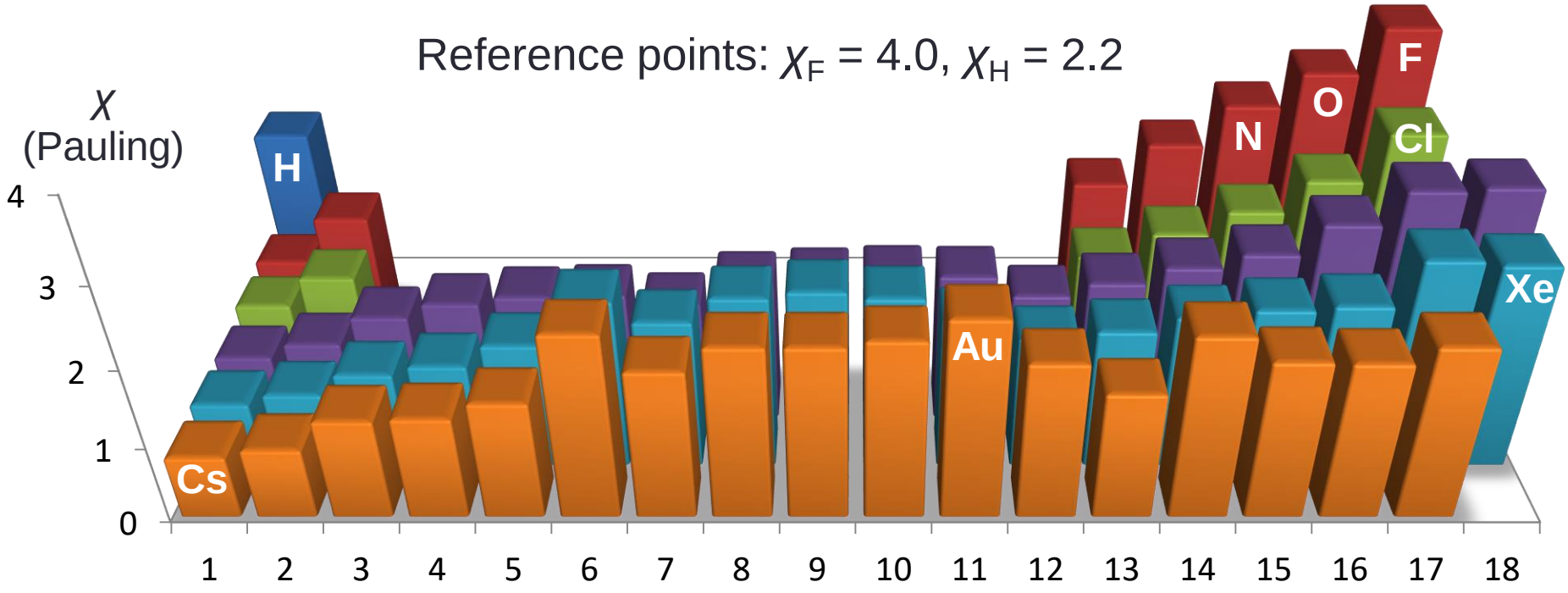
Calculating Electronegativities



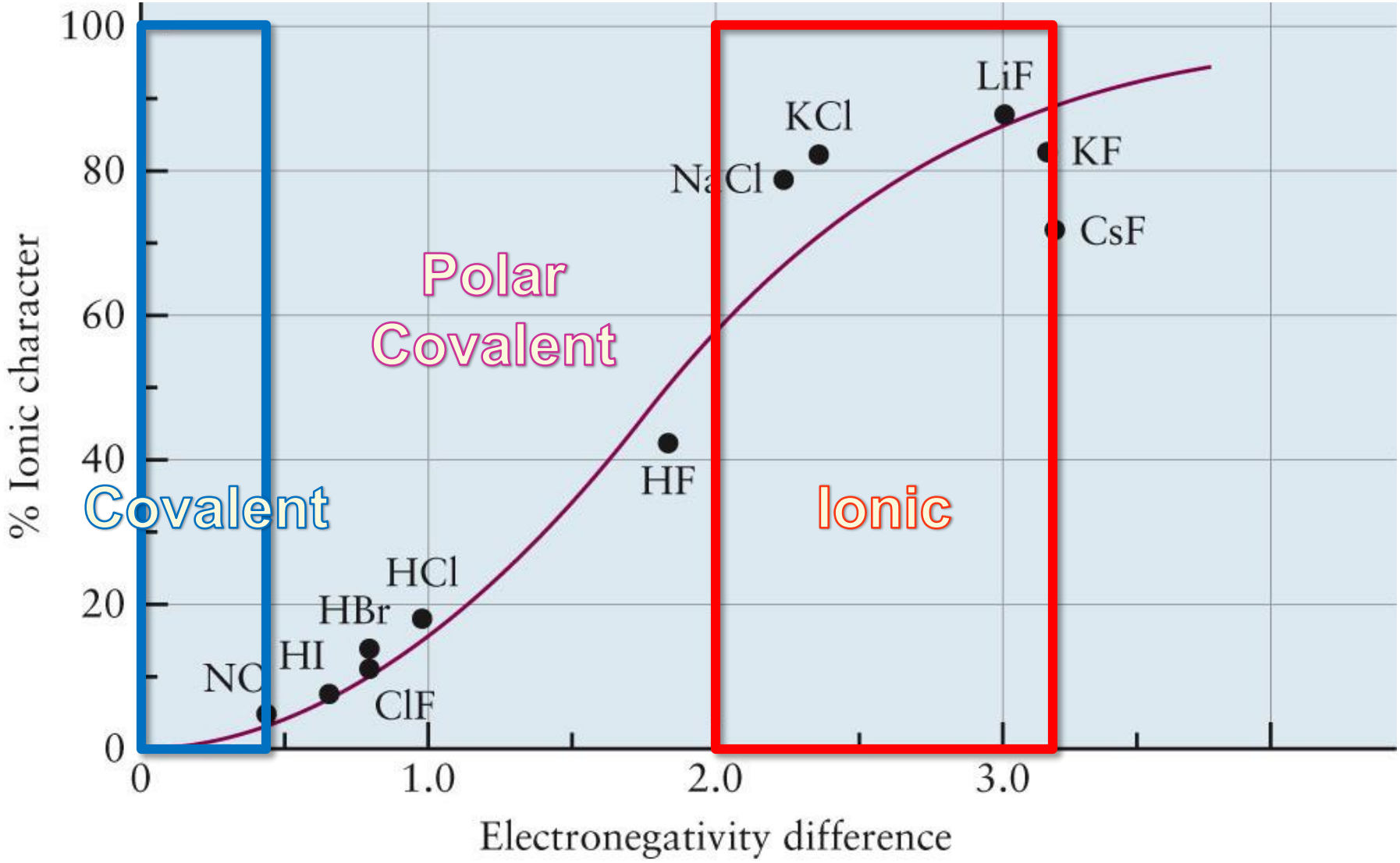
$H^{q+}—Cl^{q-}$

$$(\chi_A - \chi_B)^2 \propto q^2 \propto \Delta E$$

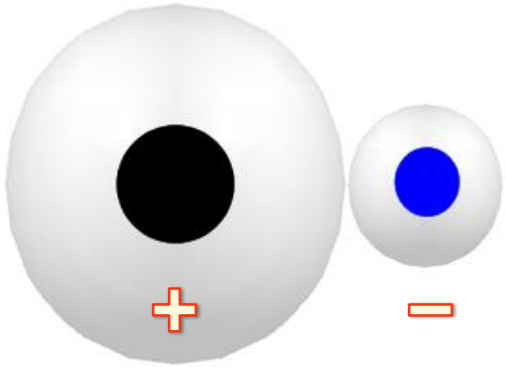
Reference points: $\chi_F = 4.0$, $\chi_H = 2.2$



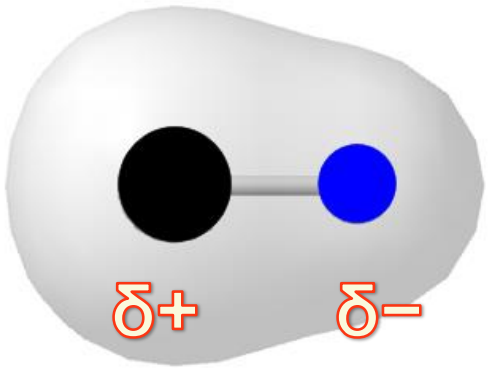
Electronegativity and Bonding



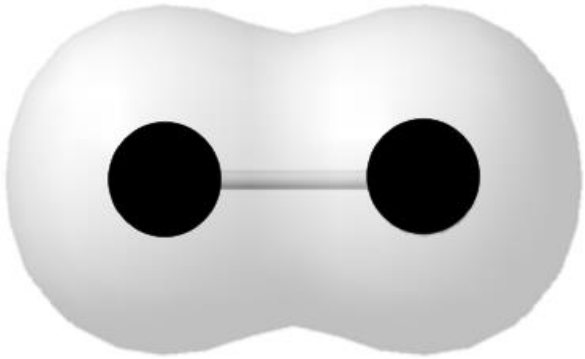
From Ionic to Covalent Bonding



Ionic

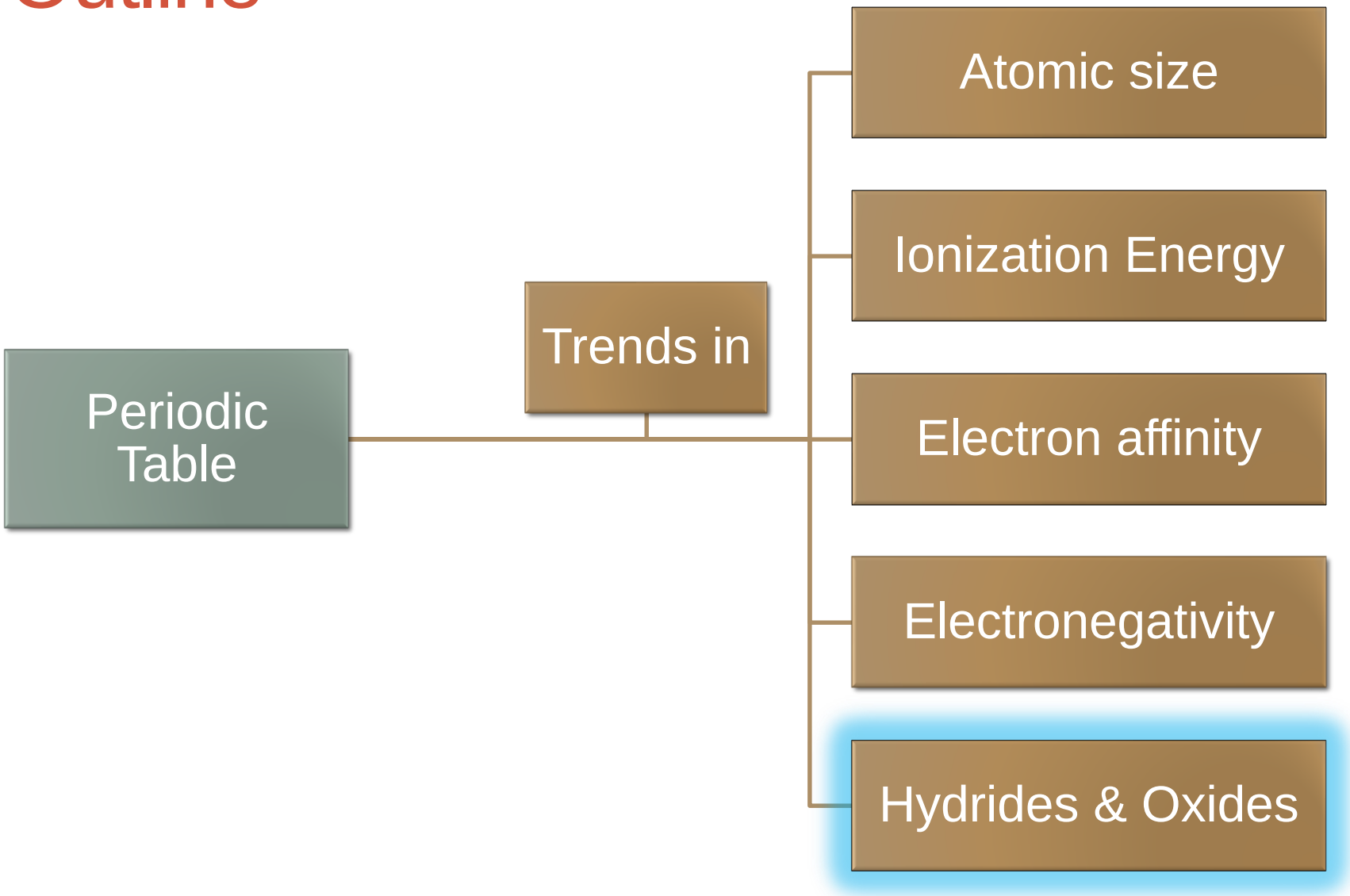


Polar Covalent



Covalent

Outline


Periodic Table
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Hydrides & Oxides

Periodic Trends in Forming Hydrides

		δ−	δ+			
LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	HF
NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl

χ = 2.20

χ = 2.55

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	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**															

Periodic Trends in Forming Oxides

δ− δ+

Li_2O BeO B_2O_3 CO_2 N_2O_5 OF_2

Na_2O MgO Al_2O_3 SiO_2 P_2O_5 SO_3 Cl_2O_7

Ionic → Covalent

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	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**															

Acid/Base Properties of Oxides

Basic:

$$Na_2O + H_2O \rightarrow Na^+(aq) + OH^-(aq)$$

Acidic:

$$Cl_2O_7 + H_2O \rightarrow ClO_4^-(aq) + H^+(aq)$$

Amphoteric 两性的:

$$Al_2O_3 + H^+(aq) \rightarrow Al^{3+}(aq) + H_2O$$

$$Al_2O_3 + OH^-(aq) + H_2O \rightarrow Al(OH)_4^-(aq)$$

aq: aqueous 水合

Most acidic: $HClO_4$

Most basic: CsOH

H																He
Li	Be	*Basic*										B	C	N	O	F	Ne
Na	Mg							*Amphoteric*				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	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Acidic

Summary

- Electronegativity
  - Mulliken: $\chi \propto \frac{1}{2}(IE_1 + EA)$
  - Pauling: $(\chi_A - \chi_B)^2 \propto q^2 \propto \Delta$
- Bonding
  - Ionic
  - Covalent / polar covalent
- Oxides and hydrides
  - Charge
  - Basic, acid, amphoteric

$\chi_F = 4.0$
$\chi_H = 2.2$

Next Lecture Series: Bonding in Molecules

Reading: OGB8 §6, YY §§3.2–3.5