FAMSE: Fundamental Aspects of Material Science and Engineering

(Electro-)catalyst oxide materials – part I

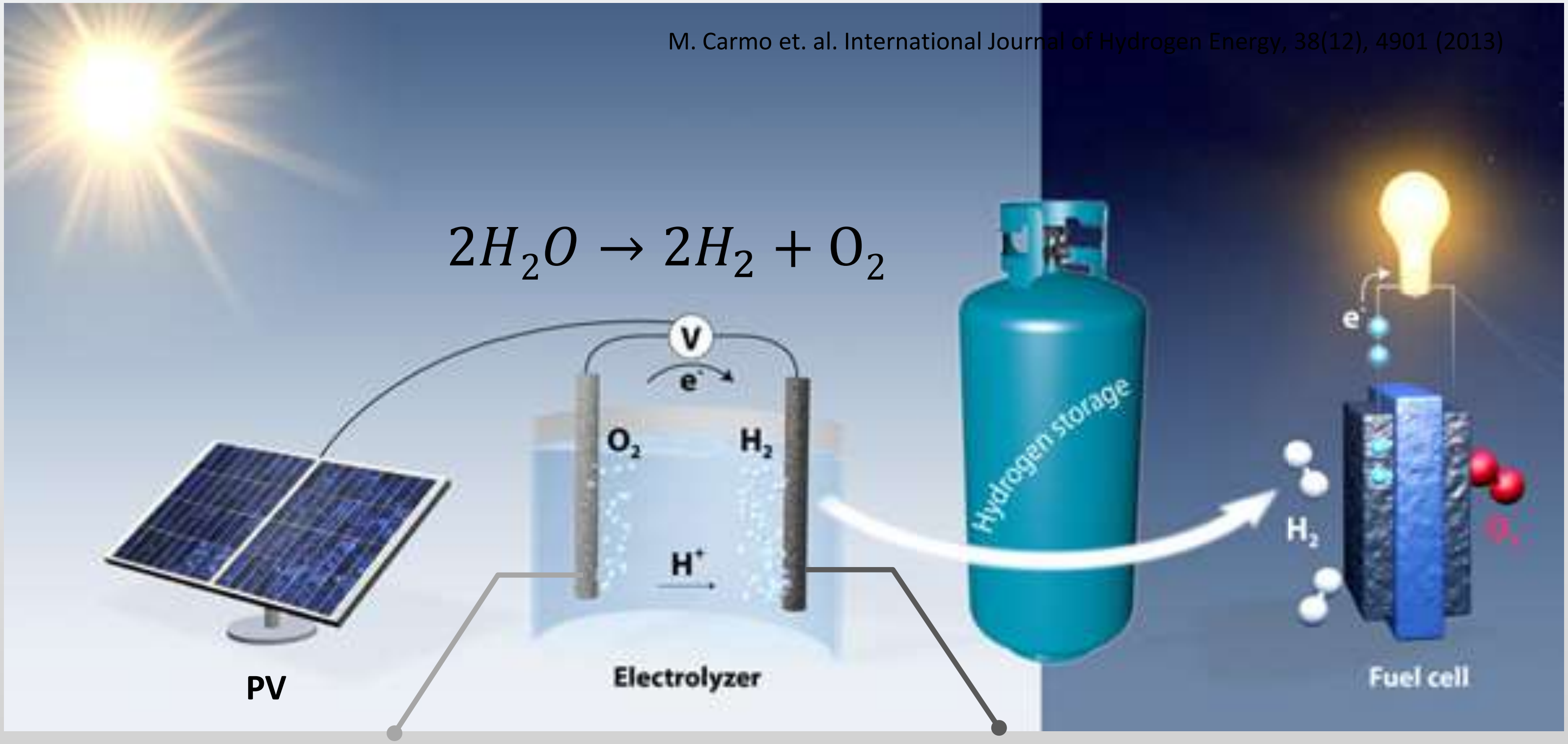
Tong Li

Atomic-scale Characterisation

Institute for Materials
Department of Mechanical Engineering
Ruhr-University Bochum

Sustainable energy cycle

- Delivery energy using hydrogen to solve the negative effects of using hydrocarbon fuels



M. Carmo et. al. International Journal of Hydrogen Energy, 38(12), 4901 (2013)

$$2H_2O \rightarrow 2H_2 + O_2$$

At anode:

Acidic $2\,H_2O \rightarrow 4H^+ + O_2 + 4e^-$

Alkaline $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

Oxygen Evolution Reaction (OER)

At cathode:

$$4\,H^+ + 4e^- \rightarrow 2H_2$$

Hydrogen Evolution Reaction (HER)

Structure of lectures

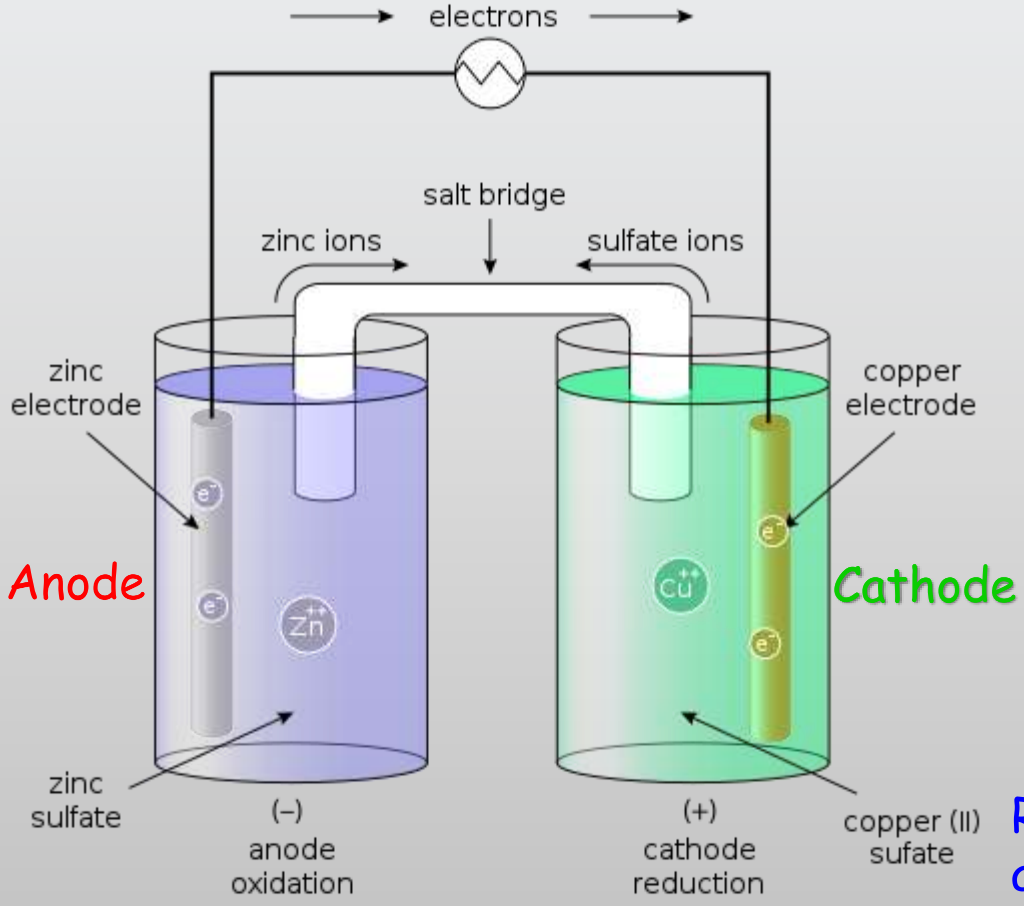
- Basics of electrochemical reactions
- (oxide) electrocatalyst
- Atomic and electronic structure
- Ionic bond
- Covalent bond
- Pauling's rule
- Oxide structure
- Descriptors of electrocatalysts' activity

Electrochemical reactions and electrocatalyst

Applications of electrochemistry

Battery – first invented by Alessandro Volta (1745 - 1817)

Voltaic cell: an electrochemical cell that uses a chemical reaction to produce electrical energy



Anode: oxidation process (losing electrons)

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

Cathode: reduction process (gaining electrons)

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

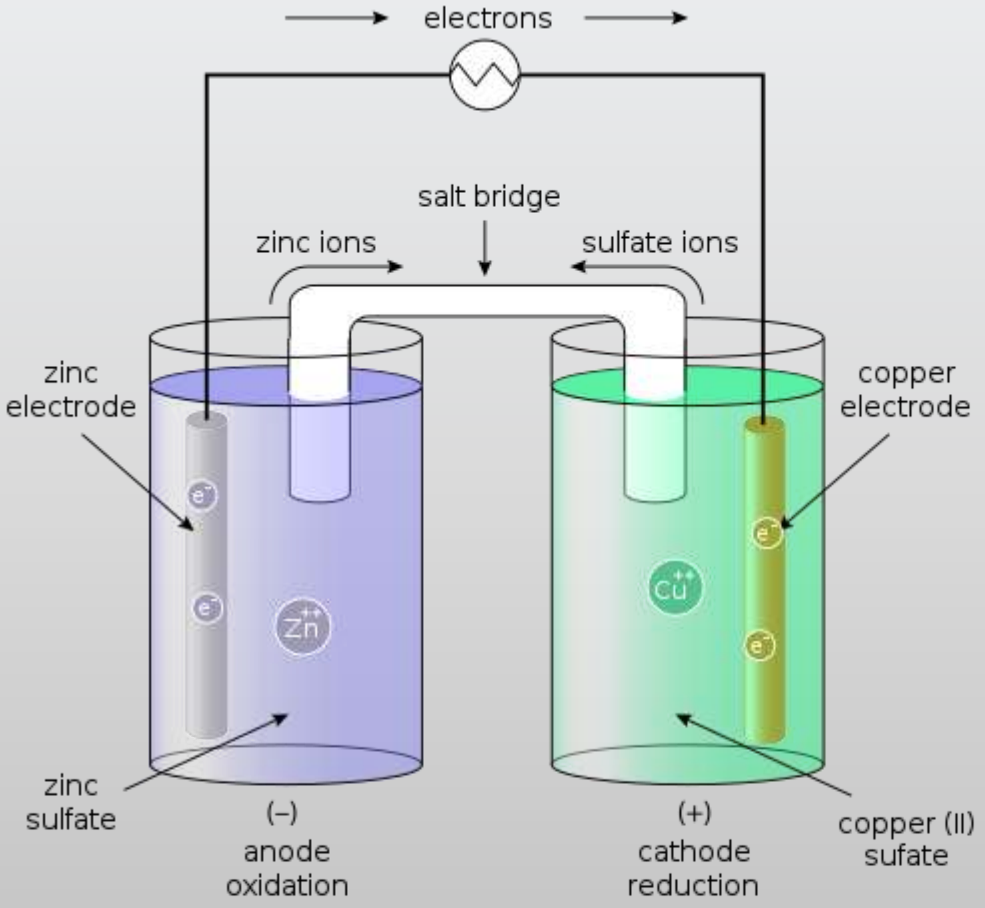
Reducing agent

Oxidizing agent

Applications of electrochemistry

Battery – first invented by Alessandro Volta (1745 - 1817)

Voltaic cell



Oxidation (anode) | Reduction (cathode)

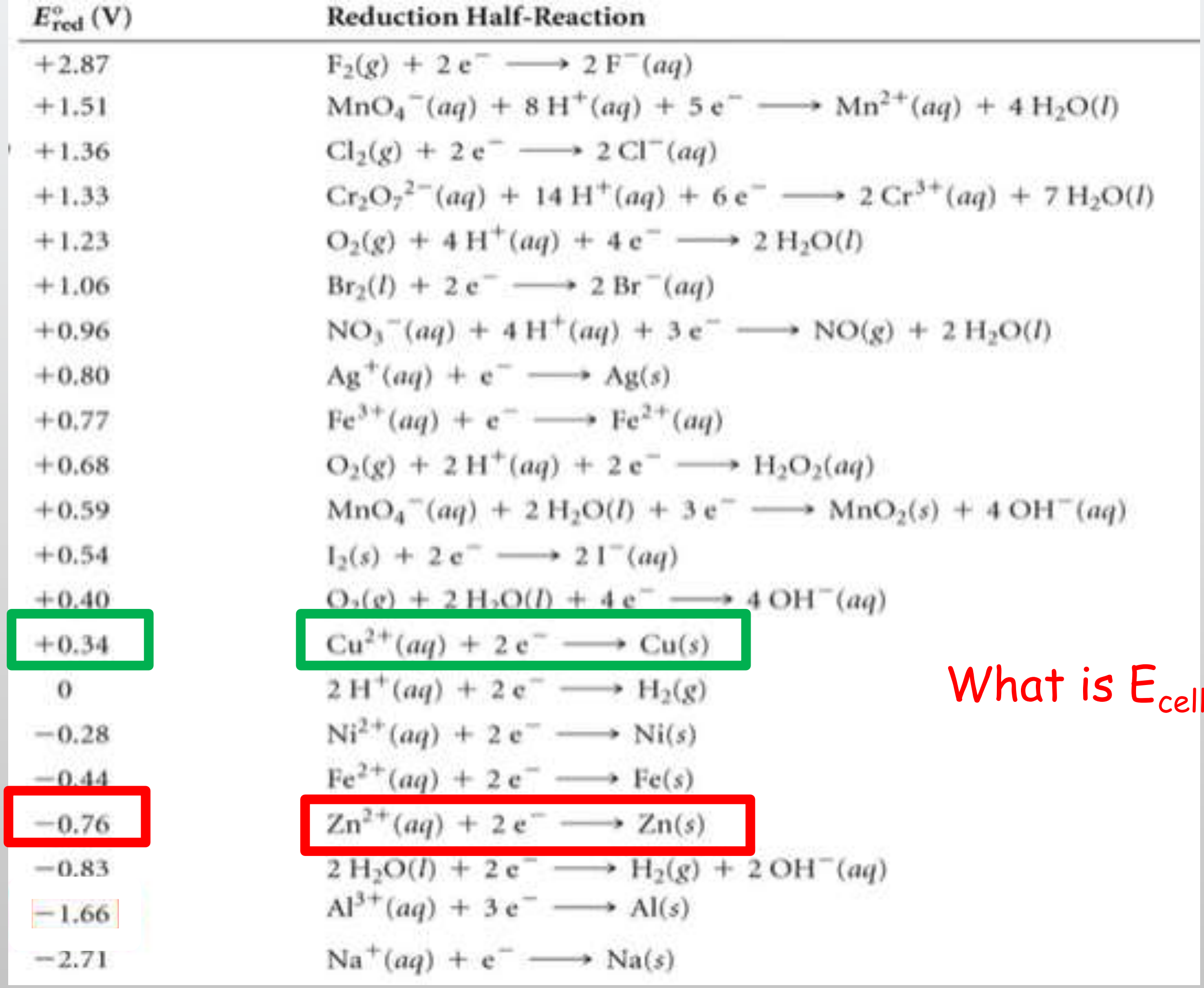
$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$$

Phase boundary | Salt bridge | Phase boundary

- As electrons moves from anode to cathode, ions travel through salt bridge
- Salt bridge is to maintain charge balance → Cations travel to cathode, anions travel to anode.

Standard reduction potential

- Standard reduction potential indicates the likelihood that a species to be reduced (measured at 298 K, 1 atm with 1 M solution (opposite to standard oxidation potential)



E°_{red} (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$

What is E_{cell}?

Oxidation (anode)

Reduction (cathode)

$$Zn_{(s)} \,|\, Zn^{2+}_{(aq)} \,\|\, Cu^{2+}_{(aq)} \,|\, Cu_{(s)}$$

$$Cell\ potential\ E_{cell}$$

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= 0.34 - (-0.76) = 1.1\ V$$

Gibbs free energy

$$\boxed{\Delta G = qE = -nFE}$$

where n is the number of moles of electrons and F is the Faraday constant (96485C/mol)

$$\boxed{\Delta G^o = -nFE^0}$$

Standard condition (1 atm, 298 K, concentration 1 mol/l)

$$E^o = 1.1\ V$$

$$= -2\left(96485\frac{C}{mole^-}\right)\left(\frac{1.1J}{C}\right)$$

$$= -212.267\ kJ/mol$$

Spontaneous reaction

Cell potential is positive, Δ G is negative, so when E is negative, Δ G is positive

Nernst equation

At non-standard conditions, what happens?

$$E = E^o - \frac{RT}{nF} lnQ$$

Q = concentration of products/reactants

R: 8.314J $k^{-1}mol^{-1}$, T = 25 °C, F is 96485C/mol

$$E = E^o - \frac{0.0257}{n} lnQ \qquad E = E^o - \frac{0.05916}{n} logQ$$

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

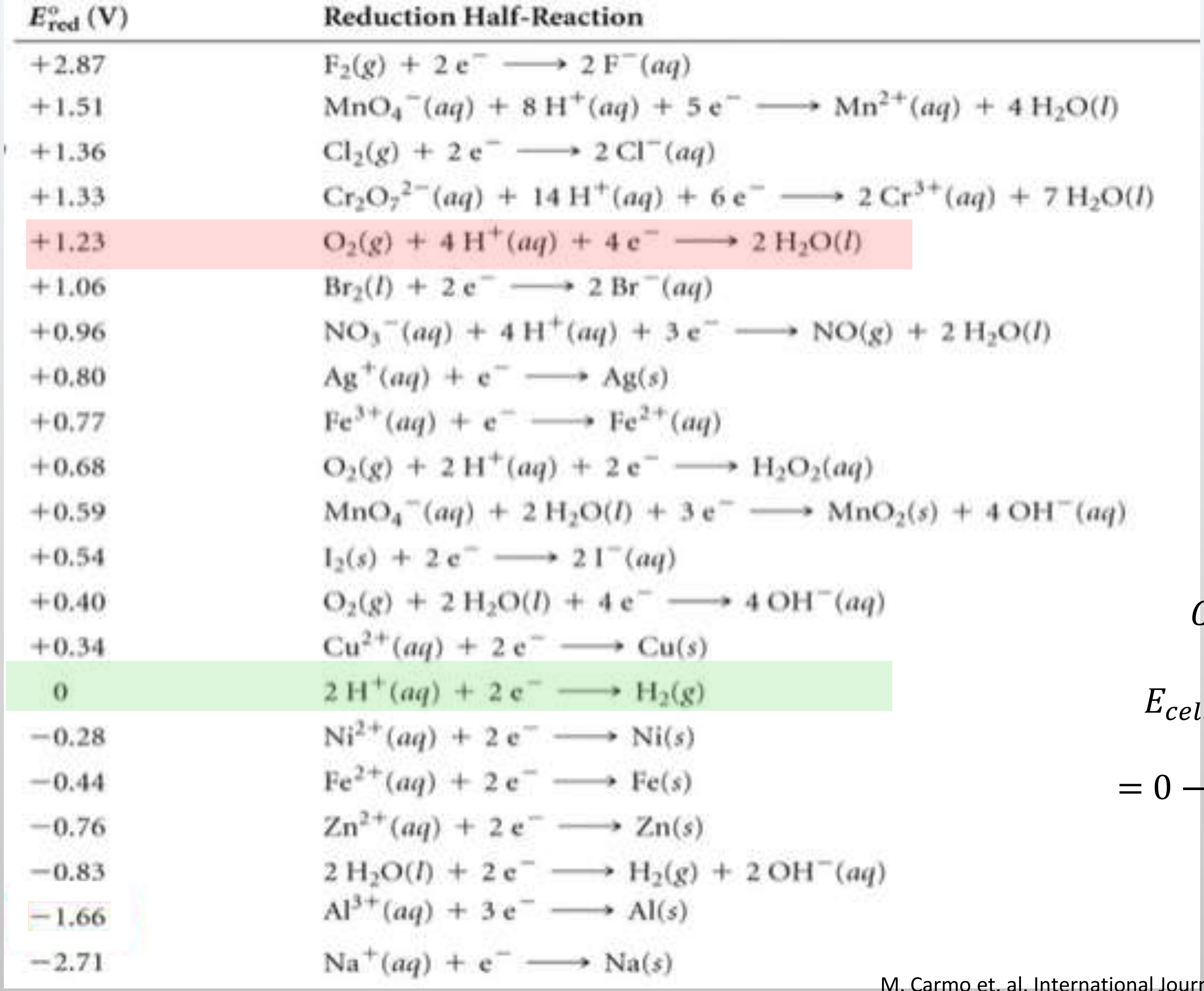
What is the cell potential?

10 M 0.01 M

$$E = E^o - \frac{0.05916}{n} logQ = 1.1 - \frac{0.0591}{2} \log\left(\frac{0.01}{10}\right) = 1.19\ V$$

→ Increasing the concentration of reactants or decreasing the concentration of products would increase the potential to a higher value → stronger driving force to drive the reaction to take place

Standard Nernstian potential of oxygen evolution reaction (OER)



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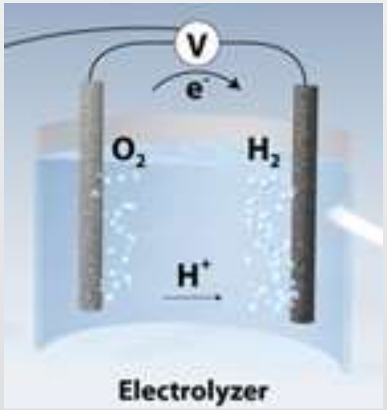
OER



Acidic solution

Cell potential E_{cell}

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= 0 - (1.23) = -1.23\ V$$

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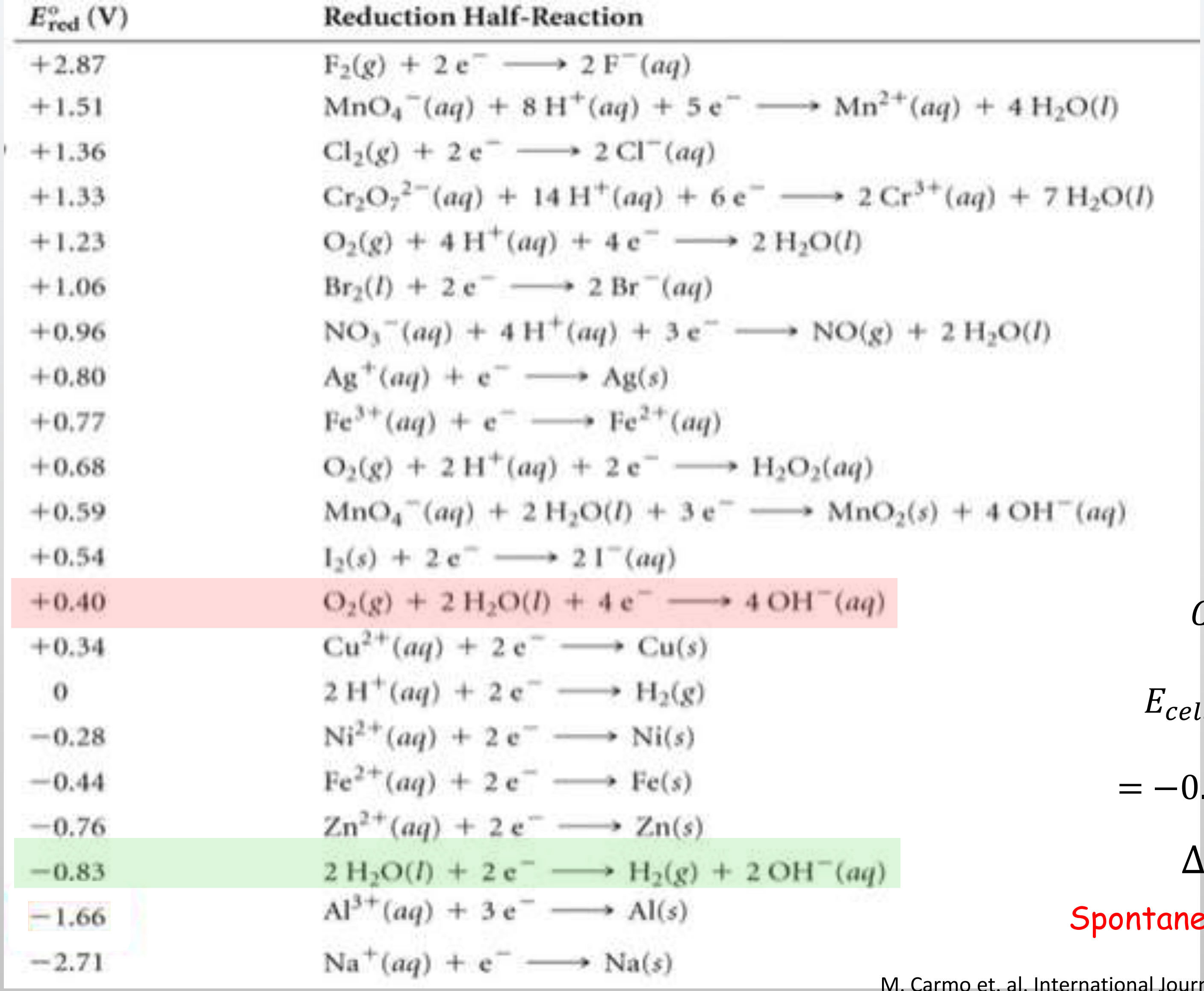
Standard Nernstian potential of oxygen evolution reaction (OER)



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+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
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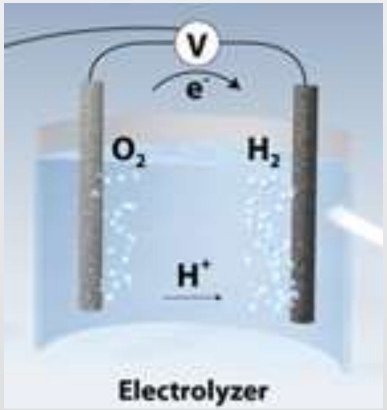
OER



Alkaline solution

Cell potential E_{cell}

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= -0.83 - (0.40) = -1.23\ V$$

$$\Delta G^o = -nFE^0$$

Spontaneous or non-spontaneous?

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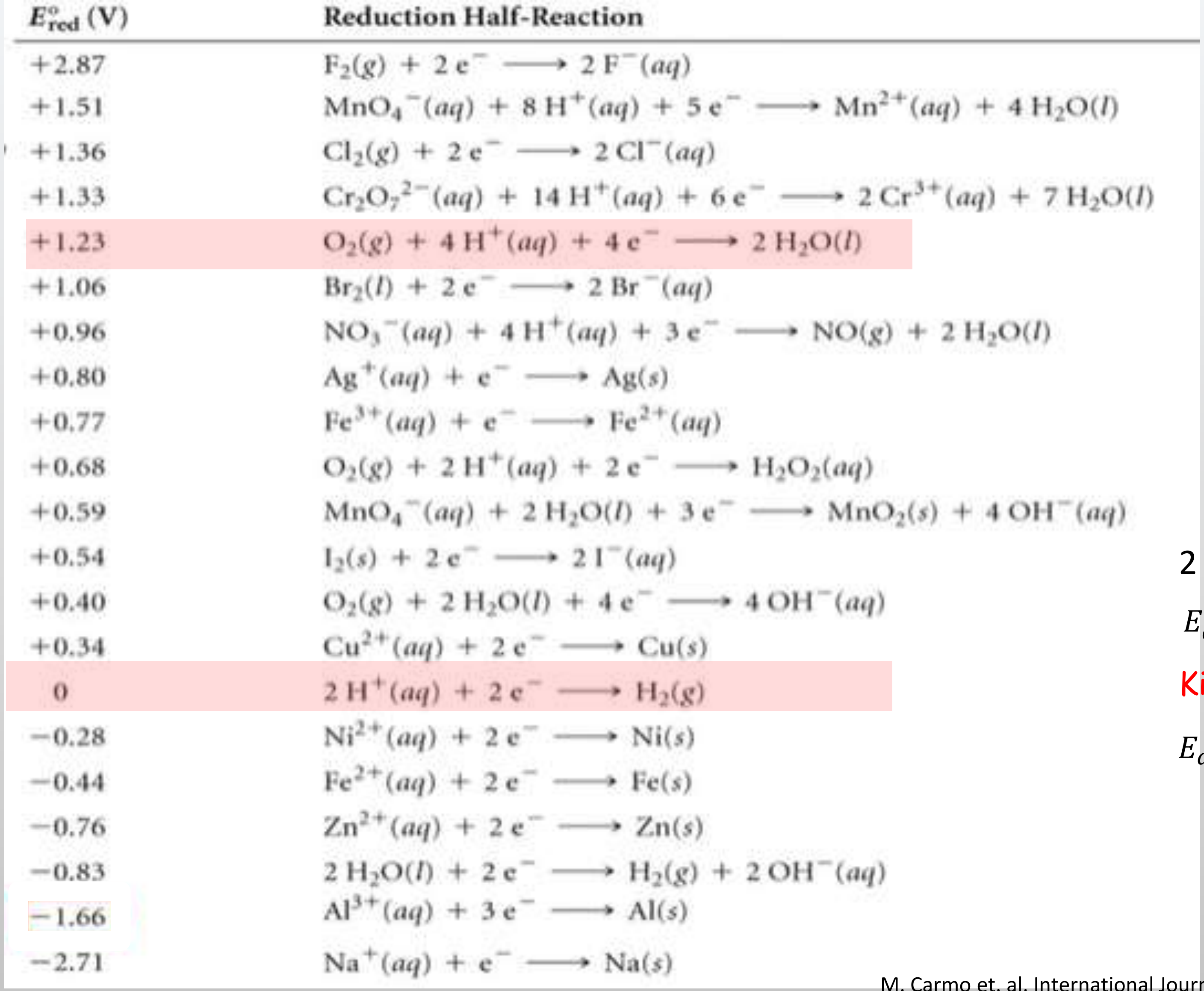
Standard Nernstian potential of oxygen evolution reaction (OER)



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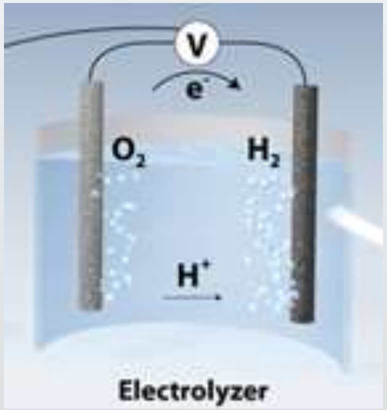
OER



At anode:

$$2\,H_2O \rightarrow 4H^+ + O_2 + 4e^-$$

$$E^o_{anode} = -1.23\ V$$

Kinetically slow

$$E_{anode} = E^o_{anode} + \eta_{anode}$$

Overpotential

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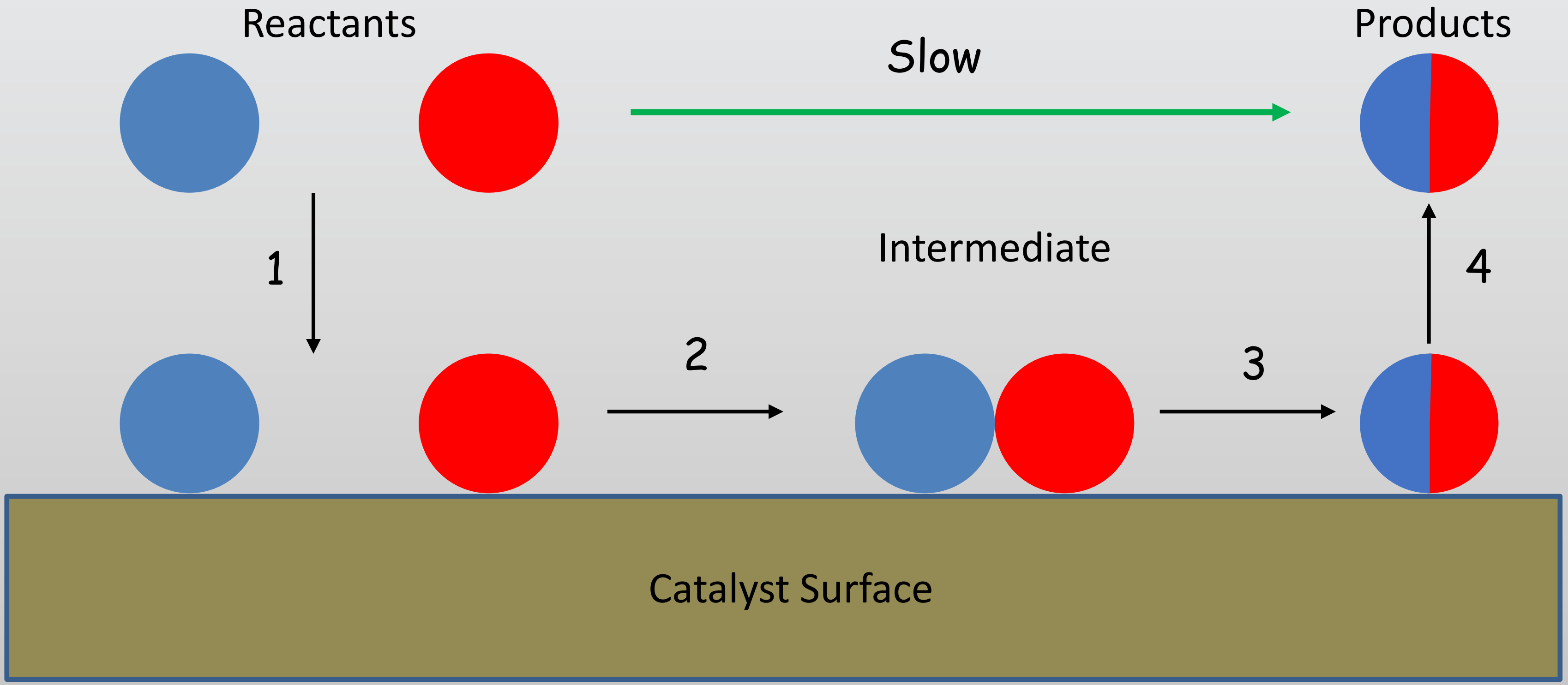
Oxide electrocatalysts

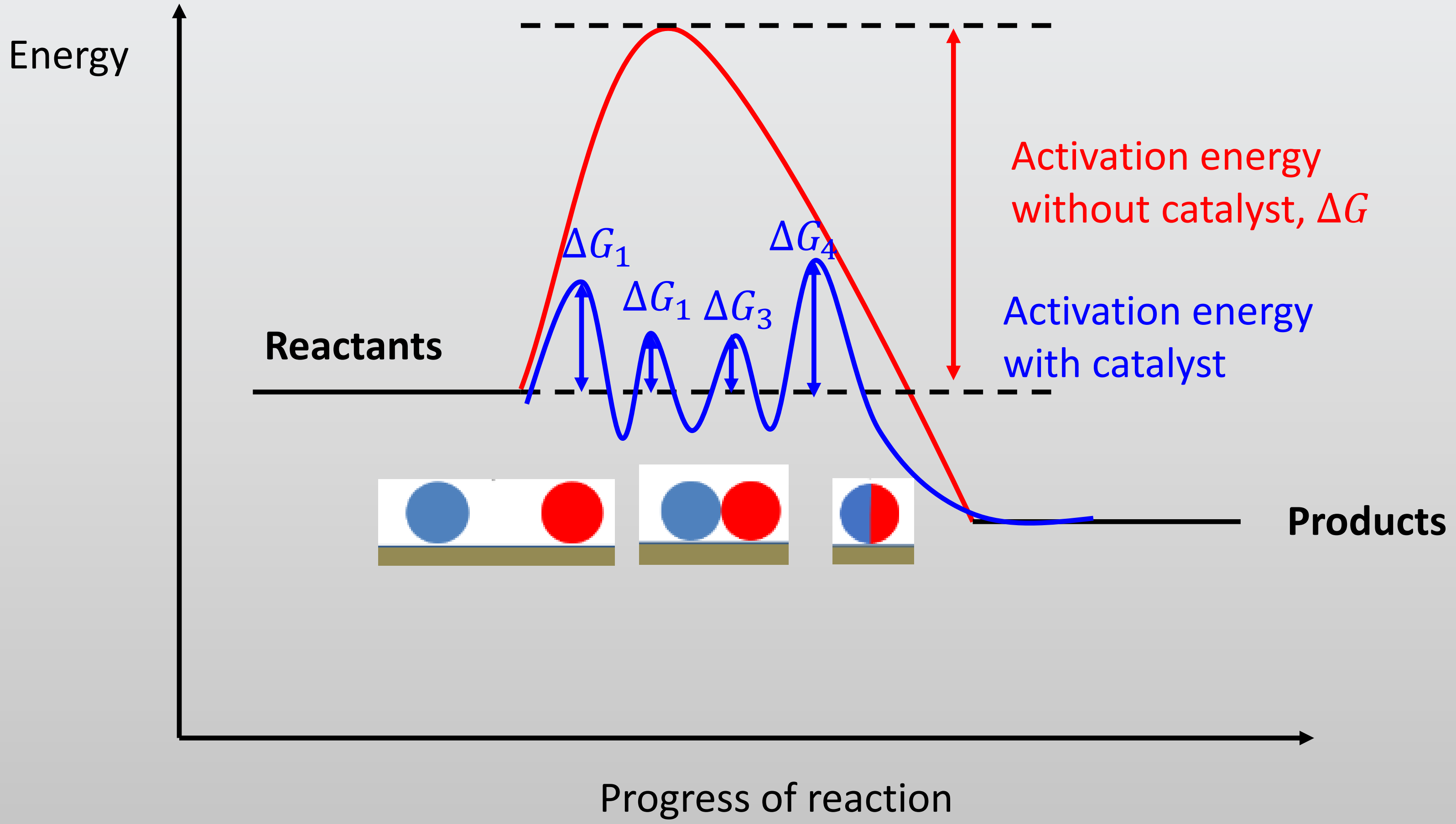
What is a catalyst?

- Catalysts are substances that can speed up/slow down chemical reactions.
- They can do this without being used up or chemically changed as the reactants turn into products.
- They have essentially the same structure and properties before and after a chemical reaction.



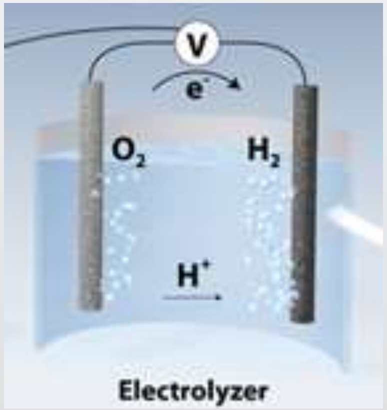
Why uses catalyst?

- Catalyst enables the reaction pathways that require lower activation energy
- It does not change the energy difference between the reactants and products



Oxygen evolution reaction

OER



At anode:

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$$

in alkaline solution

$$OH^- + * \rightarrow HO^* + e^- \quad (1)$$

$$HO^* \rightarrow O^* + e^- + H^+ \quad (2)$$

$$O^* + OH^- \rightarrow HOO^* + e^- \quad (3)$$

$$HOO^* \rightarrow * + O_2(g) + e^- + H^+ \quad (4)$$

1) In particular, OH- first adsorbs on the surface O vacancy site (equation1).
2) The adsorbed OH (OH* species) then undergoes subsequent deprotonation to form O*.
3) The following O-O bond formation step allows O* to react with another OH- to form the HOO* intermediate.
4) In the final step, O_2 is evolved through the deprotonation of HOO* with regeneration of the active site

Subprocesses and Gibbs free energy change

$$OH^- + * \rightarrow HO^* + e^- \quad (1)$$

$$HO^* \rightarrow O^* + e^- + H^+ \quad (2)$$

$$O^* + OH^- \rightarrow HOO^* + e^- \quad (3)$$

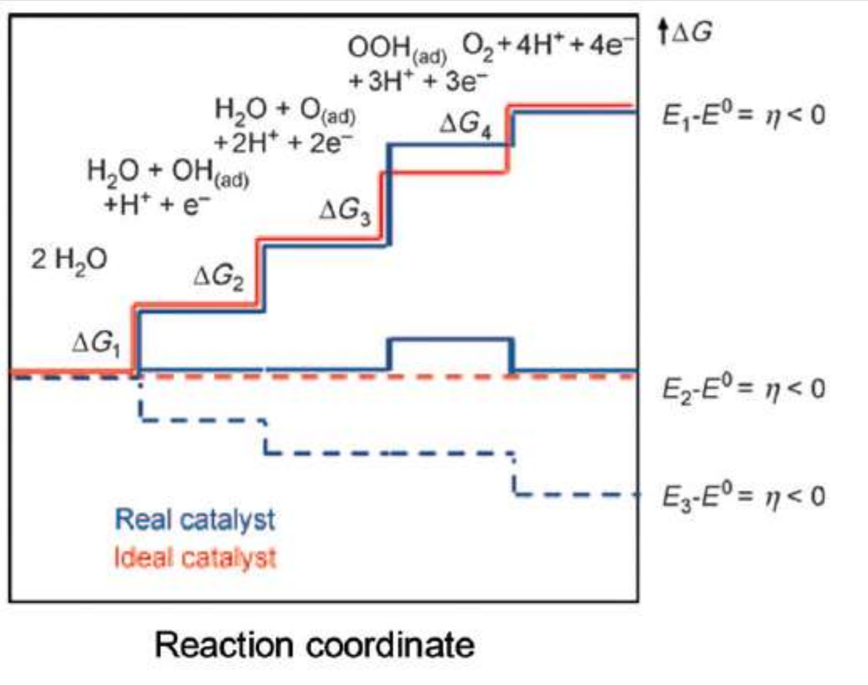
$$HOO^* \rightarrow * + O_2(g) + e^- + H^+ \quad (4)$$

$$\Delta G_1 = \Delta G_{HO*} - \Delta G_* + \frac{1}{2} G_{H_2(g)} - eU$$

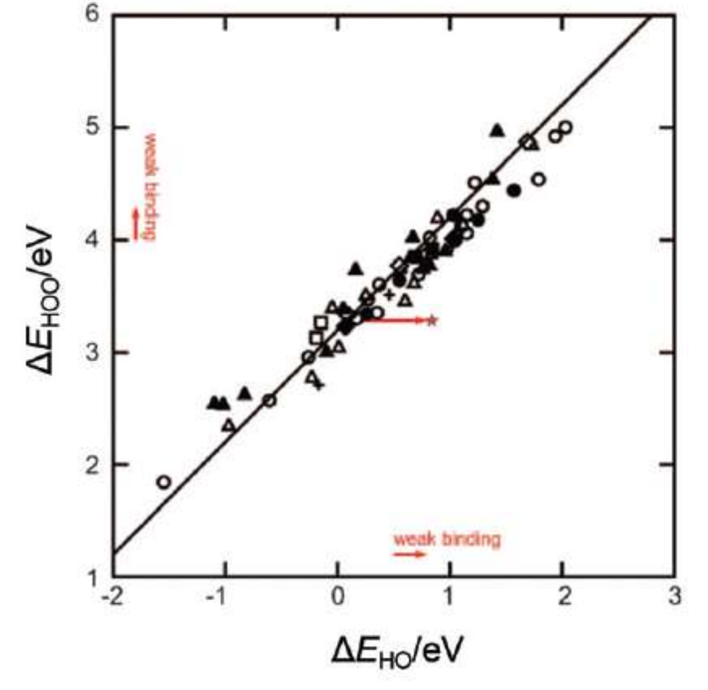
$$\Delta G_2 = \Delta G_{O*} - \Delta G_{HO*} + \frac{1}{2} G_{H_2(g)} - eU$$

$$\Delta G_3 = \Delta G_{HOO*} - \Delta G_{O*} + \frac{1}{2} G_{H_2(g)} - eU$$

$$\Delta G_4 = \Delta G_{O_2(g)} + \Delta G_* - \Delta G_{HOO*} + \frac{1}{2} G_{H_2(g)} - eU$$



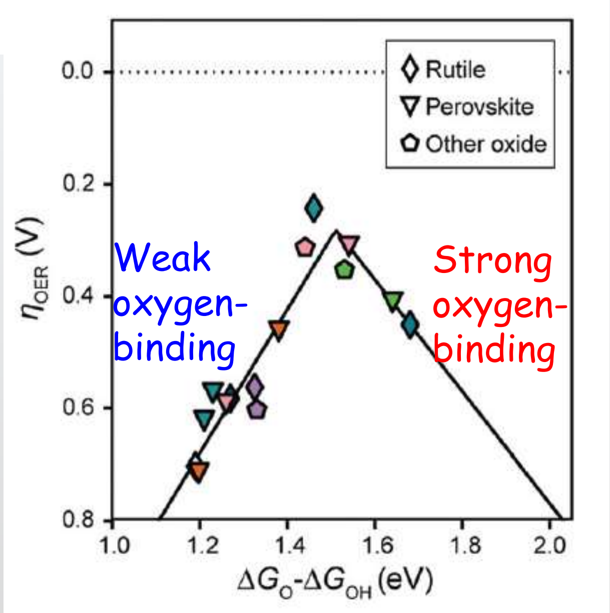
Scaling relation



$$(\Delta G_{HOO*} - \Delta G_{HO*}) = 3.2 \pm 0.2$$

Volcano plot

$\Delta G_{O*} - \Delta G_{HO*}$



Weak oxygen-binding

Strong oxygen-binding

Paul Sabatier (1854-1941, France)

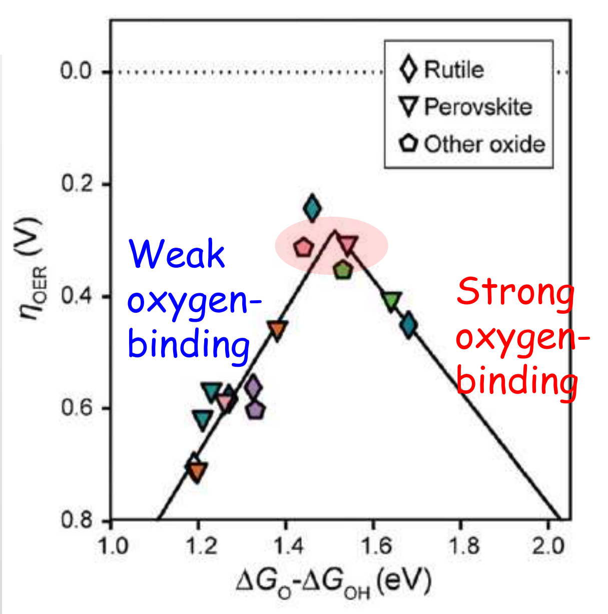
Sabatier principle:

a) If the interaction is too weak, the molecule will fail to bind to the catalyst and no reaction will take place.
b) if the interaction is too strong, the product fails to dissociate.

→ The interactions between the catalyst and the substrate should be neither too strong nor too weak

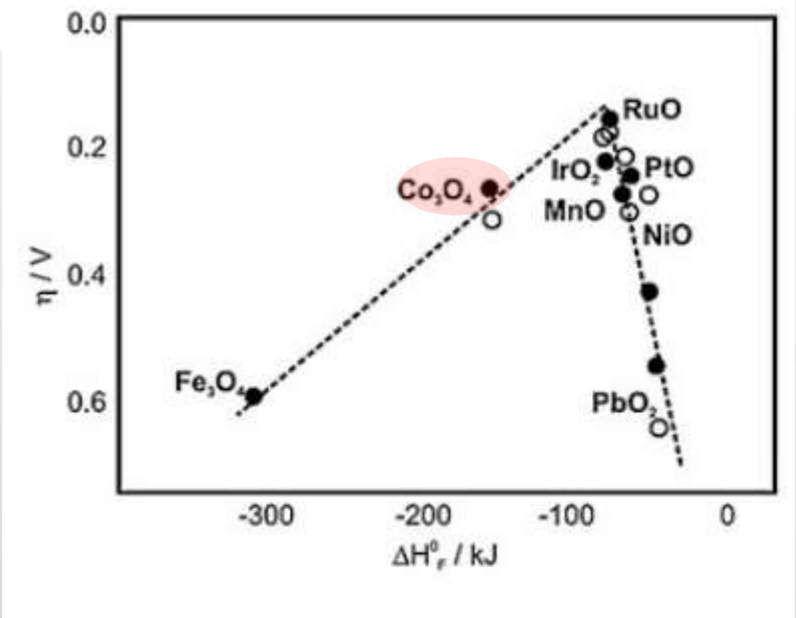
Perovskite ABO_3 & spinel oxides – AB_2O_4

$\Delta G_{O*} - \Delta G_{HO*}$



Enthalpy of lower to higher oxidation oxide

Trasatti, J. Electroanal. Chem., 111(1980) 125-131

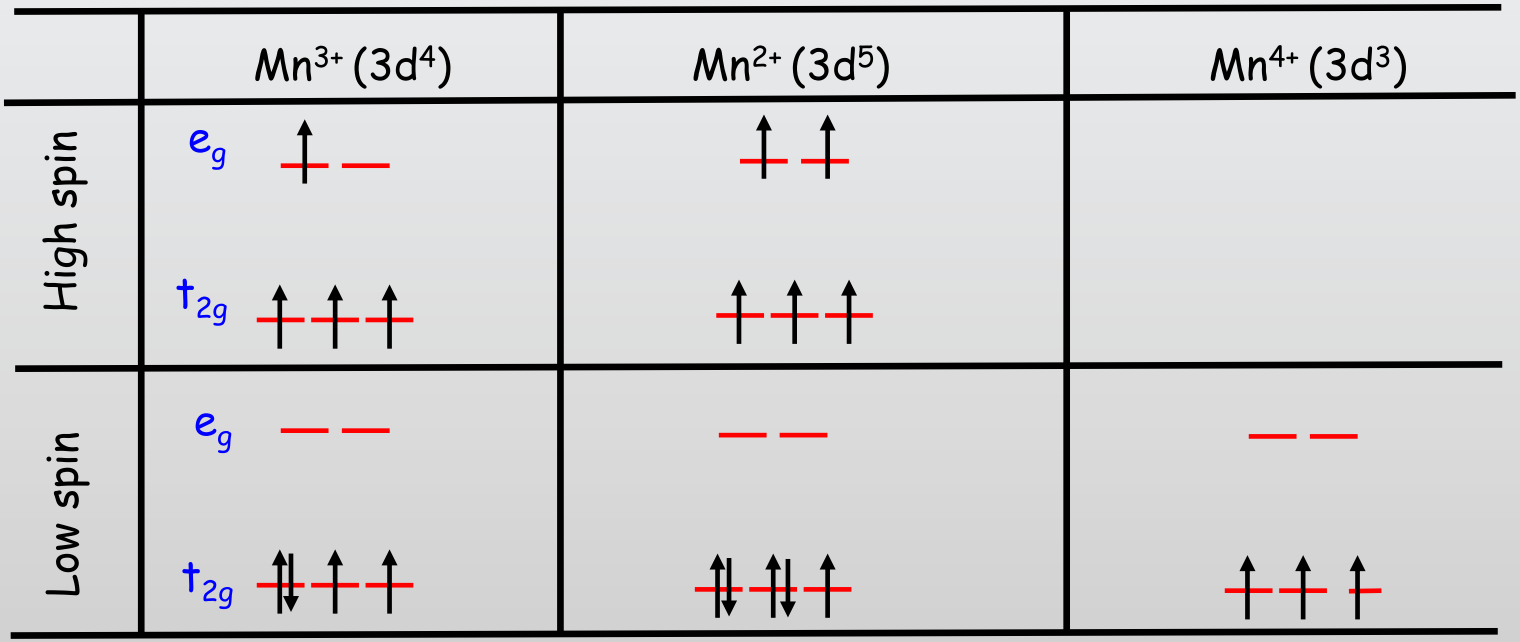


- IrO_2 and RuO_2 are active OER electrocatalysts in acidic media, but they are expensive

- Spinels and perovskites (ABO_3 , AB_2O_4) are promising

- Regulating the electronic structure can optimize the value of $\Delta G_{O*} - \Delta G_{HO*}$ → substituting with foreign elements, creating vacancies, tuning the strain and engineering the interface

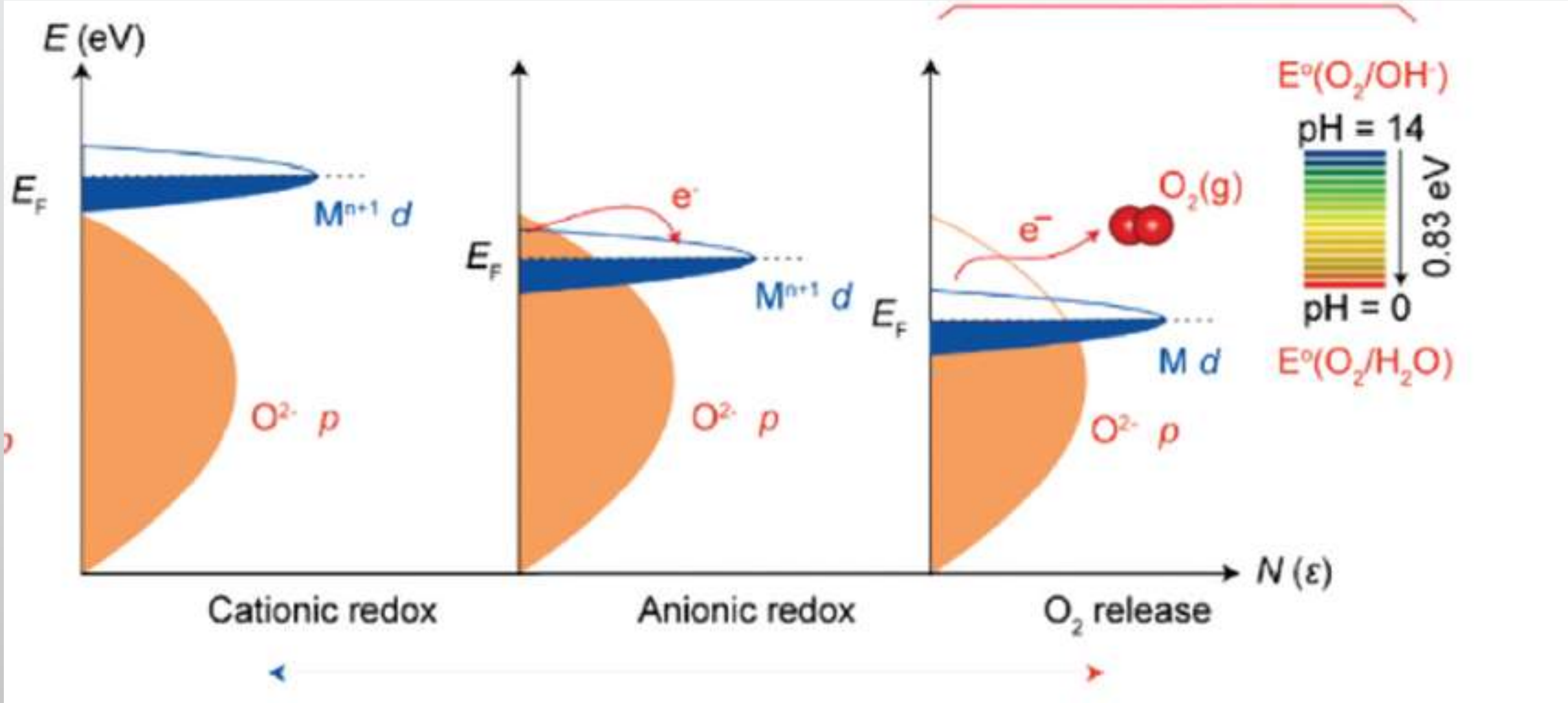
e_g orbital occupancy: The lower the eg occupancy, the stronger the binding of oxygen



		Mn^{3+} ($3d^4$)	Mn^{2+} ($3d^5$)	Mn^{4+} ($3d^3$)
High spin	e_g	↑ —	↑ ↑	
	t_{2g}	↑ ↑ ↑	↑ ↑ ↑	
Low spin	e_g	— —	— —	— —
	t_{2g}	↑↓ ↑ ↑	↑↓ ↑↓ ↑	↑ ↑ ↑

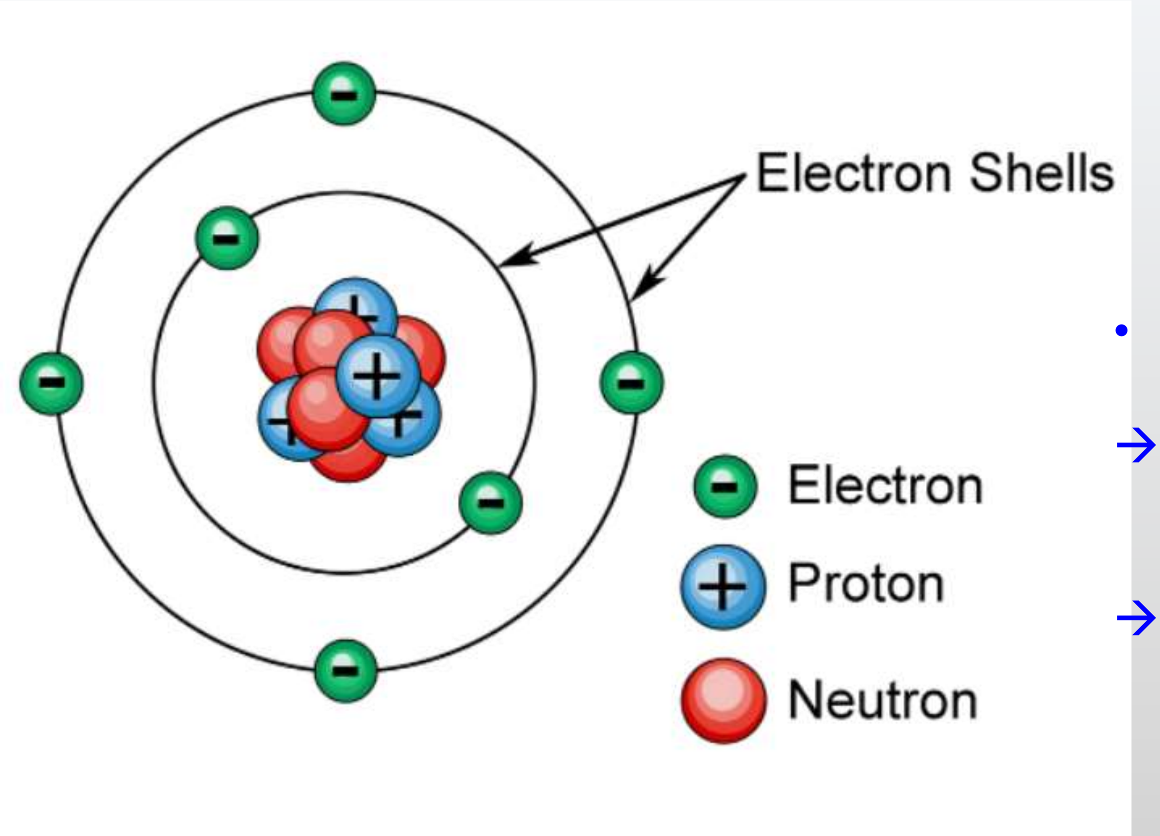
Metal-oxygen covalency

- Increasing the electronegativity of transition metal typically moves the metal d state close to O 2p state → decreasing the binding dissociation bonds of M-O → improving OER activity



Atomic/electronic structure of atoms

Atomic structure



- What is this element?

→ It contains 6 neutrons and 6 protons

→ It is orbited by 6 electrons

Atomic number (Z) = number of protons

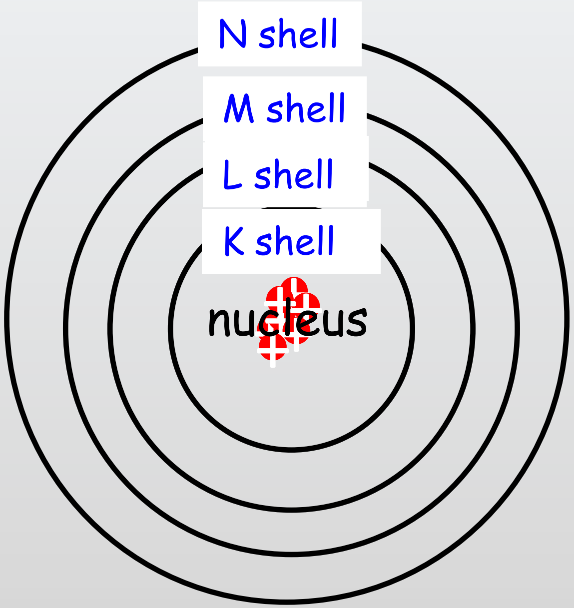
Mass number (A) = sum of protons and neutrons

Isotopes = protons + neutrons

^{12}C = 98,89% (abundance)
^{13}C = 1,109%
^{14}C = 1 ppt (part per trillion)

Electron shells

- Electrons’ orbit is quantized with a discrete level K, L, M, N is the principal quantum number n



- *orbitals are the regions of space in which electrons are most likely to be found.*

Second derivative with respect to X

Schrodinger Wave Function

$$\frac{\partial^2\psi}{\partial X^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Position

Energy

Potential energy

Wave function: the probability of finding electrons at certain energy levels within an atom

	Symbol	Possible values
Principal quantum number	n	1, 2, 3, 4, …n
Angular momentum quantum number	l	0,1, 2,3, …(n-1)
Magnetic quantum number	m_l	-l, …-1, 0, 1, …, l
Spin quantum number	m_s	+1/2, -1/2

- Principle quantum number n : energy of an electron and size of the orbital

- Angular momentum quantum number l: divides the shells into smaller groups of orbitals (subshells), 0, 1, 2, 3, 4, 5 → s, p, d, f, g, h (the energy of subshell increases with l) → determines shape of the orbital

- Magnetic quantum number m_l: orientation in space of an orbital of a given energy n and shape l (individual orbitals)

- Spin quantum number m_s: orientation of the spin axis of an electron (up or down)

Electrons in subshells

- Angular momentum quantum number s, p, d, f, g, h, i, j etc indicates the shapes of orbital

Sub - shell	l	Maximum electrons 2(2l+1)
s	0	2
p	1	6
d	2	10
f	3	14

n	**l (l = n-1)**	**M_l (-l, …l)**	**Number of orbitals**	**Orbital name**	**Number of electrons 2(2l+1)**
1	0	0	1	1s	2
2					
3					
4					

n	l (l = n-1)	M_l (-l, …l)	Number of orbitals	Orbital name	Number of electrons 2(2l+1)
1	0	0	1	1s	2
2	0	0	1	2s	2
	1	-1, 0, 1	3	2p	6
3	0	0	1	3s	2
	1	-1, 0, 1	3	3p	6
	2	-2, -1, 0, 1, 2	5	3d	10
4	0	0	1	4s	2
	1	-1, 0, 1	3	4p	6
	2	-2, -1, 0, 1, 2	5	4d	10
	3	-3, -2, -1, 0, 1, 2, 3	7	4f	14

FAMSE: Fundamental Aspects of Material Science and Engineering

(Electro-)catalyst oxide materials – part II

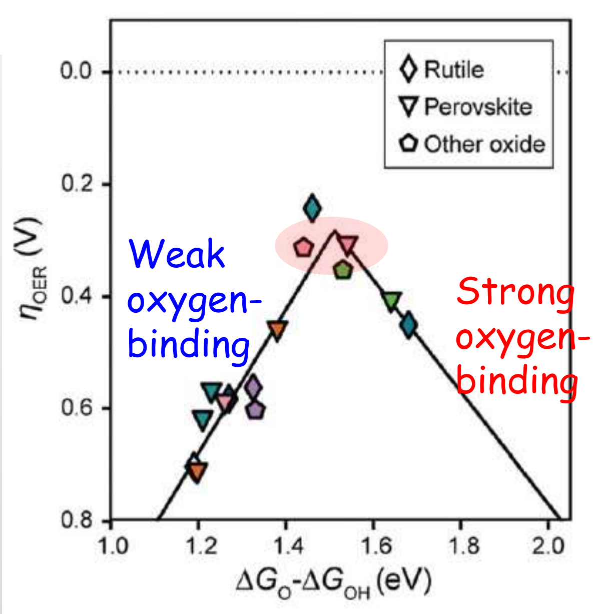
Tong Li

Atomic-scale Characterisation

Institute for Materials
Department of Mechanical Engineering
Ruhr-University Bochum

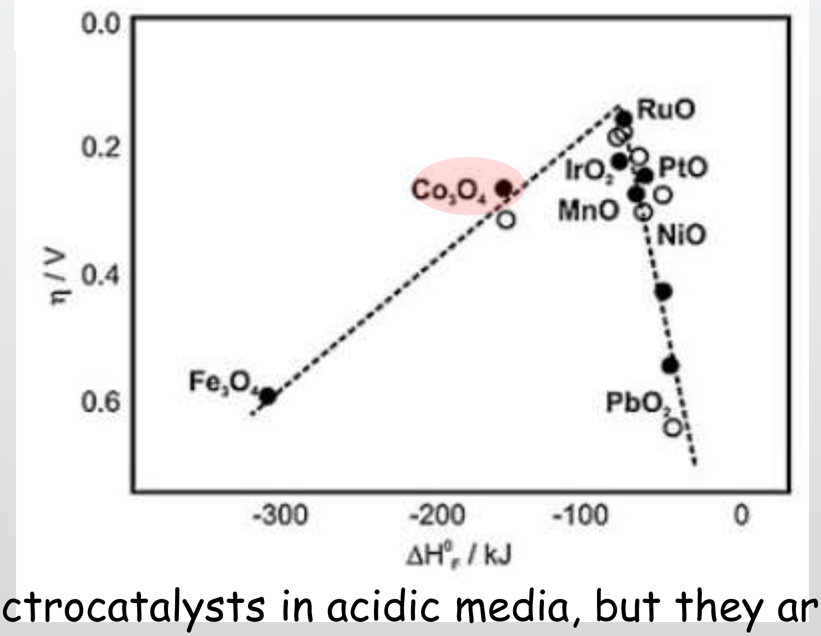
Perovskite ABO_3 & spinel oxides – AB_2O_4

$\Delta G_{O*} - \Delta G_{HO*}$



Enthalpy of lower to higher oxidation oxide

Trasatti, J. Electroanal. Chem., 111(1980) 125-131



- IrO_2 and RuO_2 are active OER electrocatalysts in acidic media, but they are expensive

- Spinels and perovskites (ABO_3 , AB_2O_4) are promising

- Design strategies:

1) e_g orbital occupancy → the higher the e_g occupancy, the better OER activity
2) Increasing metal-oxygen covalency → improving OER activity, why?
3) Substitution of foreign elements
4) Tetrahedral and octahedral sites, which is more active for OER?

Electron orbitals

	Symbol	Possible values
Principal quantum number	n	1, 2, 3, 4, …n
Angular momentum quantum number	l	0,1, 2,3, …(n-1)
Magnetic quantum number	m_l	-l, …-1, 0, 1, …, l
Spin quantum number	m_s	+1/2, -1/2

- Principle quantum number n : energy of an electron and size of the orbital
- Angular momentum quantum number l: divides the shells into smaller groups of orbitals (subshells), 0, 1, 2, 3, 4, 5 → s, p, d, f, g, h (the energy of subshell increases with l) → determines shape of the orbital
- Magnetic quantum number m_l: orientation in space of an orbital of a given energy n and shape l (individual orbitals)
- Spin quantum number m_s: orientation of the spin axis of an electron (up or down)

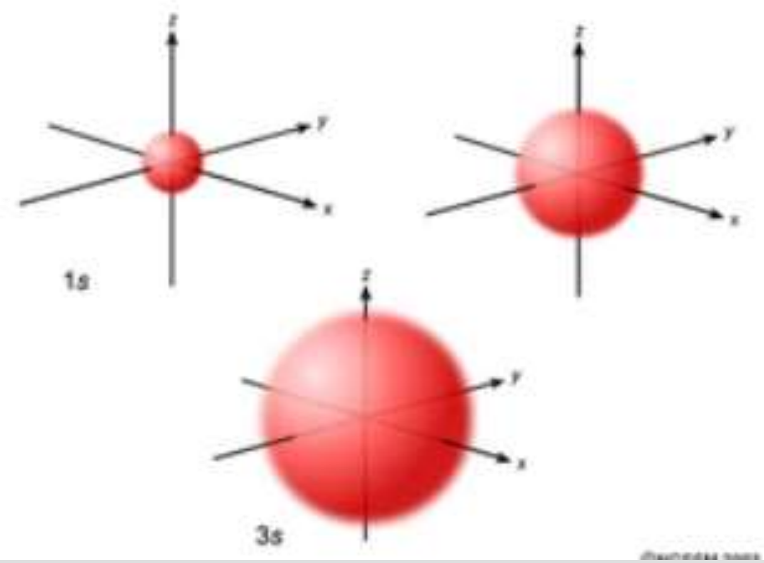
Principle quantum number

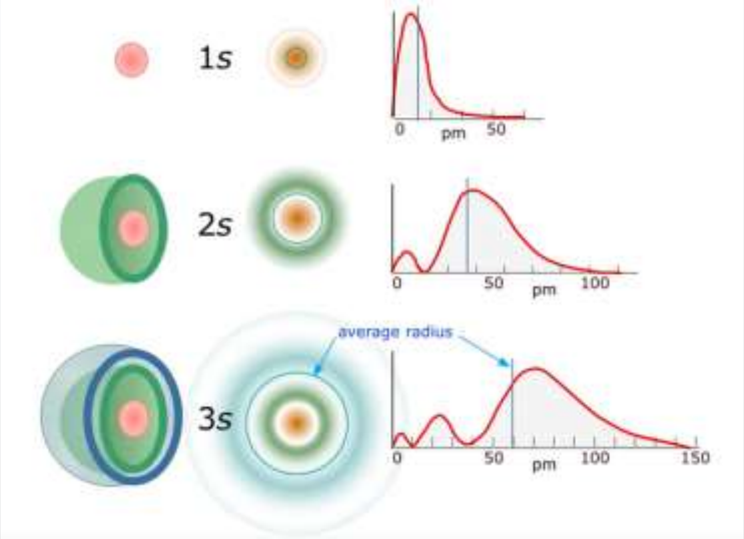
Angular momentum quantum number

Magnetic quantum number

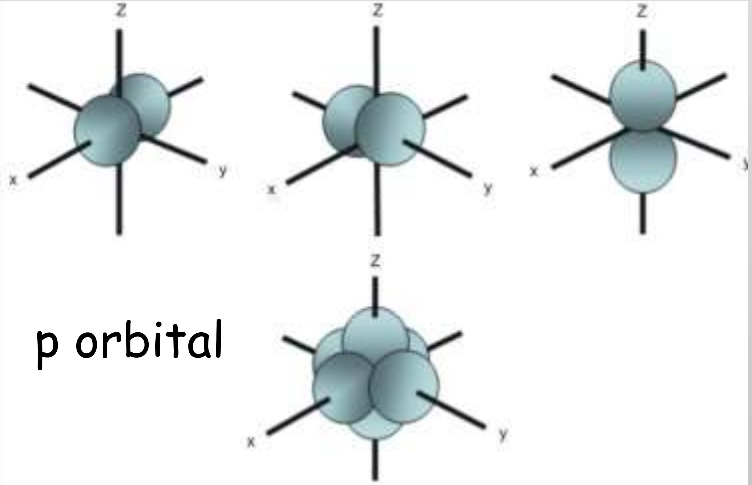
n	l (l = n-1)	M_l (-l, …l)	Number of orbitals	Orbital name	Number of electrons 2(2l+1)
1	0	0	1	1s	2
2	0	0	1	2s	2
	1	-1, 0, 1	3	2p	6
3	0	0	1	3s	2
	1	-1, 0, 1	3	3p	6
	2	-2, -1, 0, 1, 2	5	3d	10
4	0	0	1	4s	2
	1	-1, 0, 1	3	4p	6
	2	-2, -1, 0, 1, 2	5	4d	10
	3	-3, -2, -1, 0, 1, 2, 3	7	4f	14

s, p orbitals





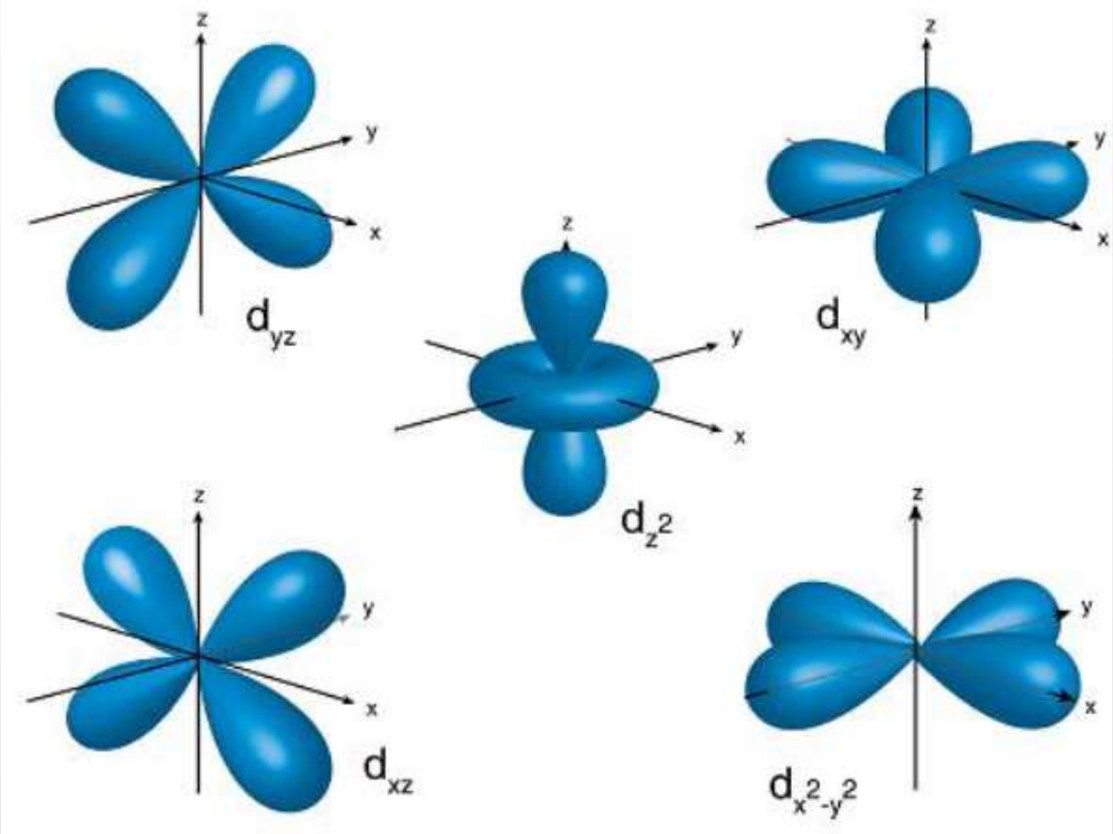
s orbitals: spherically symmetric around the nucleus of the atom. As energy level increases, the electrons are located further from nucleus



p orbital

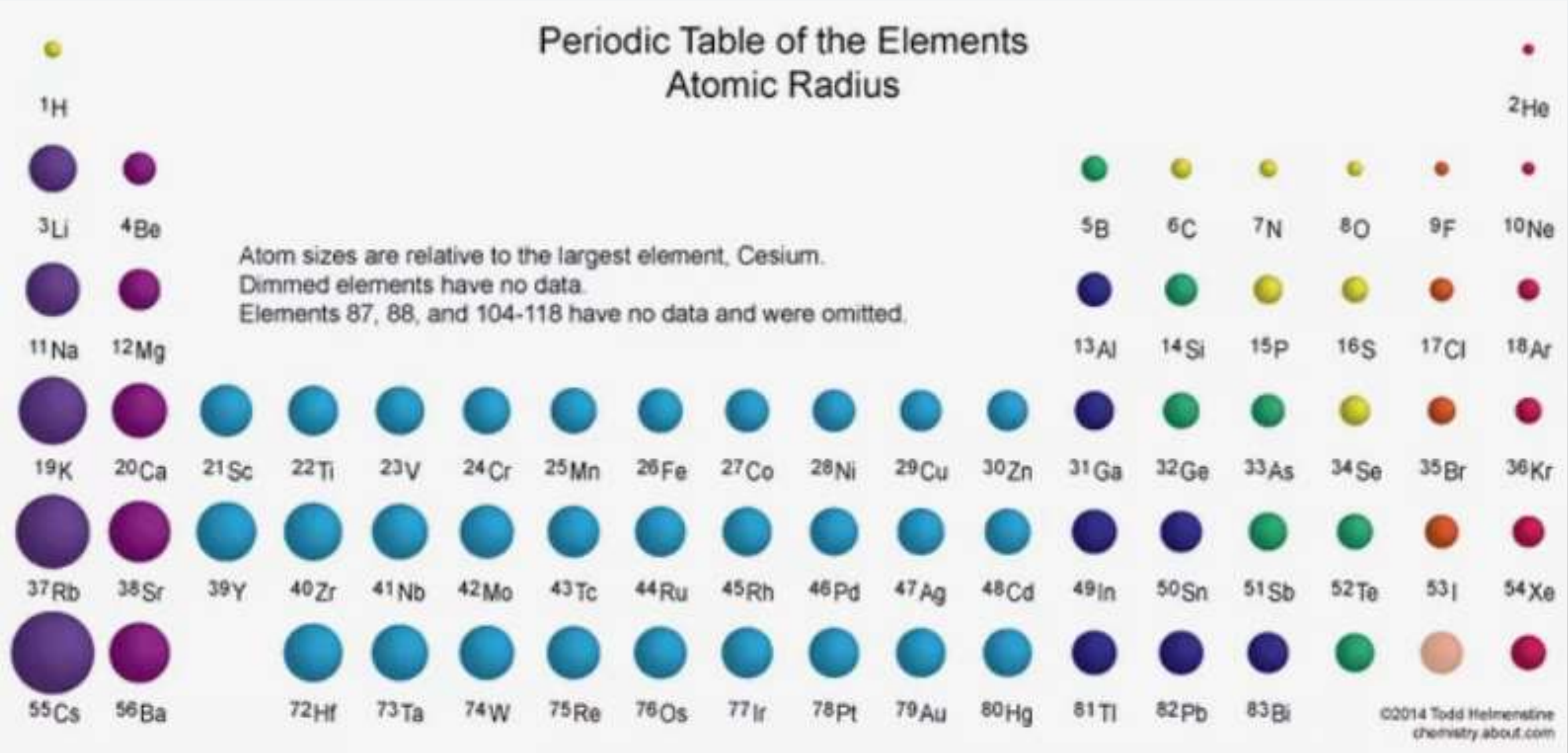
p orbitals: three equivalent p orbitals p_x, p_y and p_z. the p orbitals starts to appear at the 2nd energy level, called $2p_x$, $2p_y$, $2p_z$.

d orbitals



- d orbitals → $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{x^2-y^2}$, $3d_{z^2}$
- $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ indicate that the orbitals lie in the x-y, x-z and y-z planes; each orbital has four lobes and each lobe points between the axes
- $3d_{x^2-y^2}$, manifest the lobes points along the axes
- $3d_{z^2}$ looks like p obital wearing a doughnut around its waist
- d orbital appears at the third energy level

Periodic Table/electron configuration



Periodic Table of the Elements
Atomic Radius

Atom sizes are relative to the largest element, Cesium.
Dimmed elements have no data.
Elements 87, 88, and 104-118 have no data and were omitted.

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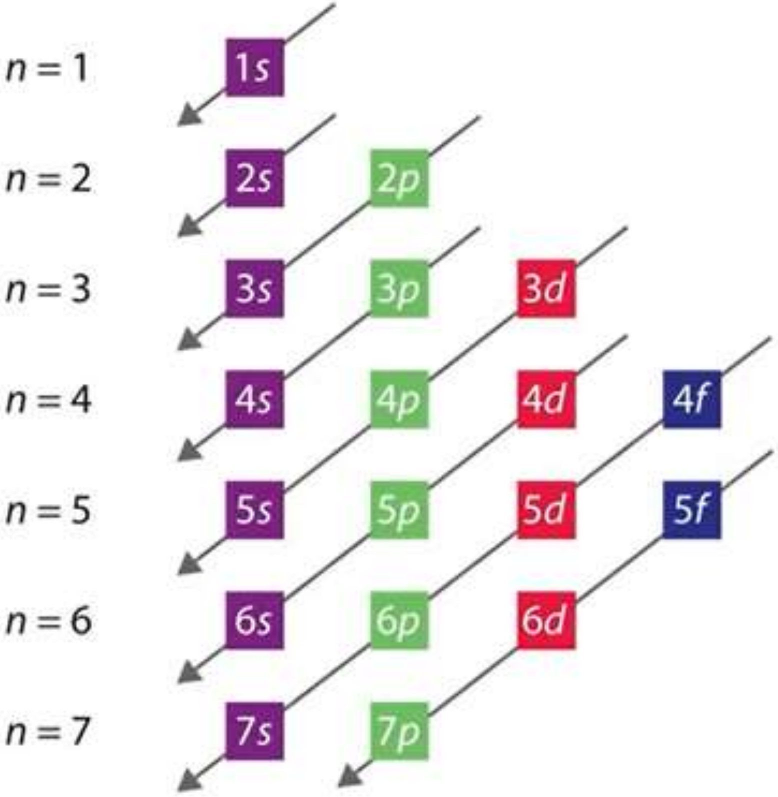
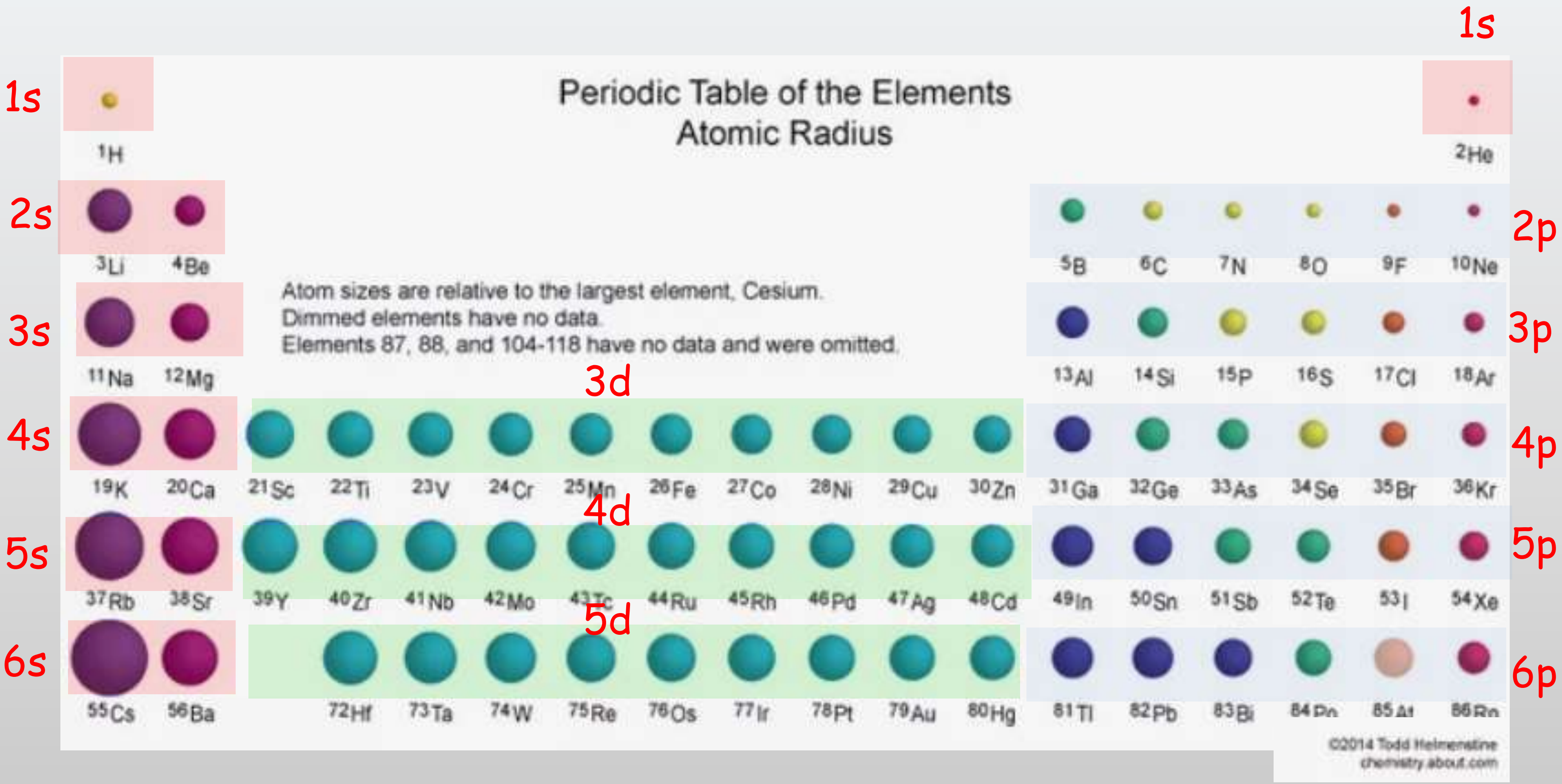
n	l (l = n-1)	M_l (-l, …l)	Number of orbitals	Orbital name	Number of electrons 2(2l+1)	
1				1s	2	2
2				2s	2	8
				2p	6	
3				3s	2	8
				3p	6	
				3d	10	10
4				4s	2	2
				4p	6	6
				4d	10	
				4f	14	



(arrows indicate the next shell that should be filled by electrons)

Periodic Table



Atom sizes are relative to the largest element, Cesium.
Dimmed elements have no data.
Elements 87, 88, and 104-118 have no data and were omitted.

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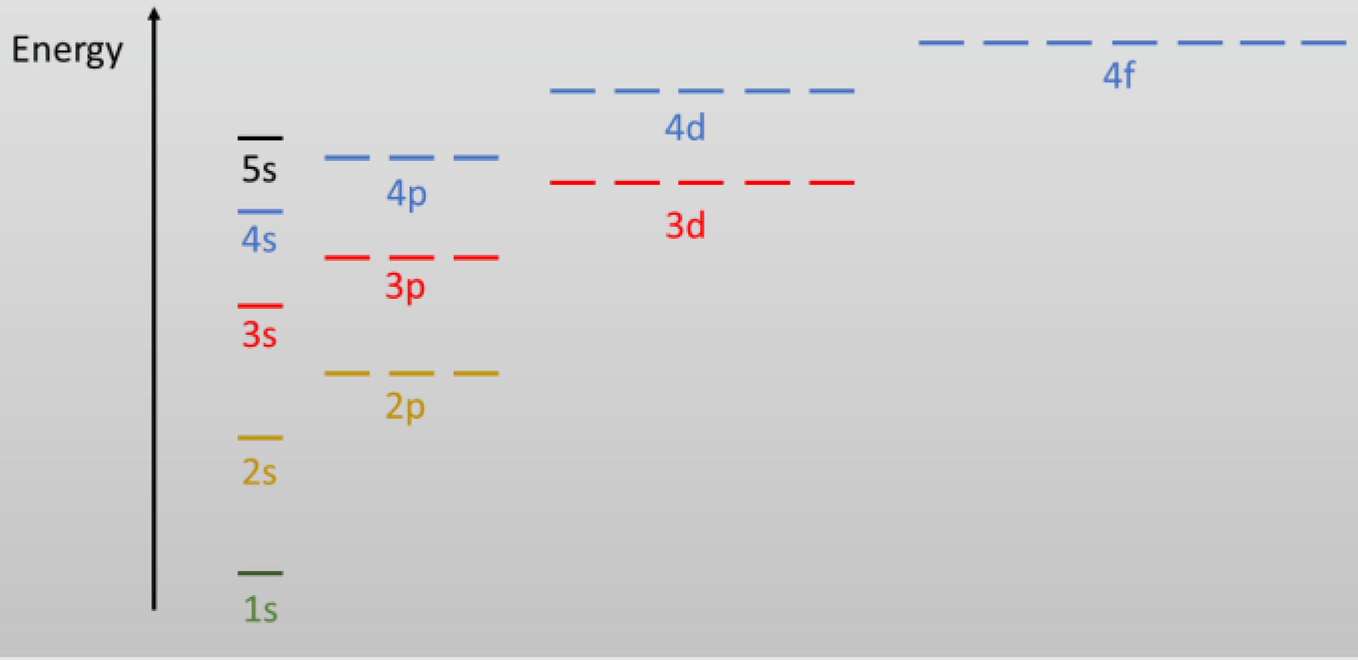
Orbital energy levels & electron filling principle

1) Aufbau principle: electrons fill subshells of the lowest available energy, followed by the subshells with higher energy

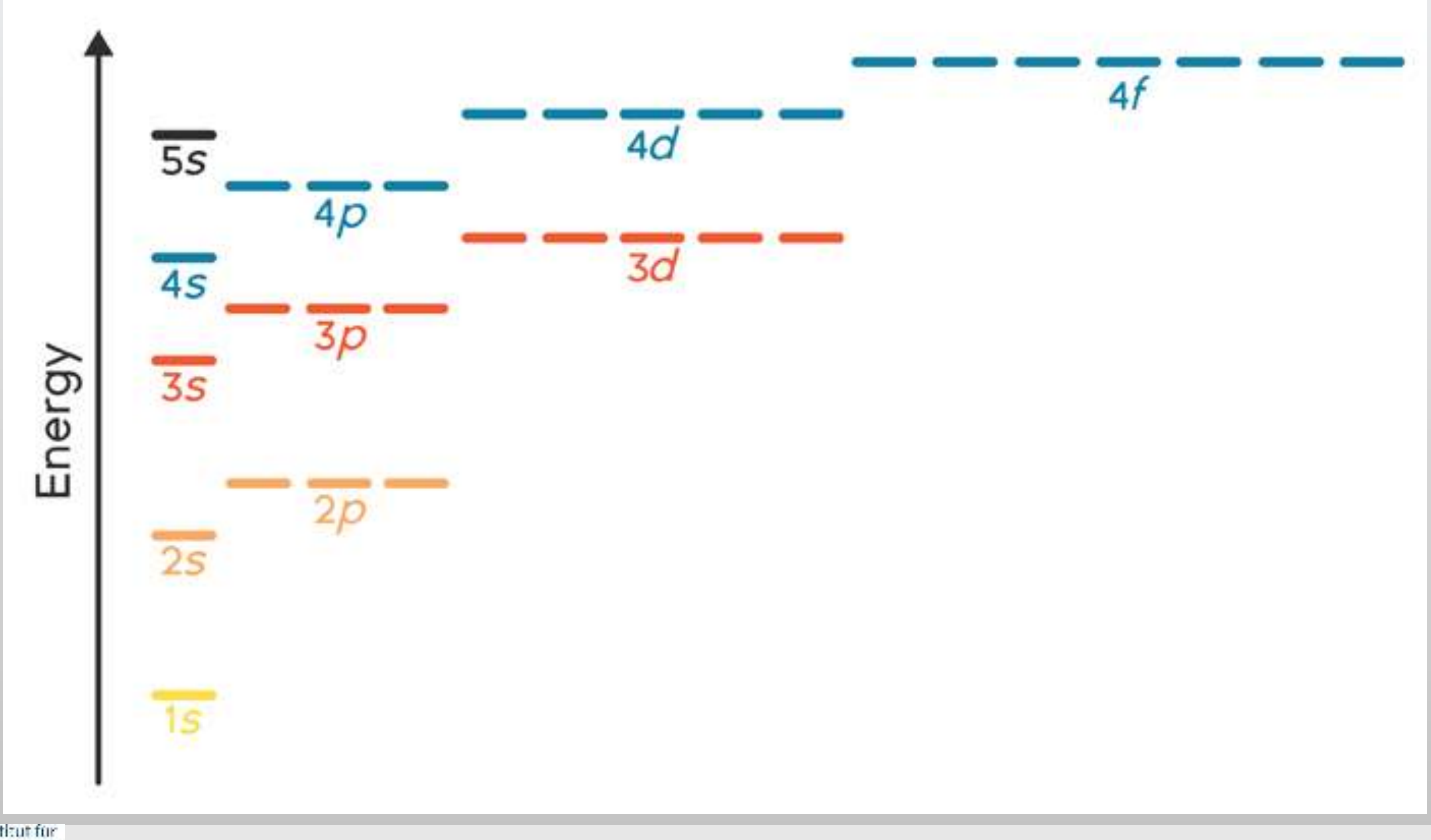
2) Hund's rule: if multiple orbital of the same energy are available, electrons occupy different orbital singly before any are occupied doubly

3) Pauli exclusion principle: electron that occupy the same orbital must have different spins



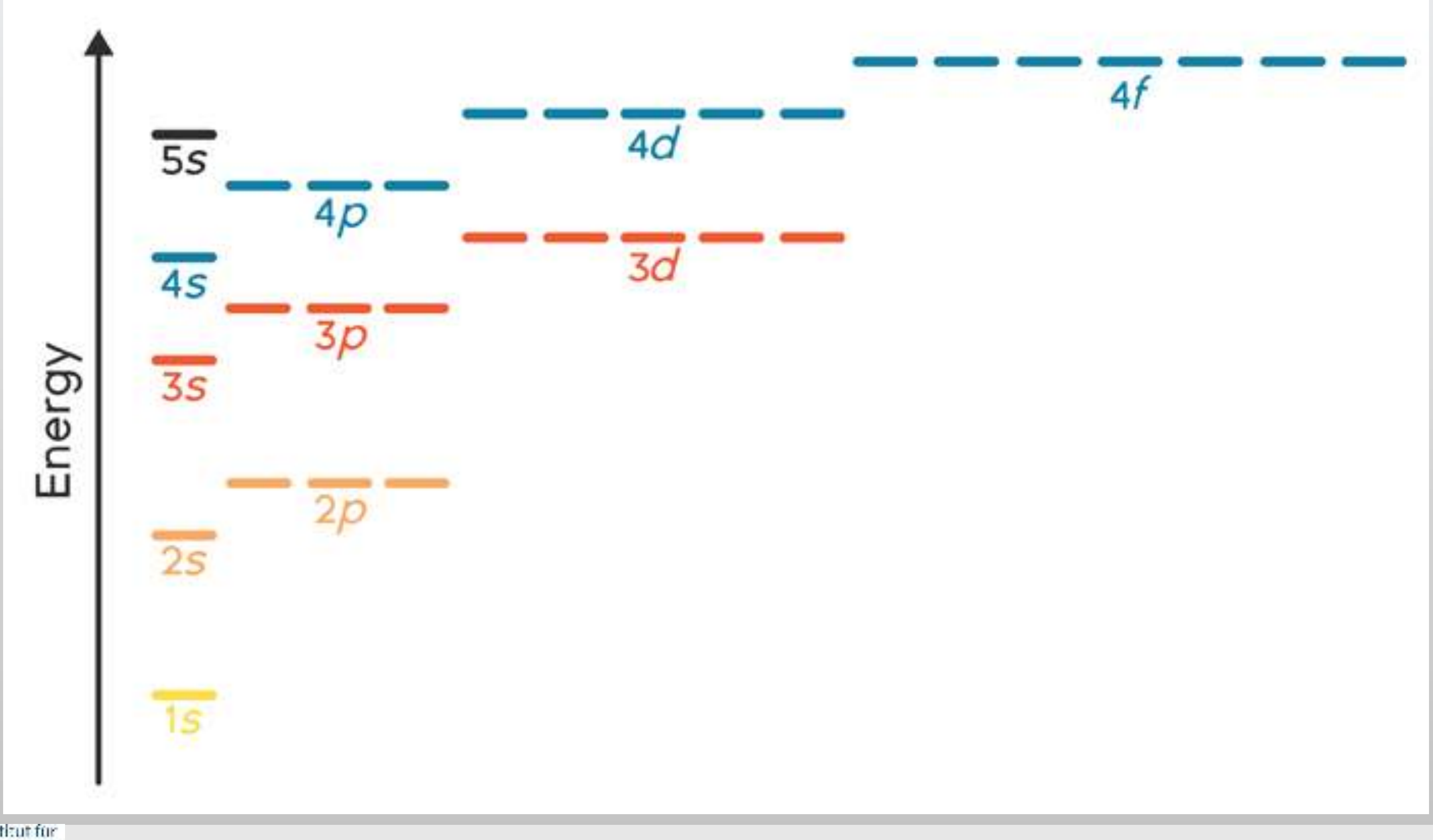
Electronic configuration of S

S: $1s^2 2s^2 2p^6 3s^2 3p^4$



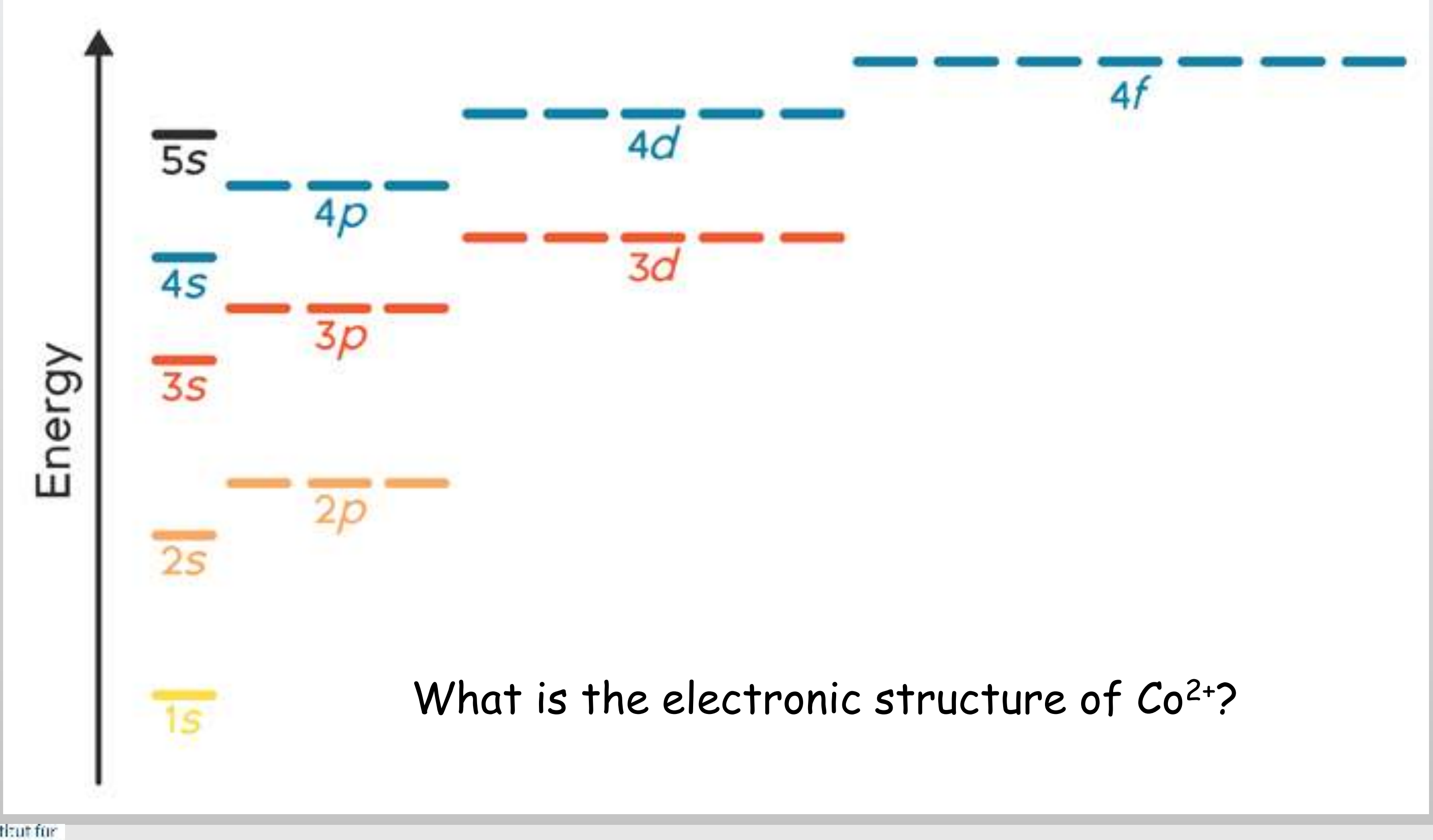
Electronic configuration of Co

Co: 1s 2s 2p 3s 3p 4s 3d



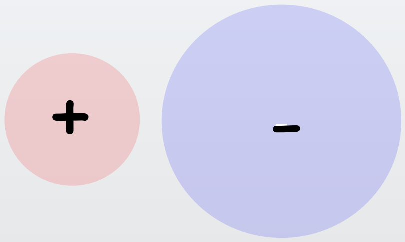
Electronic configuration of Co^{2+}

Co: 1s 2s 2p 3s 3p 4s 3d

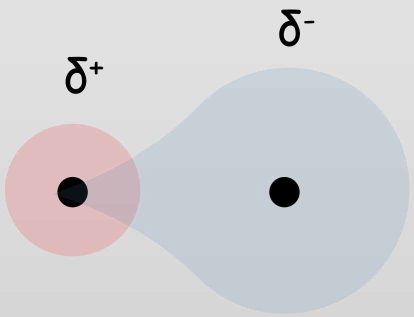


What is the electronic structure of Co^{2+}?

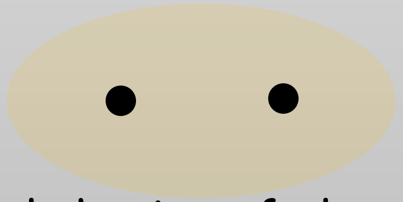
Chemical bonds



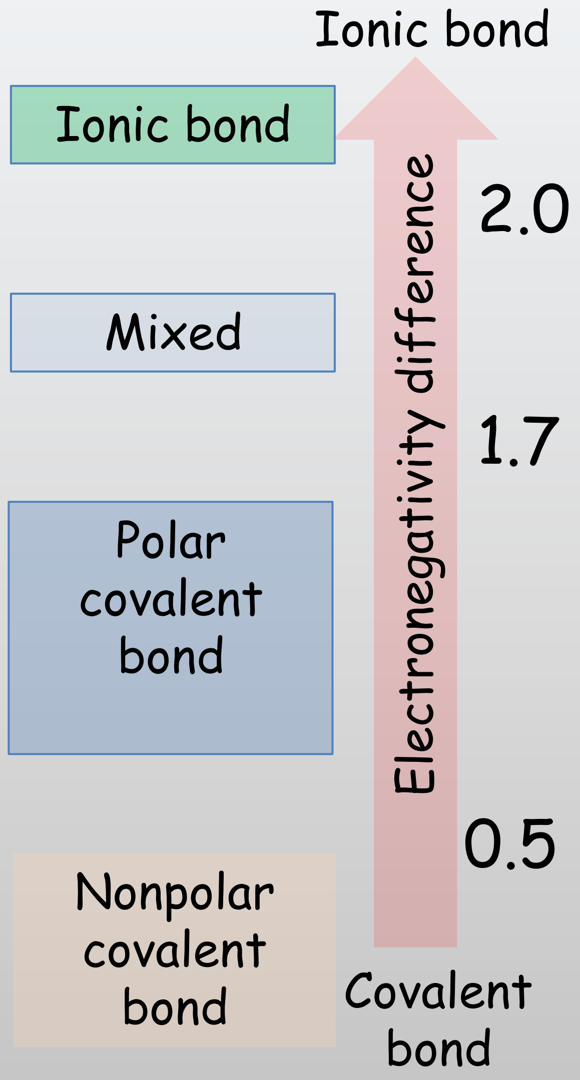
No sharing of electrons



Unequal sharing of electrons



Equal sharing of electrons



Ionic bond

Ionic bond

2.0

Mixed

1.7

Polar covalent bond

Electronegativity difference

0.5

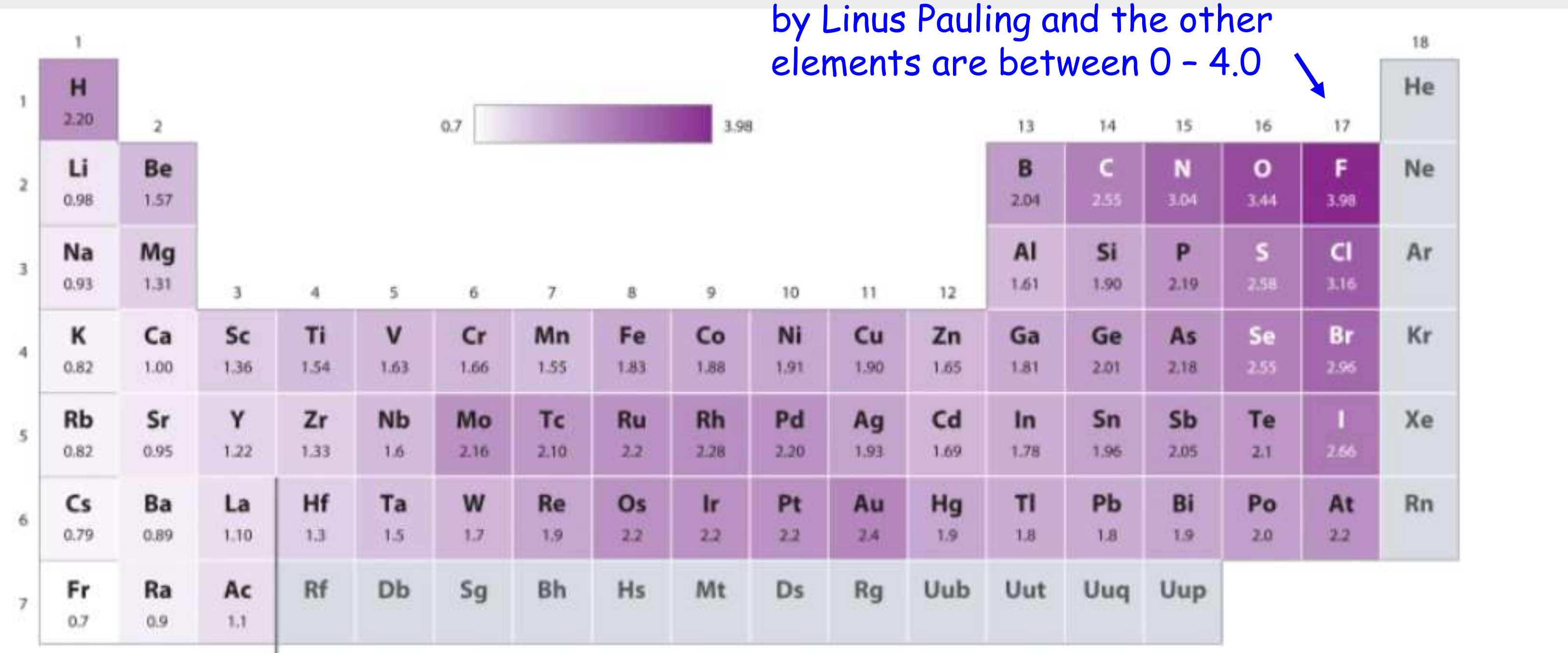
Nonpolar covalent bond

Covalent bond

Electronegativity χ

- The tendency or ability of the atoms to attract electrons from the other elements (electron acceptor)

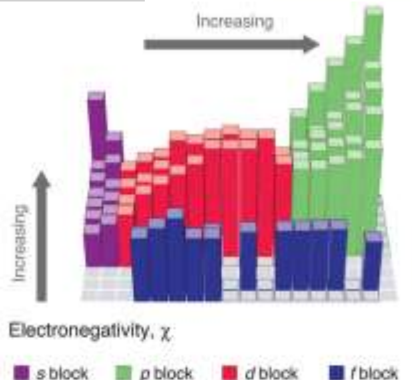
F is arbitrarily set at 4.0 (3.98) by Linus Pauling and the other elements are between 0 – 4.0



0.7 3.98

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** 2.20																	**He**
2	**Li** 0.98	**Be** 1.57											**B** 2.04	**C** 2.55	**N** 3.04	**O** 3.44	**F** 3.98	**Ne**
3	**Na** 0.93	**Mg** 1.31											**Al** 1.61	**Si** 1.90	**P** 2.19	**S** 2.58	**Cl** 3.16	**Ar**
4	**K** 0.82	**Ca** 1.00	**Sc** 1.36	**Ti** 1.54	**V** 1.63	**Cr** 1.66	**Mn** 1.55	**Fe** 1.83	**Co** 1.88	**Ni** 1.91	**Cu** 1.90	**Zn** 1.65	**Ga** 1.81	**Ge** 2.01	**As** 2.18	**Se** 2.55	**Br** 2.96	**Kr**
5	**Rb** 0.82	**Sr** 0.95	**Y** 1.22	**Zr** 1.33	**Nb** 1.6	**Mo** 2.16	**Tc** 2.10	**Ru** 2.2	**Rh** 2.28	**Pd** 2.20	**Ag** 1.93	**Cd** 1.69	**In** 1.78	**Sn** 1.96	**Sb** 2.05	**Te** 2.1	**I** 2.66	**Xe**
6	**Cs** 0.79	**Ba** 0.89	**La** 1.10	**Hf** 1.3	**Ta** 1.5	**W** 1.7	**Re** 1.9	**Os** 2.2	**Ir** 2.2	**Pt** 2.2	**Au** 2.4	**Hg** 1.9	**Tl** 1.8	**Pb** 1.8	**Bi** 1.9	**Po** 2.0	**At** 2.2	**Rn**
7	**Fr** 0.7	**Ra** 0.9	**Ac** 1.1	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Uub**	**Uut**	**Uuq**	**Uup**			

Ce 1.12	**Pr** 1.13	**Nd** 1.14	**Pm**	**Sm** 1.17	**Eu**	**Gd** 1.20	**Tb**	**Dy** 1.22	**Ho** 1.23	**Er** 1.24	**Tm** 1.25	**Yb**	**Lu** 1.0
Th 1.3	**Pa** 1.5	**U** 1.7	**Np** 1.3	**Pu** 1.3	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**



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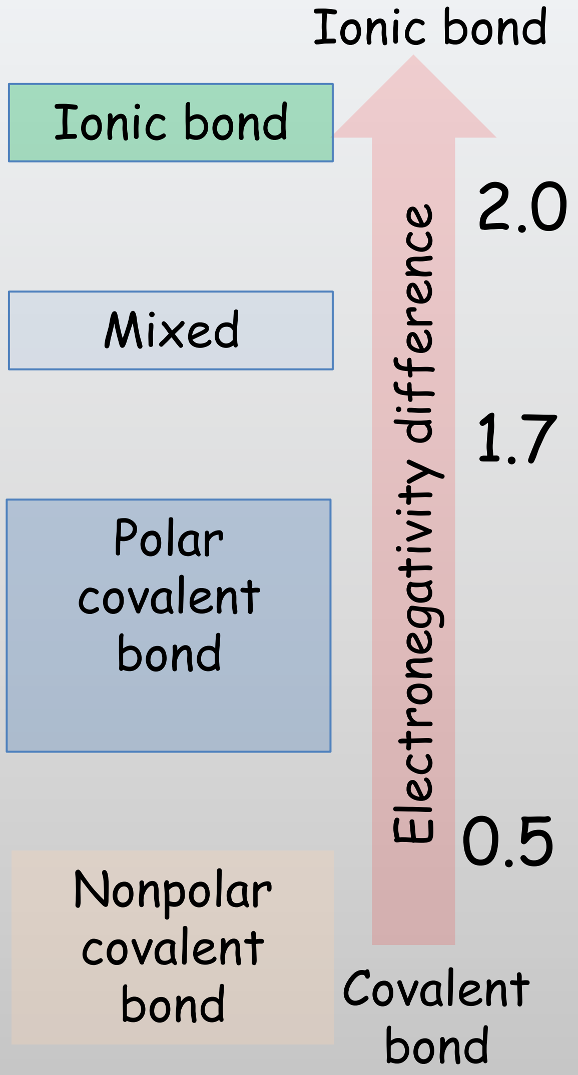
Chemical bonds

- Chemical bonds → electronegativity

a) Difference in electronegativity > 2 → ionic bond → electrostatic attraction and forming ionic bond

b) Difference in electronegativity < 1.7, no electrons are stolen but the electrons are shared between nucleus

- Polar covalent bond (difference in electronegativity > 0.5) → electron density towards to the one who has higher electronegativity → slight electron excess in one element compared to the other
- Nonpolar covalent bond (difference in electronegativity < 0.5) → electrons are shared more evenly, the atoms have no partial charges

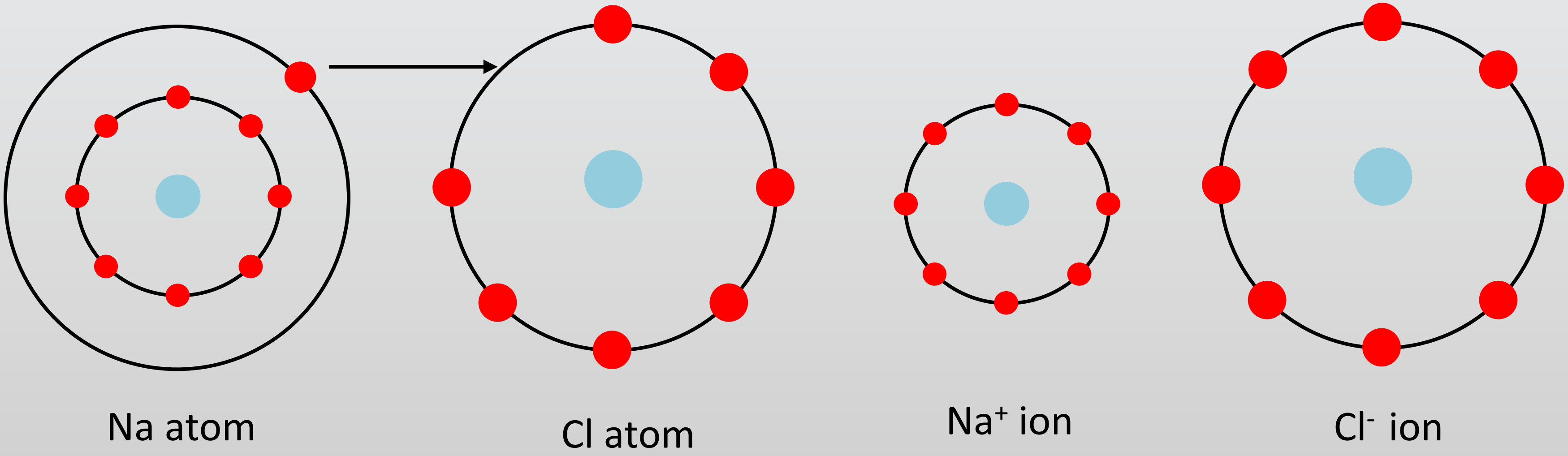


Ionic bond

Ionic bond

- Chemical bonds → electronegativity

a) Difference in electronegativity > 2 → ionic bond → electrostatic attraction and forming ionic bond

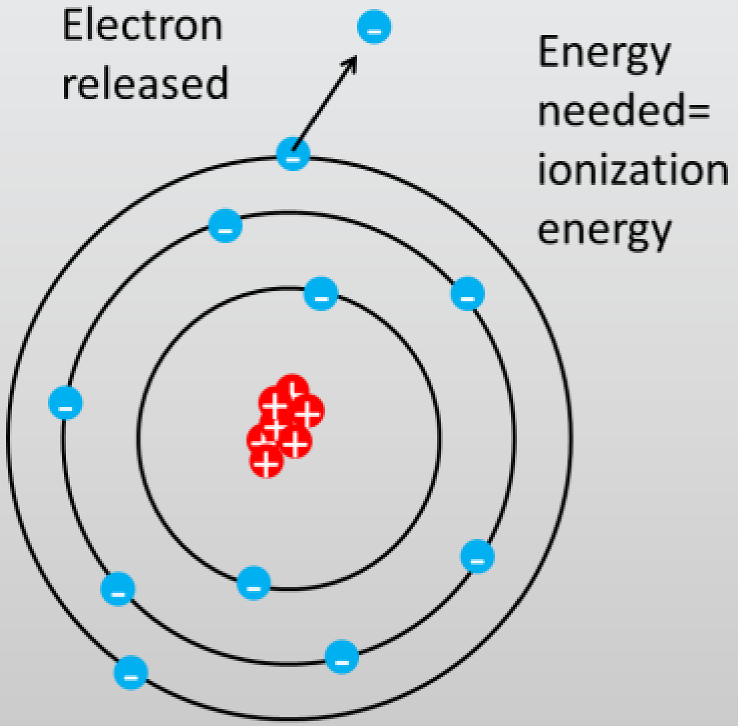


- Ionic bonding results from the transfer of electrons → making the ionic compound stable due to the **electrostatic attraction** between positive and negative ions

Oxides

Most oxides have ionic character which involves **exchange of electrons**

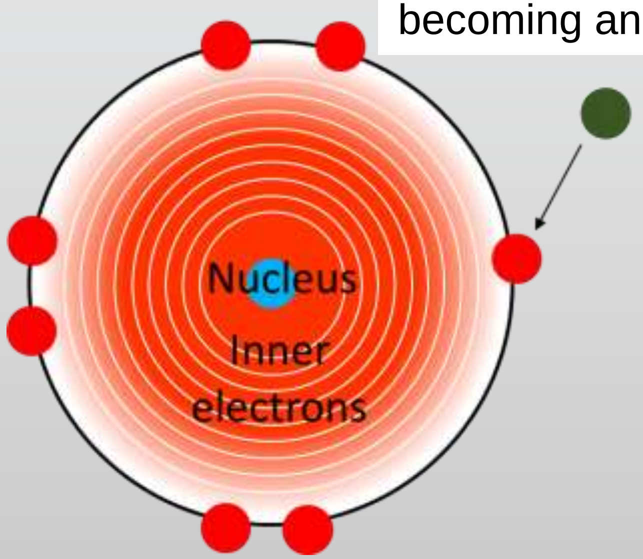
Ionization energy



Remove an electron → cation

Electron affinity

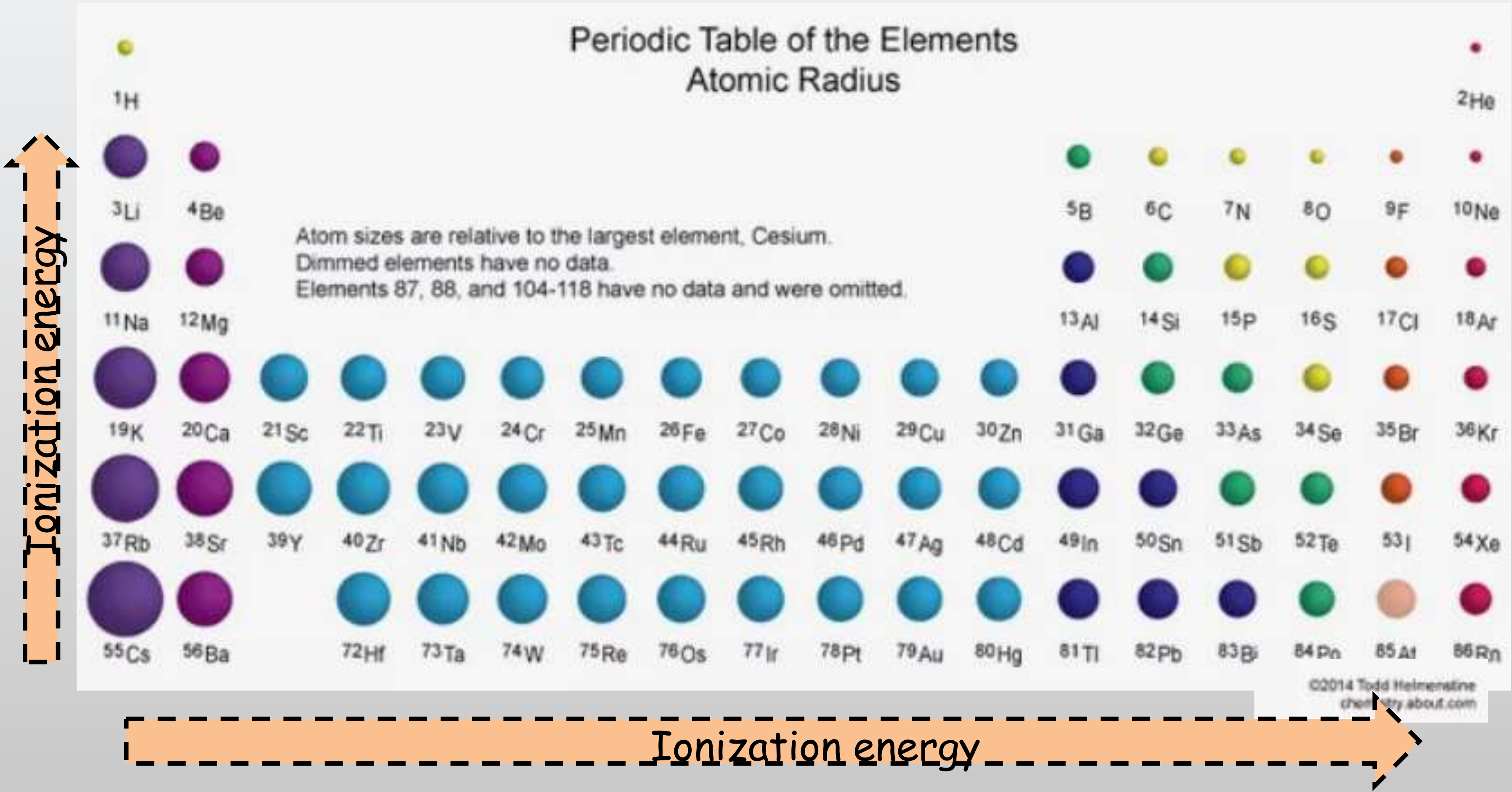
Energy change when a neutral atom receive an electron, becoming an anion



Accept an electron → anion

Ionization energy

- Energy required to remove an electron from an atom



Periodic Table of the Elements
Atomic Radius

Atom sizes are relative to the largest element, Cesium.
Dimmed elements have no data.
Elements 87, 88, and 104-118 have no data and were omitted.

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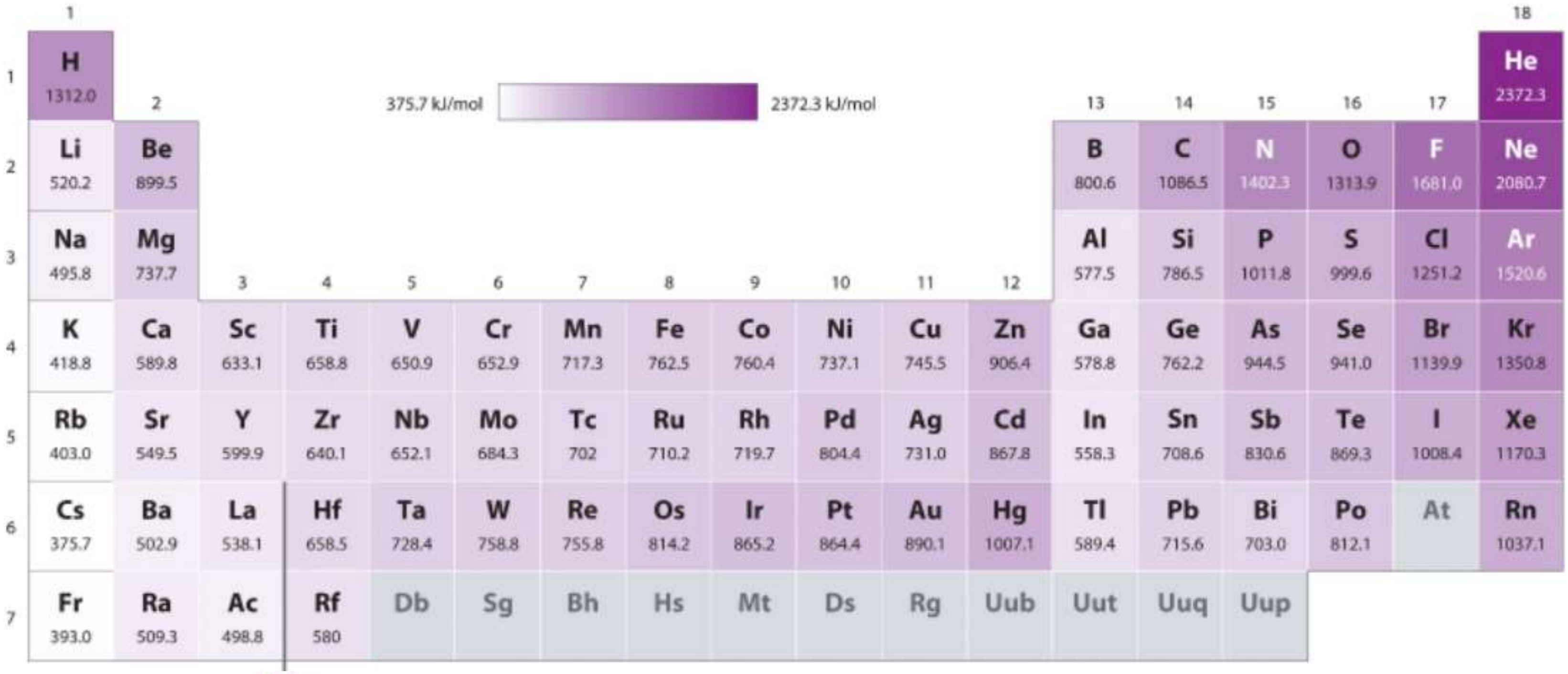
Coulomb's law gives the electrostatic forces between e.g., protons and electrons :

$$F = k\frac{Q_1 Q_2}{r^2}$$

Ionization energy

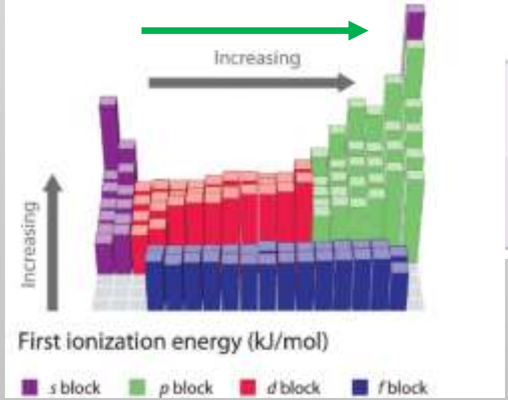
How does the d orbital energy level change?



375.7 kJ/mol – 2372.3 kJ/mol

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** 1312.0																	**He** 2372.3
2	**Li** 520.2	**Be** 899.5											**B** 800.6	**C** 1086.5	**N** 1402.3	**O** 1313.9	**F** 1681.0	**Ne** 2080.7
3	**Na** 495.8	**Mg** 737.7											**Al** 577.5	**Si** 786.5	**P** 1011.8	**S** 999.6	**Cl** 1251.2	**Ar** 1520.6
4	**K** 418.8	**Ca** 589.8	**Sc** 633.1	**Ti** 658.8	**V** 650.9	**Cr** 652.9	**Mn** 717.3	**Fe** 762.5	**Co** 760.4	**Ni** 737.1	**Cu** 745.5	**Zn** 906.4	**Ga** 578.8	**Ge** 762.2	**As** 944.5	**Se** 941.0	**Br** 1139.9	**Kr** 1350.8
5	**Rb** 403.0	**Sr** 549.5	**Y** 599.9	**Zr** 640.1	**Nb** 652.1	**Mo** 684.3	**Tc** 702	**Ru** 710.2	**Rh** 719.7	**Pd** 804.4	**Ag** 731.0	**Cd** 867.8	**In** 558.3	**Sn** 708.6	**Sb** 830.6	**Te** 869.3	**I** 1008.4	**Xe** 1170.3
6	**Cs** 375.7	**Ba** 502.9	**La** 538.1	**Hf** 658.5	**Ta** 728.4	**W** 758.8	**Re** 755.8	**Os** 814.2	**Ir** 865.2	**Pt** 864.4	**Au** 890.1	**Hg** 1007.1	**Tl** 589.4	**Pb** 715.6	**Bi** 703.0	**Po** 812.1	**At**	**Rn** 1037.1
7	**Fr** 393.0	**Ra** 509.3	**Ac** 498.8	**Rf** 580	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Uub**	**Uut**	**Uuq**	**Uup**			

Pr 528.1	**Nd** 533.1	**Pm** 538.6	**Sm** 544.5	**Eu** 547.1	**Gd** 593.4	**Tb** 565.8	**Dy** 573.0	**Ho** 581.0	**Er** 589.3	**Tm** 596.7	**Yb** 603.4	**Lu** 523.5
Pa 568	**U** 597.6	**Np** 604.5	**Pu** 581.4	**Am** 576.4	**Cm** 578.1	**Bk** 598.0	**Cf** 606.1	**Es** 619	**Fm** 627	**Md** 635	**No** 642	**Lr** 472.8



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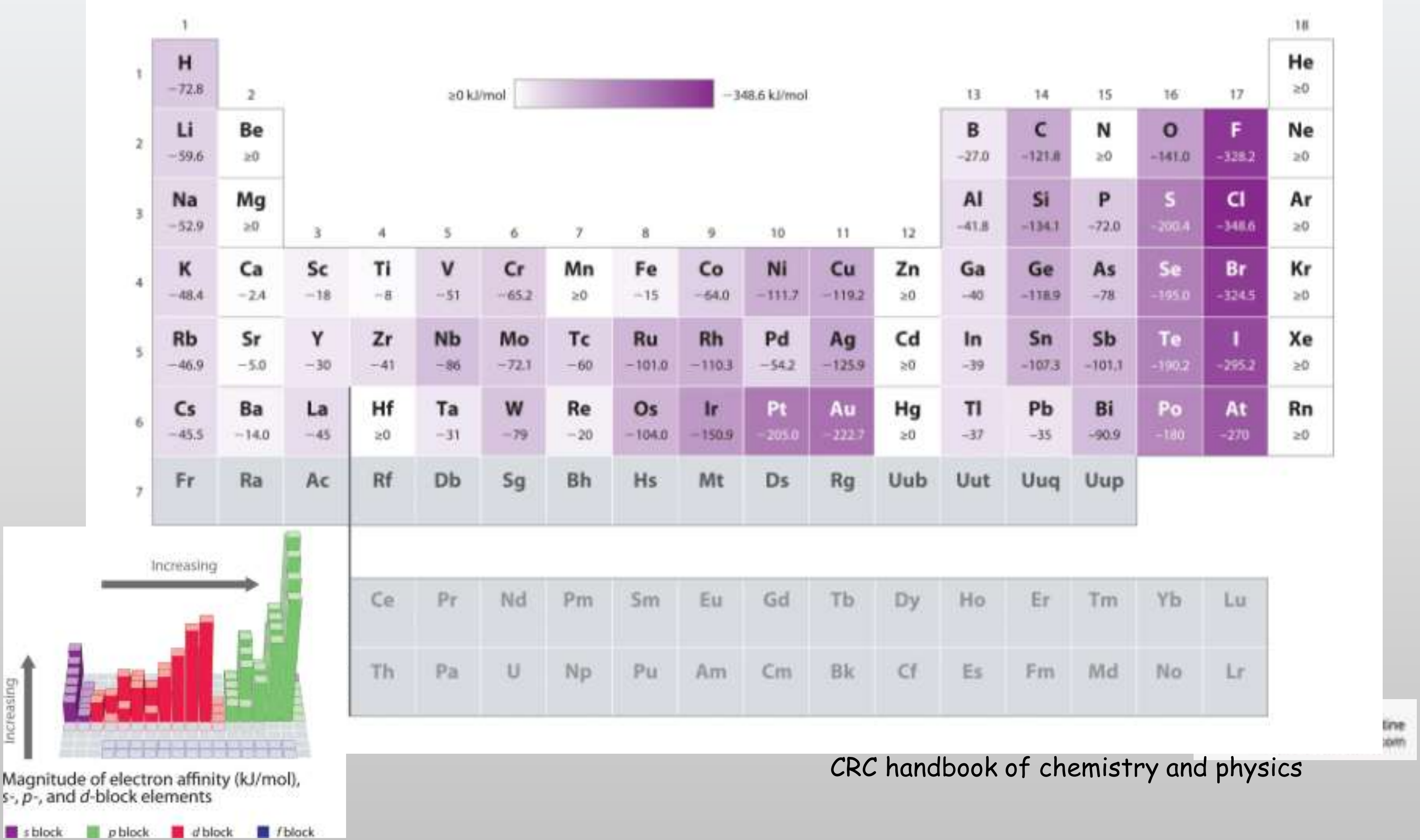
Electron affinity

- Electron affinity is the change in energy of a neutral atom when an electron is added to the atom to form a negative ion



≥0 kJ/mol 🟪 −348.6 kJ/mol

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** −72.8																	**He** ≥0
2	**Li** −59.6	**Be** ≥0											**B** −27.0	**C** −121.8	**N** ≥0	**O** −141.0	**F** −328.2	**Ne** ≥0
3	**Na** −52.9	**Mg** ≥0											**Al** −41.8	**Si** −134.1	**P** −72.0	**S** −200.4	**Cl** −348.6	**Ar** ≥0
4	**K** −48.4	**Ca** −2.4	**Sc** −18	**Ti** −8	**V** −51	**Cr** −65.2	**Mn** ≥0	**Fe** −15	**Co** −64.0	**Ni** −111.7	**Cu** −119.2	**Zn** ≥0	**Ga** −40	**Ge** −118.9	**As** −78	**Se** −195.0	**Br** −324.5	**Kr** ≥0
5	**Rb** −46.9	**Sr** −5.0	**Y** −30	**Zr** −41	**Nb** −86	**Mo** −72.1	**Tc** −60	**Ru** −101.0	**Rh** −110.3	**Pd** −54.2	**Ag** −125.9	**Cd** ≥0	**In** −39	**Sn** −107.3	**Sb** −101.1	**Te** −190.2	**I** −295.2	**Xe** ≥0
6	**Cs** −45.5	**Ba** −14.0	**La** −45	**Hf** ≥0	**Ta** −31	**W** −79	**Re** −20	**Os** −104.0	**Ir** −150.9	**Pt** −205.0	**Au** −222.7	**Hg** ≥0	**Tl** −37	**Pb** −35	**Bi** −90.9	**Po** −180	**At** −270	**Rn** ≥0
7	**Fr**	**Ra**	**Ac**	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Uub**	**Uut**	**Uuq**	**Uup**			
				Ce	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	
				Th	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**	

Magnitude of electron affinity (kJ/mol), s-, p-, and d-block elements

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Ionic bond energy

How to calculate ionic bond energy?

e.g., Formation of NaCl from neutral Na and Cl atoms

$Na\,(g) \rightarrow Na^{+}\,(g) + e^{-}$ ΔE = ionization energy = 494 kJ/mol

$Cl\,(g) + e^{-} \rightarrow Cl^{-}\,(g)$ ΔE = electron affinity = -349 kJ/mol

$Na\,(g) + Cl\,(g) \rightarrow Na^{+}\,(g) + Cl^{-}\,(g)$ ΔE = 145 kJ/mol

→ Need energy

!! The electronic attraction between Na^+ and Cl^-

Ionic bond energy

Using Coulomb's law, the Coulombic potential energy is:

$$E_{potential} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r}$$

z = ion charges
r = separation distance between ions
ε_0 = permittivity of free space
e=charge of an electron

For NaCl, r = 2.36 Å, e=1.602 x 10^{-19} C, ε_0=8.854 x $10^{-12}C^2$/Jm,
Avogadro's constant = 6.022 x 10^{23} mol^{-1}

What is the Coulomb potential (unit: kj/mol)?

$$E_{potential} = \frac{(+1)(-1)\left(1.602 \times 10^{-19}\ C\right)^2}{4\times 3.14\ \times 8.854\ \times 10^{-12}\ C^2 J^{-1} m^{-1}\ \times 2.34\ \times 10^{-10} m} \times \frac{kJ}{1000} \times \frac{6.022\times 10^{23}}{mol} = -589\ kJ$$

Madelung constant:

Ionic bond energy

- Ionic bond
- e.g., Formation of NaCl from neutral Na and Cl atoms

$Na\ (g) \rightarrow Na^+\ (g) + e^-$ ΔE = ionization energy = 494 kJ/mol

$Cl\ (g) + e^- \rightarrow Cl^-\ (g)$ ΔE = -electron affinity = -349 kJ/mol

$Na\ (g) + Cl\ (g) \rightarrow Na^+\ (g) + Cl^-\ (g)$ ΔE = 145 kJ/mol

→ Need energy

!! The electronic attraction between Na+ and Cl- is -589 kJ/mol

Net energy change $Na\ (g) + Cl\ (g) \rightarrow NaCl$ ΔE = -444 kJ/mol

→ Favored reaction

ΔE measured = -411 kJ/mol

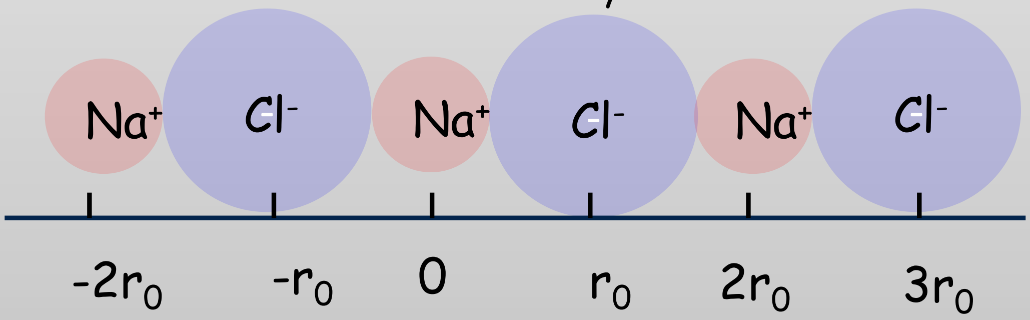
Ionic bond energy

Using Coulomb's law, the Coulombic potential energy is:

$$E_{potential} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r}$$

z = ion charges
r = separation distance between ions
ε_0 = permittivity of free space
e=charge of an electron

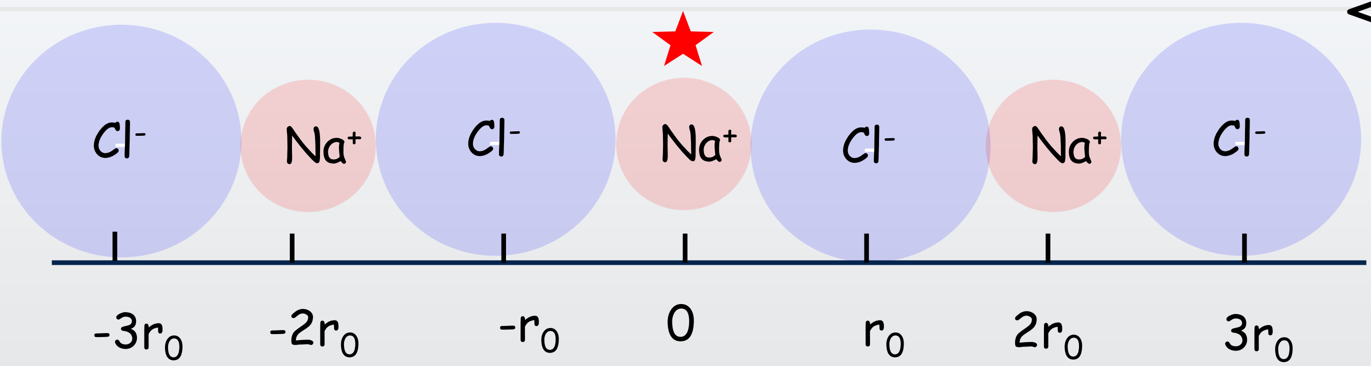
Madelung constant → accounts for short-range and long-range geometric facets of forces between two interacting species


1D NaCl crystal

Madelung constant:

Madelung constant

1D NaCl crystal



Based on : $E_{pot} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r}$

z = ion charges
r = separation distance between ions
ε_0 = permittivity of free space

1) First nearest neighbor of Na⁺: $E_1 = \frac{-e^2}{4\pi\varepsilon_0 r_0} + \frac{-e^2}{4\pi\varepsilon_0 r_0} = \frac{-2e^2}{4\pi\varepsilon_0 r_0}$

2) Second nearest neighbor of Na⁺: $E_2 = \frac{e^2}{4\pi\varepsilon_0 2r_0} + \frac{e^2}{4\pi\varepsilon_0 2r_0} = \frac{2e^2}{4\pi\varepsilon_0 2r_0}$

3) Third nearest neighbor of Na⁺: $E_2 = \frac{-e^2}{4\pi\varepsilon_0 3r_0} + \frac{-e^2}{4\pi\varepsilon_0 3r_0} = -\frac{2e^2}{4\pi\varepsilon_0 3r_0}$

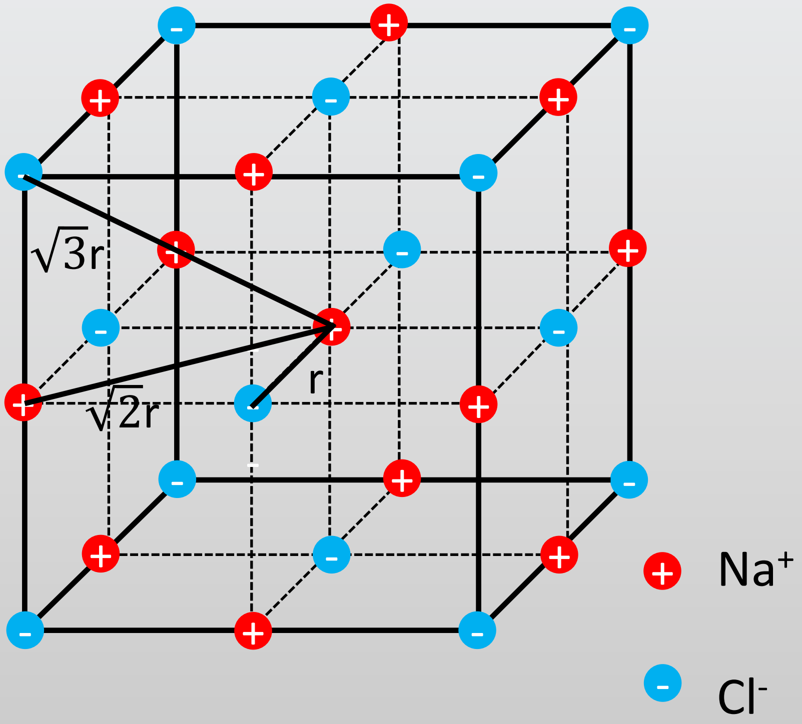
… …

Total energy: $$E = -\frac{e^2}{4\pi\varepsilon_0 r_0}\left[2\left(1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\cdots\right)\right]$$

2ln2 → Madelung constant

Madelung constant

3D NaCl crystal



1) First nearest neighbors: 6 Cl^- at r_0
2) Second nearest neighbors: 12 Na+ at $\frac{r_0}{\sqrt{2}}$
3) Third nearest neighbors; 8 Cl- at $\frac{r_0}{\sqrt{3}}$

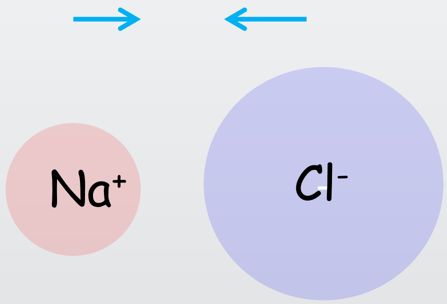
…

$$E = -\frac{e^2}{4\pi\varepsilon_0 r_0}\left[\frac{6}{1}-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}+\cdots\right]$$

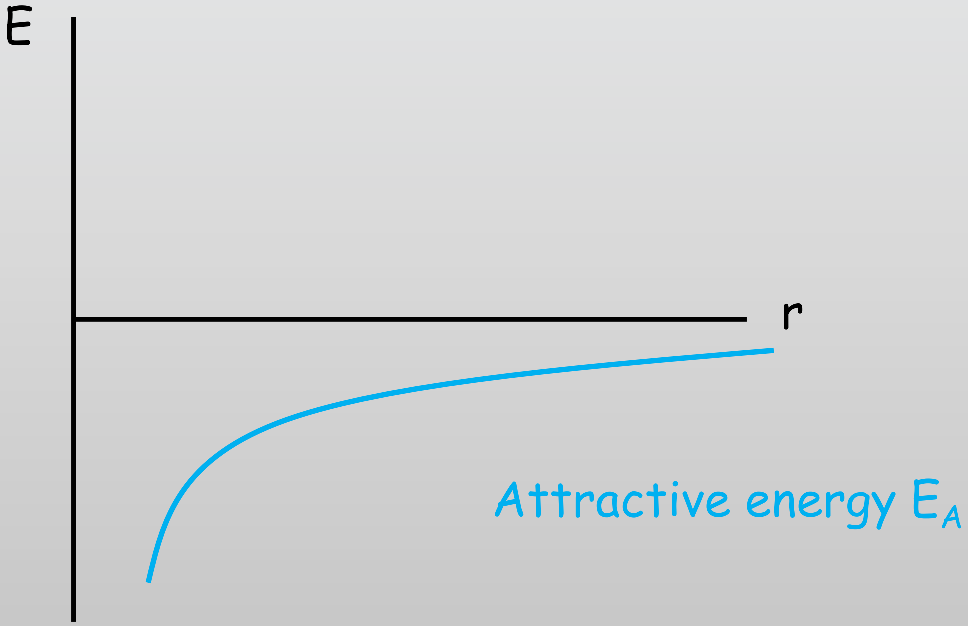
$$\downarrow$$

1.74756 for NaCl

Ionic bond energy



Attractive forces

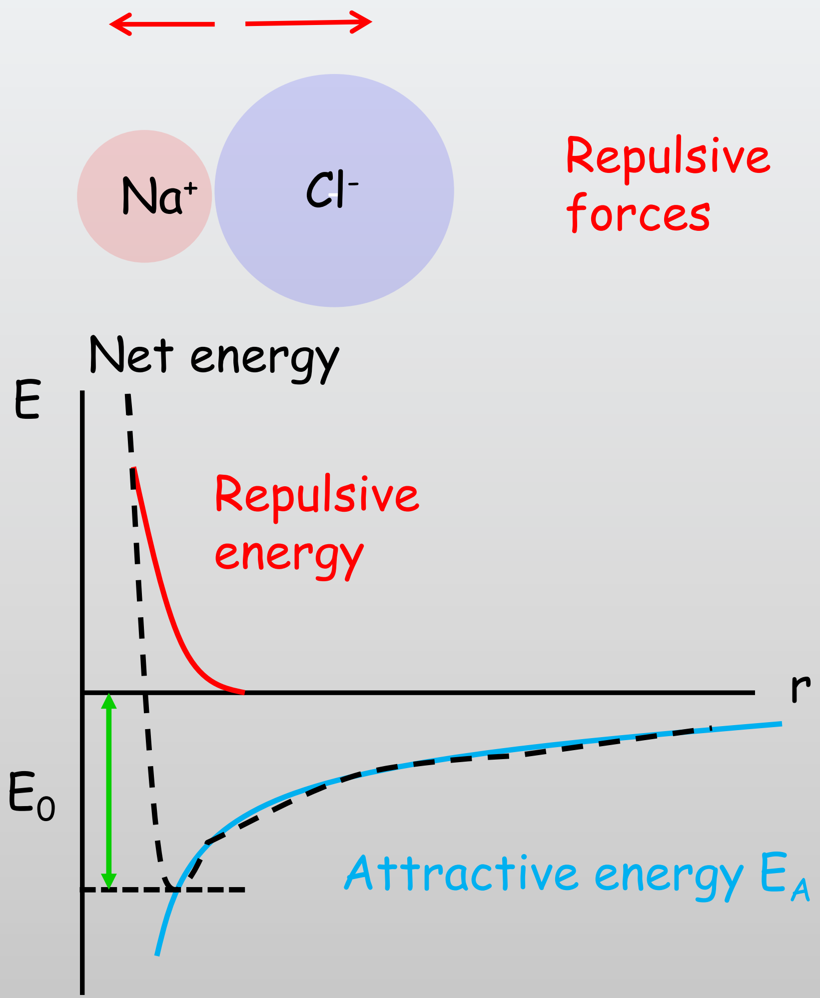


a) Using Coulomb's law, the Coulombic potential energy is:

$$E_A = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r}$$

z = ion charges
r = separation distance between ions
ε_0 = permittivity of free space

Ionic bond energy



a) Using Coulomb's law, the Coulombic potential energy is:

$$E_A = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r}$$

z = ion charges
r = separation distance between ions
ε_0 = permittivity of free space

b) Born equation to consider the repulsive forces due to two charged species being in proximity:

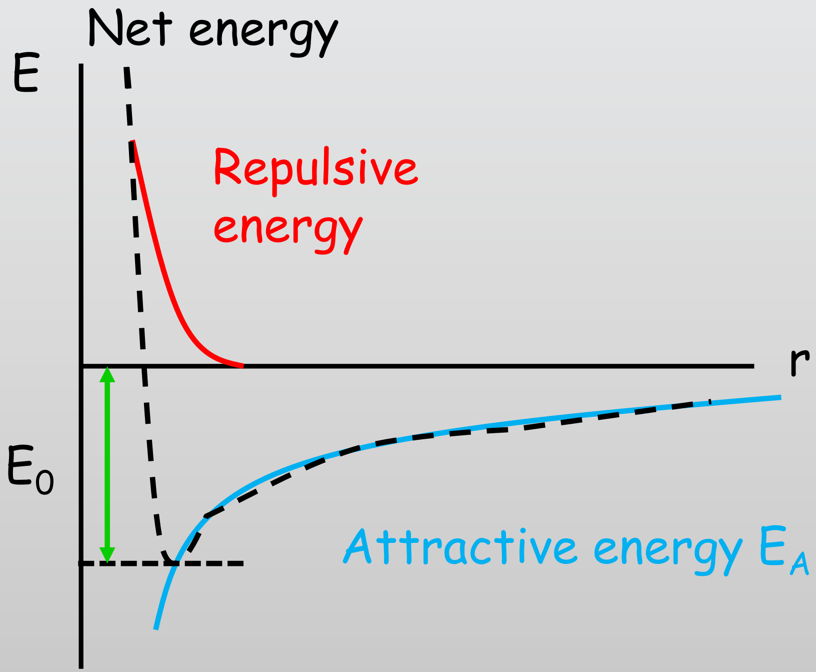
$$E_r = \frac{B}{r^n}$$

B = constant
n = born exponent, between 6-12, depending on the principal quantum number

Ionic bond energy

$$E_{net} = E_A + E_r = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n}$$

z = ion charges
r = separation distance between ions
ε_0 = permittivity of free space
B = constant
n = born exponent, between 6-12



The constant B from Borne equation can be estimated by the minimum energy level

$$E_{bond} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r}(1 - \frac{1}{n})$$

Considering Madelung constant a,

$$E_{sum} = \frac{z_1\ z_2\ e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)\alpha$$

Lattice energy

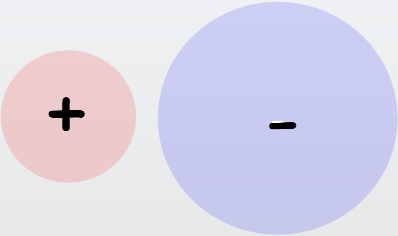
For a mol of crystalline solid,

lattice energy = E bond energy x Madelung constant x Avogadro constant

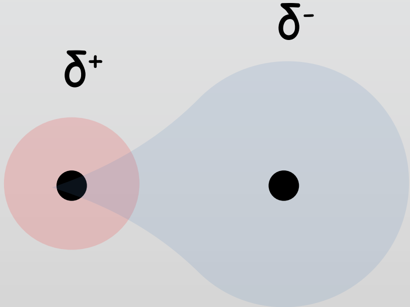
$$E_{sum} = \frac{N_A z_1\ z_2\ e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)\alpha$$

- N_A: Avogadro constant
- a: Madelung constant for a lattice
- z_1 and z_2 are the charge numbers of cation and anion
- e is elemental charge, 1.6022 x 10-19 C
- ε_0 is permittivity of free space
- r_0 is the distance to the closest ion
- n is the born exponent

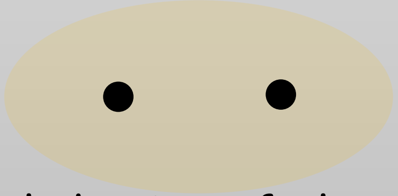
Chemical bonds



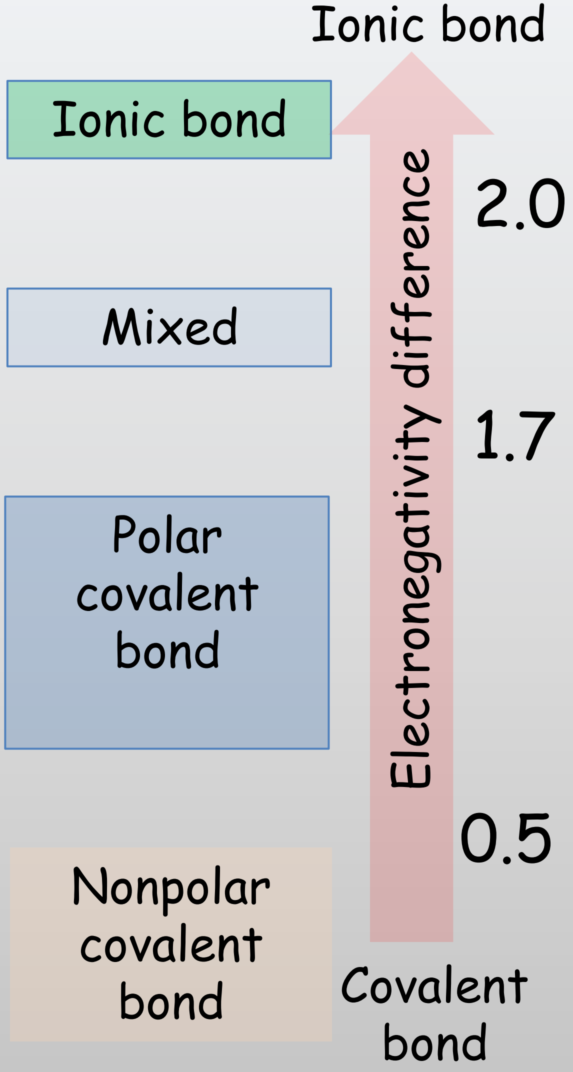
No sharing of electrons



Unequal sharing of electrons



Equal sharing of electrons

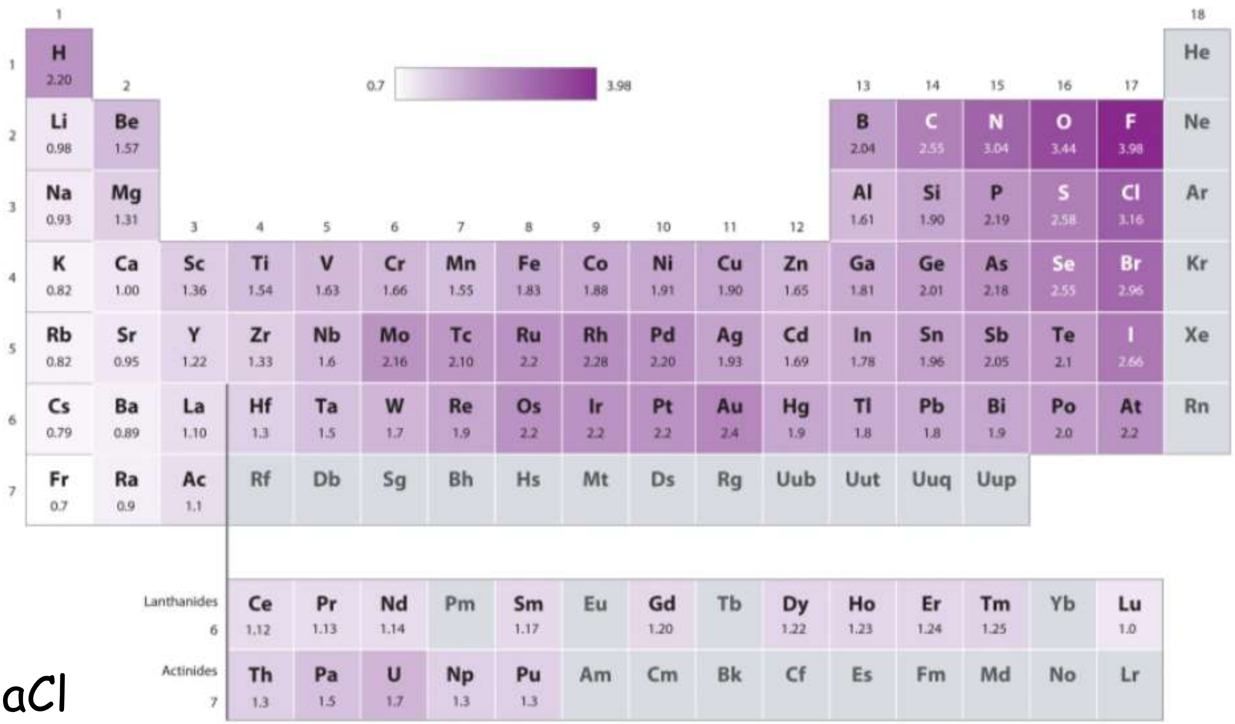


No clear cut! Degree of ionic character

Fraction of ionic character can be calculated by electronegativity values:

$$IC = 1 - \exp[-0.25(X_M - X_x)^2]$$

X is the electronegativities of the element in a compound MX



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

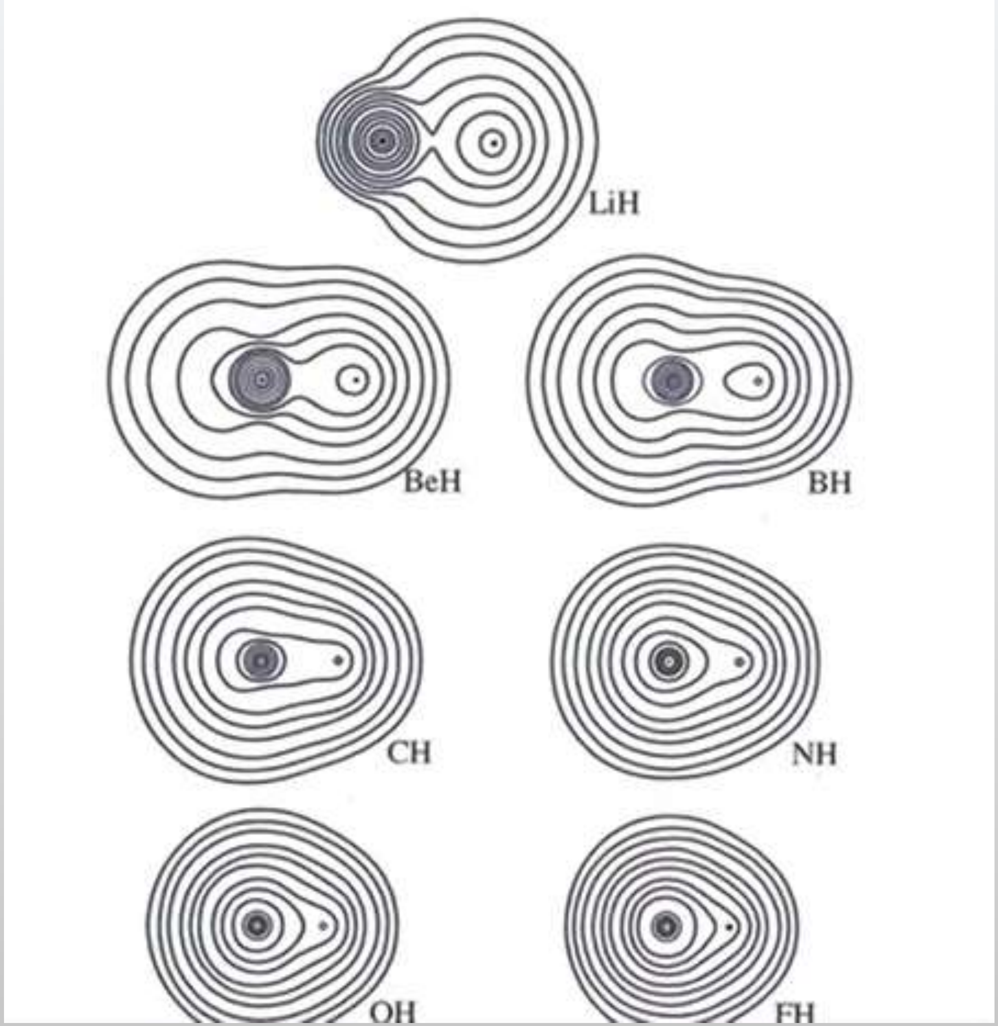
Lanthanides 6	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.0
Actinides 7	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

For NaCl

IC = 0,67 or 67% → this compound is 2/3 ionic (a fair degree of convent bonding)

Covalent bond

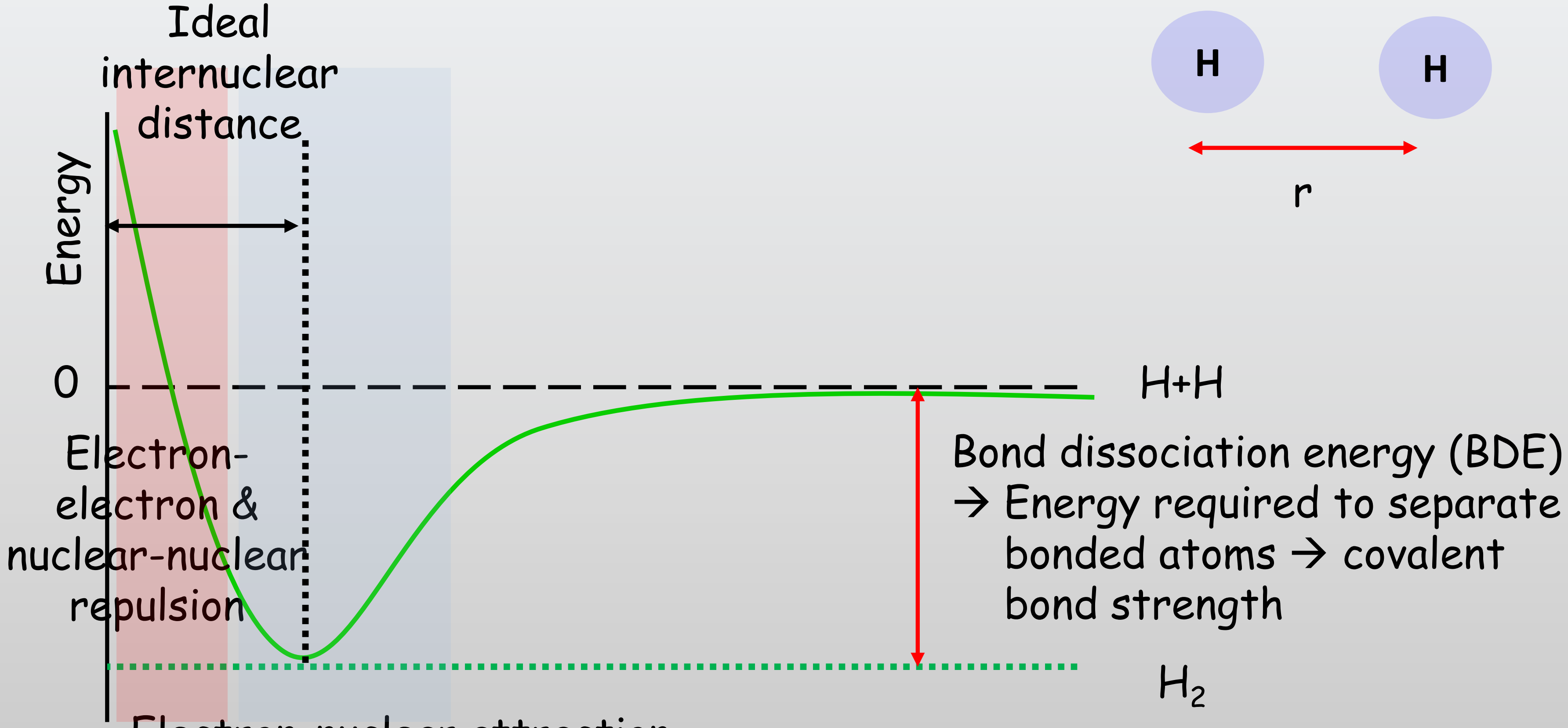
Covalent bond



Electrons shared and spend more time between nucleus → molecular orbital

Covalent bond – valence bond theory

- Covalent bond: a pair of electrons shared between two atoms



Ideal internuclear distance

Electron-electron & nuclear-nuclear repulsion

Bond dissociation energy (BDE)
→ Energy required to separate bonded atoms → covalent bond strength

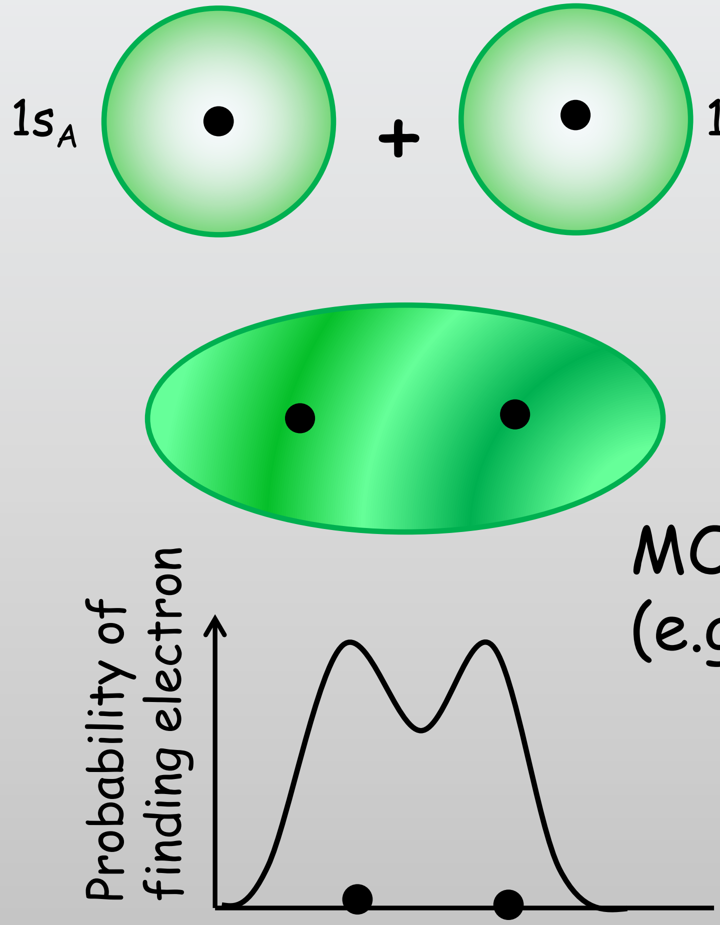
Electron-nuclear attraction
Sharing electrons → ideal internuclear distance

Molecular orbitals (MO)

Combination of atomic orbitals (AO) gives rise to molecular orbitals (MO)

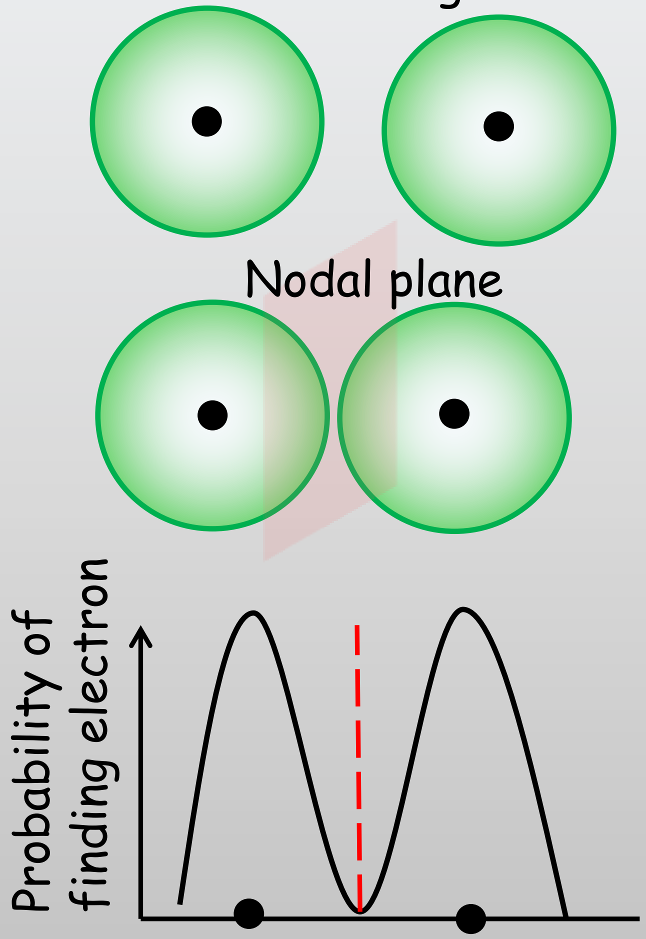
Constructive interference of AOs→ Bonding MO

Destructive interference → anti-bonding MO



Electrons localized

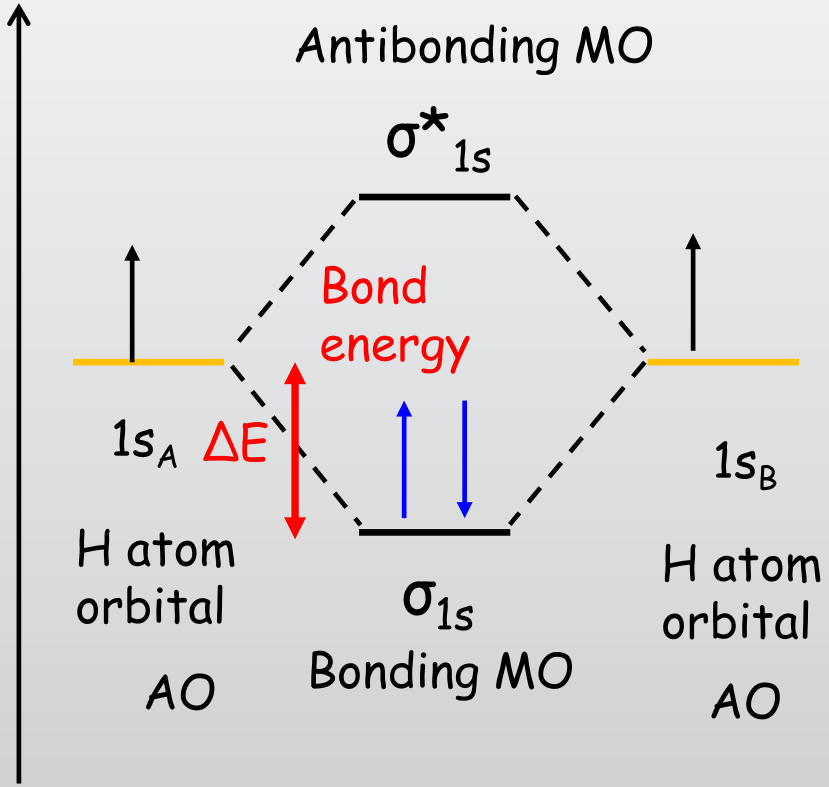
MO (e.g., σ)

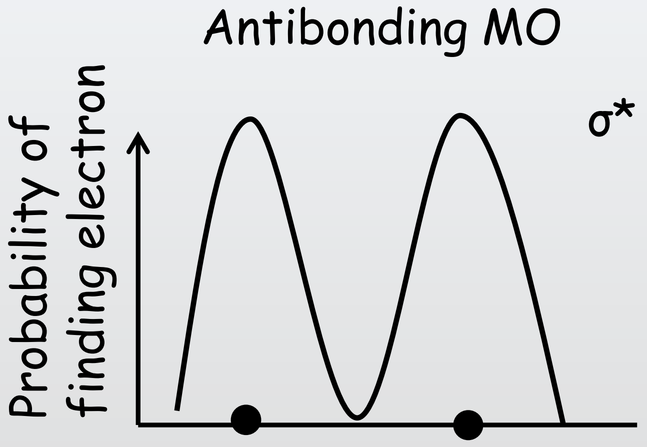


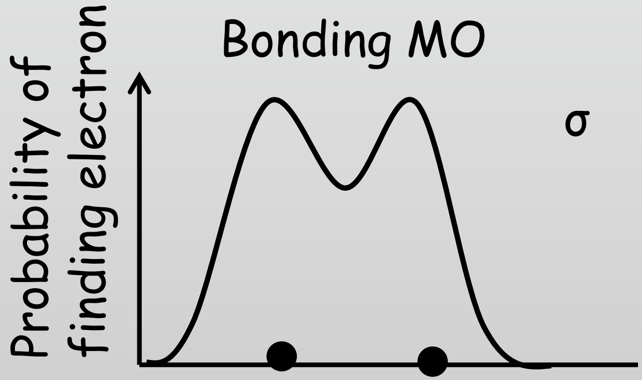
Electrons delocalized

σ*

Molecular orbitals (MO)





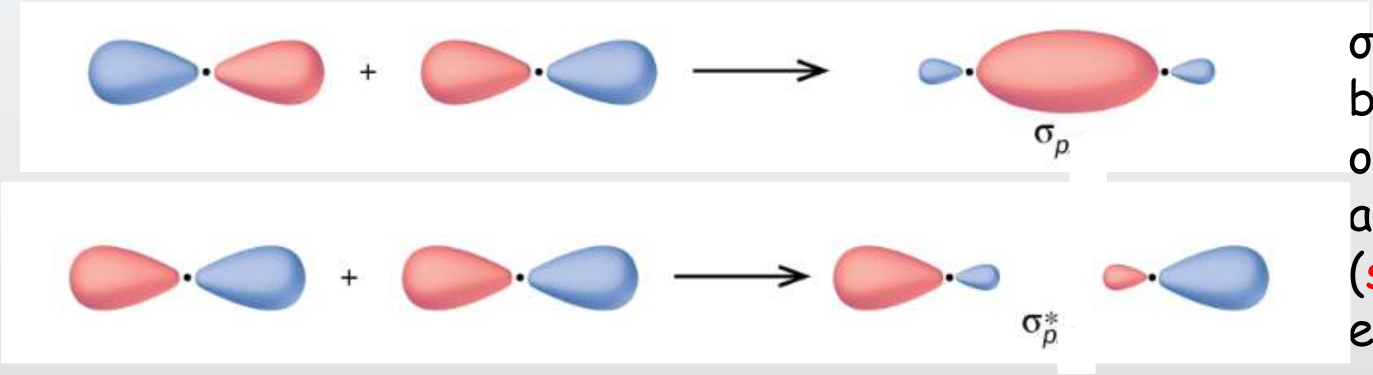


Anti-bonding molecular orbitals are less stable and have higher energy

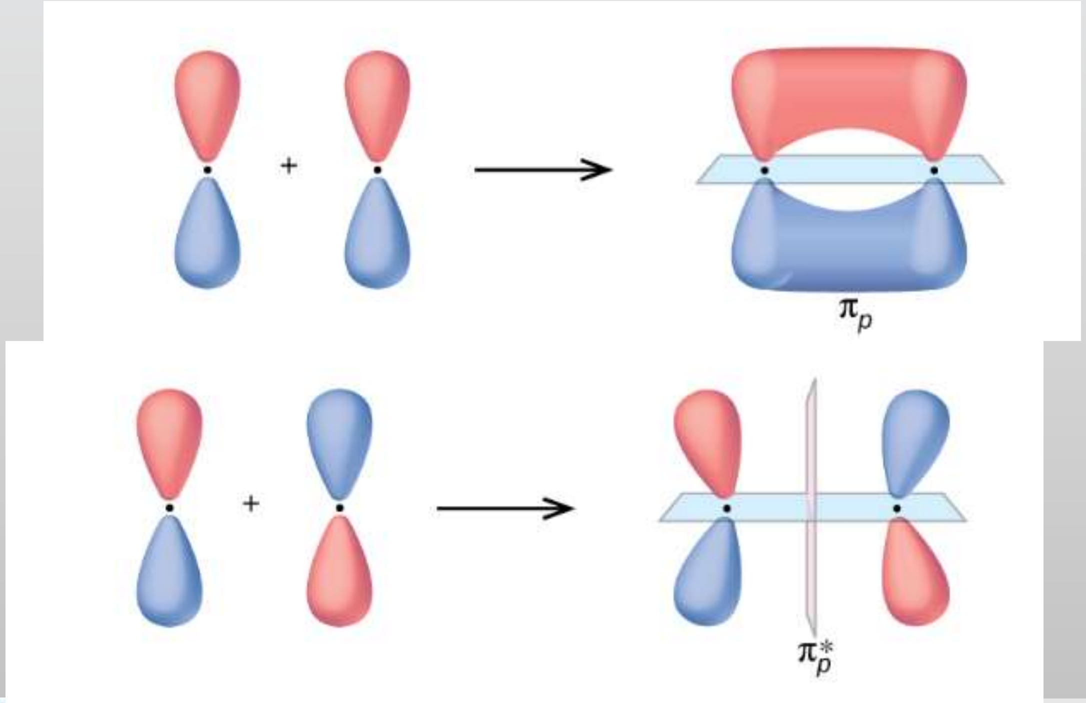
Bond order = $\frac{1}{2}$(No. of bonding electrons – No. of anti-bonding electrons)

→ Bond order indicates the number of covalent bond

Molecular orbitals (MO) of p orbitals



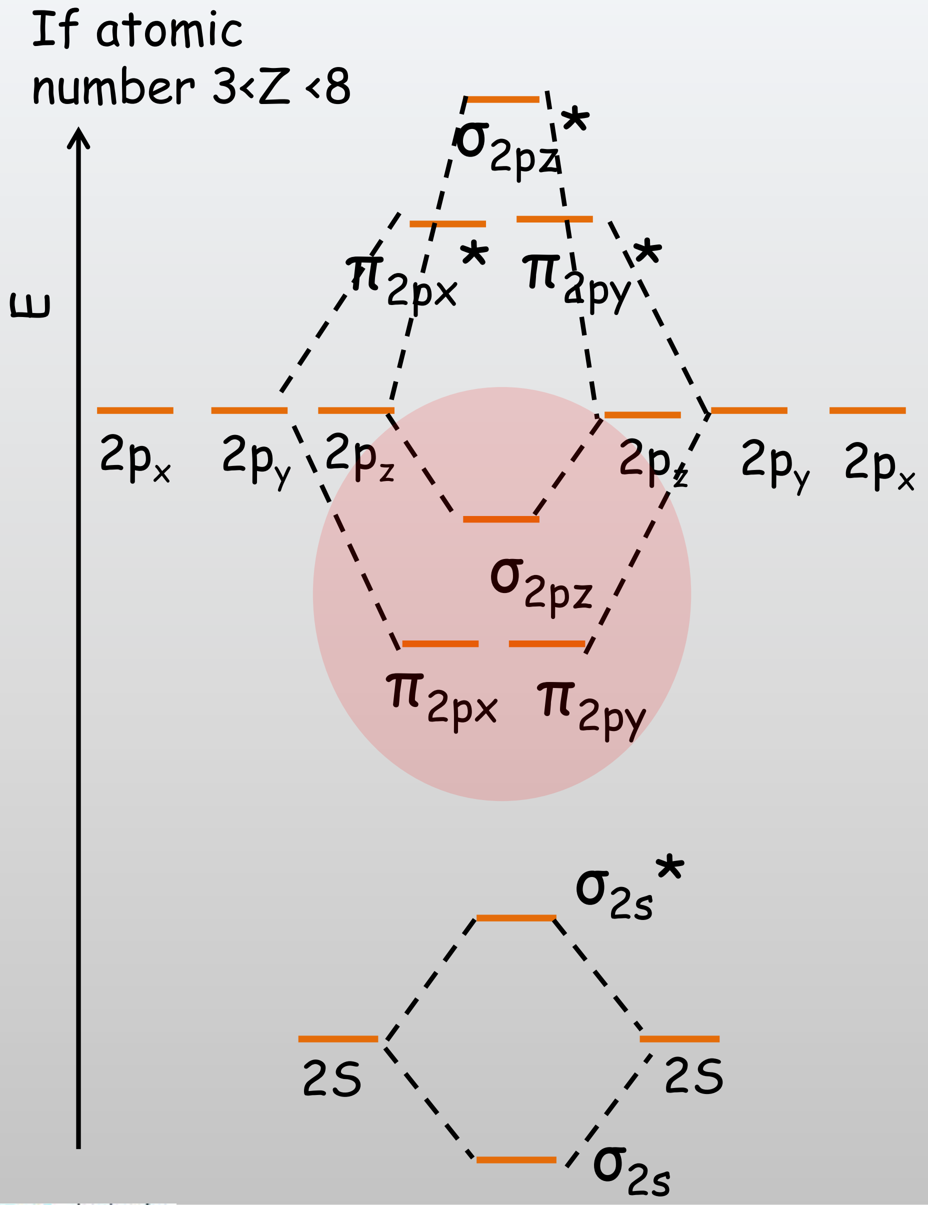
σ bond are formed by end-to-end overlapping of atomic orbitals (stronger → electrons along the axis of nucleus of atoms)

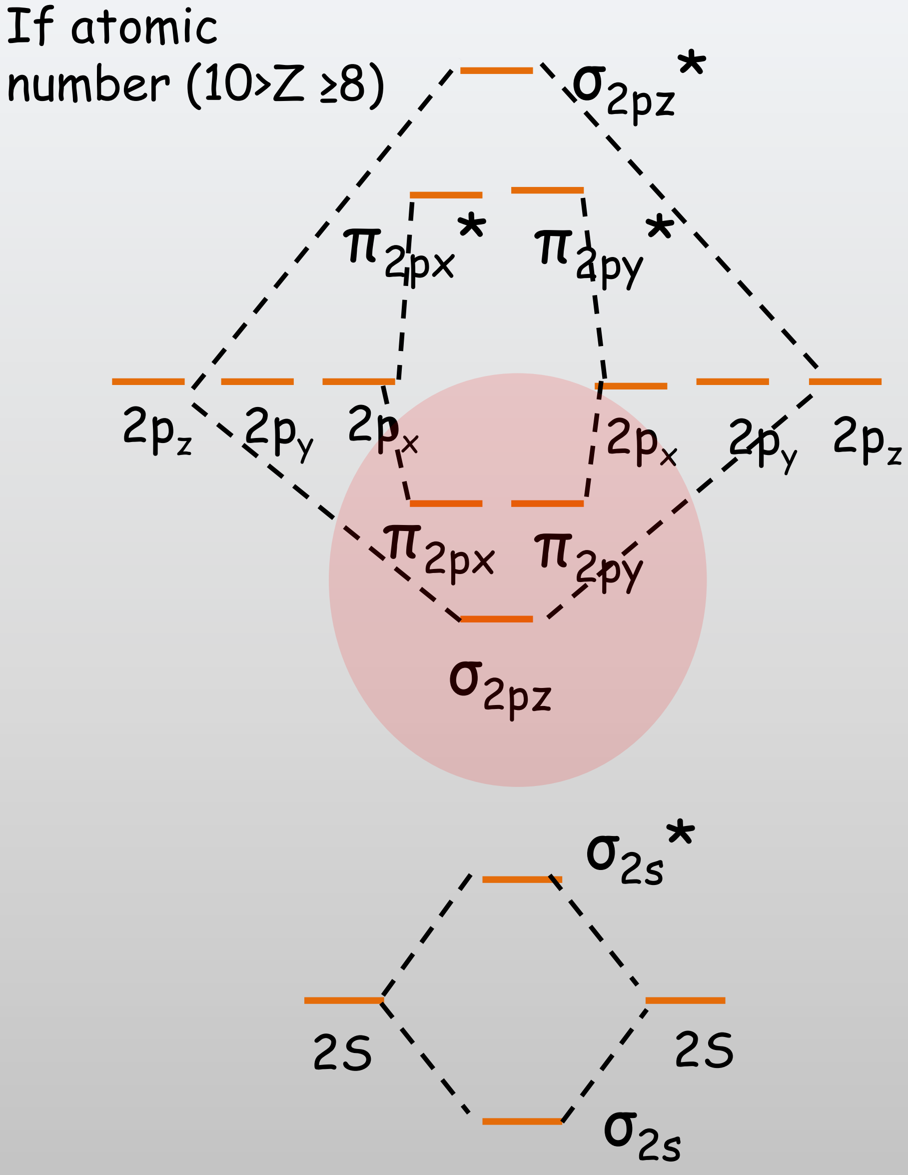


π bond are formed by lateral (x, y) overlapping of atom orbital (unhybridized p orbitals) (weaker→ electrons concentrate above or below the axis of nucleus of atoms)

(Courtesy of chem libretexts)

Molecular orbitals (MO)





Covalent bond strength

Bond	Bond Energy (kJ)	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	N=N	418	Si–Cl	359
H–P	320	N≡N	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
C=C	611	O–O	140	P–I	215
C≡C	837	O=O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C=N	615	O–Si	370	S–Br	215
C≡N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C=O	741	O–I	200	Cl–I	210
C≡O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Bond strength is quantified by bond dissociation energy (BDE)

→ the energy required to break a specific covalent bond in one mole of gaseous molecules

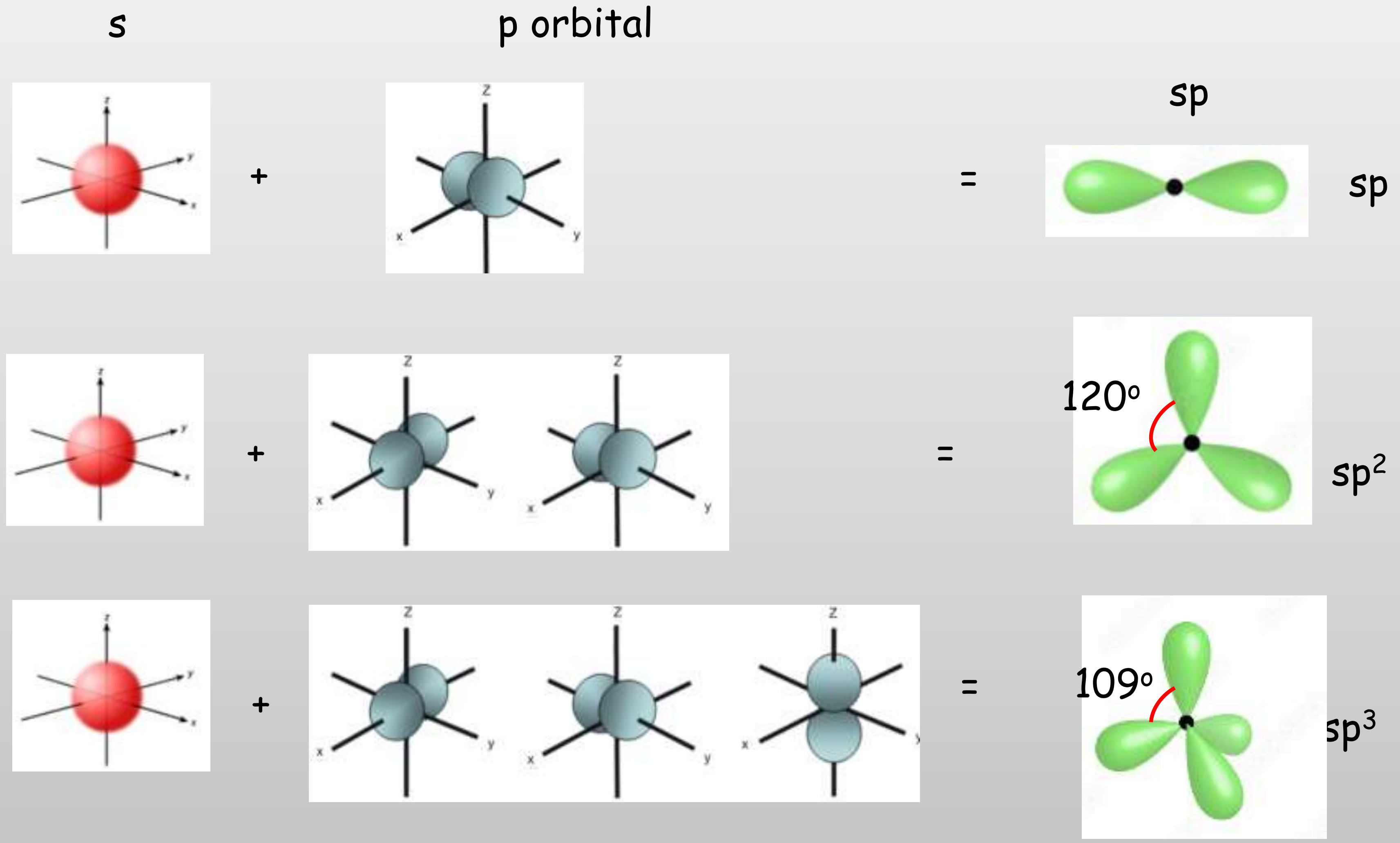
→ E.g., H_2 (g) → 2H (g) $\Delta H^o = 436$ kJ

→ When one bonds to various atoms in a group, the bond strength typically decreases as we move down to the group

→ Triple bond > double bond > single bond

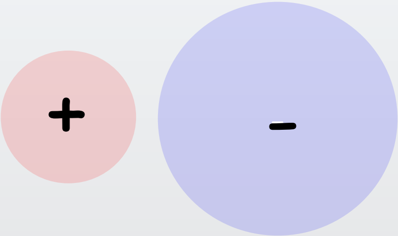
Hybridization

Hybridization model explains molecules with double or triple bonds

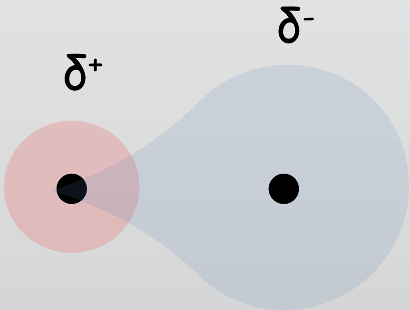


(credit of Natros)

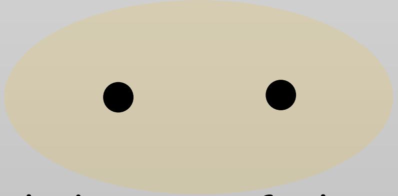
Chemical bonds



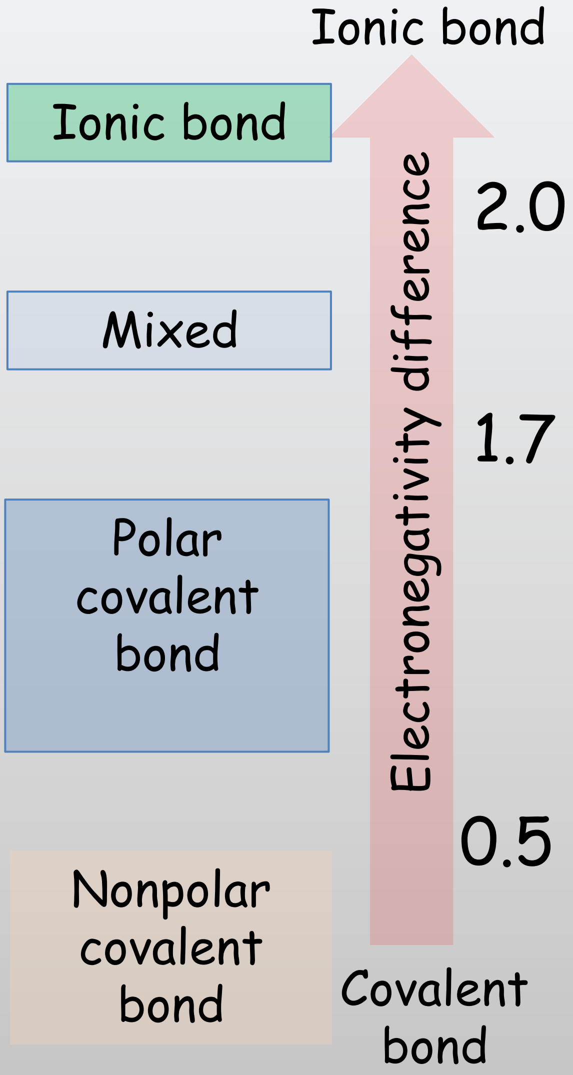
No sharing of electrons



Unequal sharing of electrons



Equal sharing of electrons



Ionic bond

Ionic bond

2.0

Mixed

1.7

Polar covalent bond

Electronegativity difference

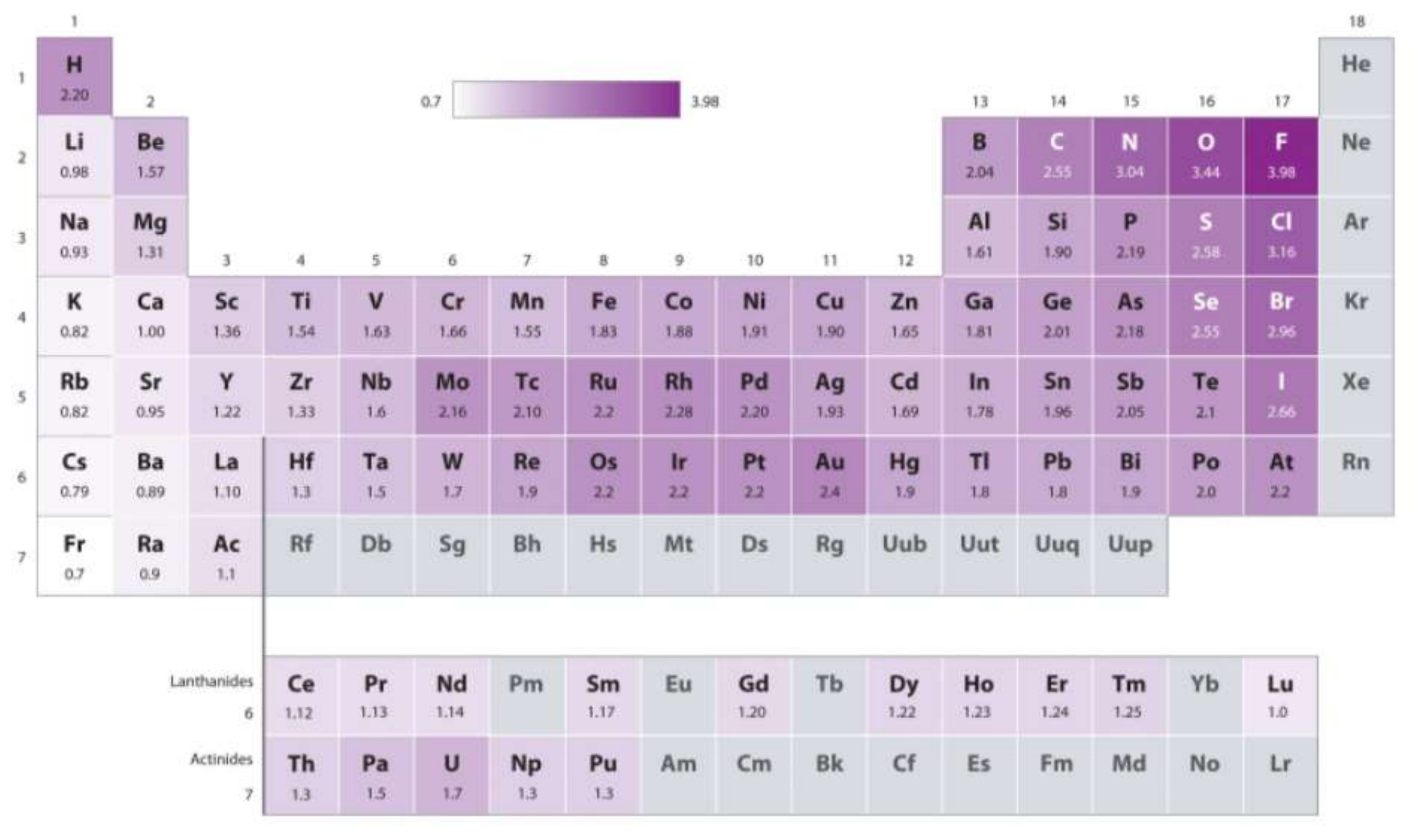
0.5

Nonpolar covalent bond

Covalent bond

Electronegativity

- What kind of Co-O, Fe-O and Ni-O bond?
- What is the trend in bond strength among Co-O, Fe-O and Ni-O?



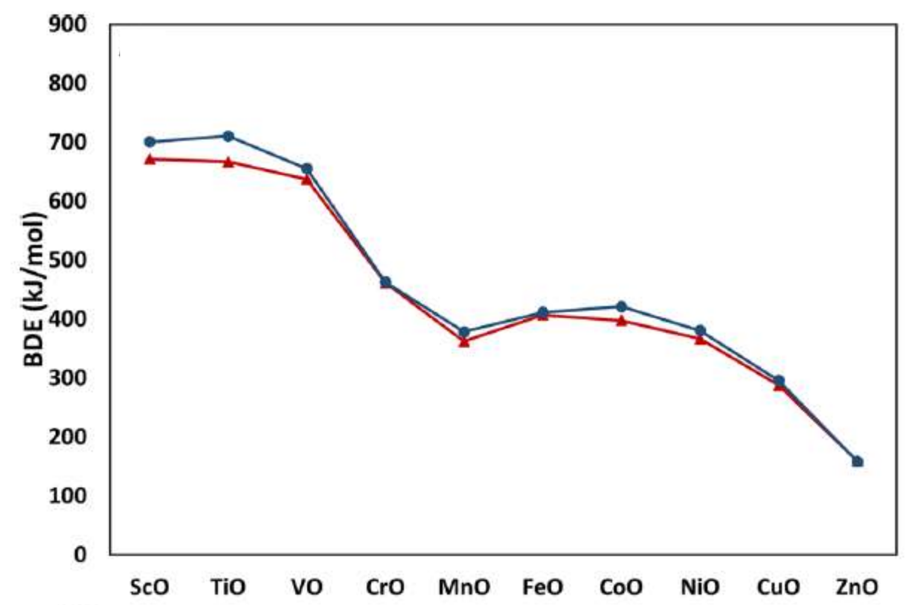
0.7 — 3.98

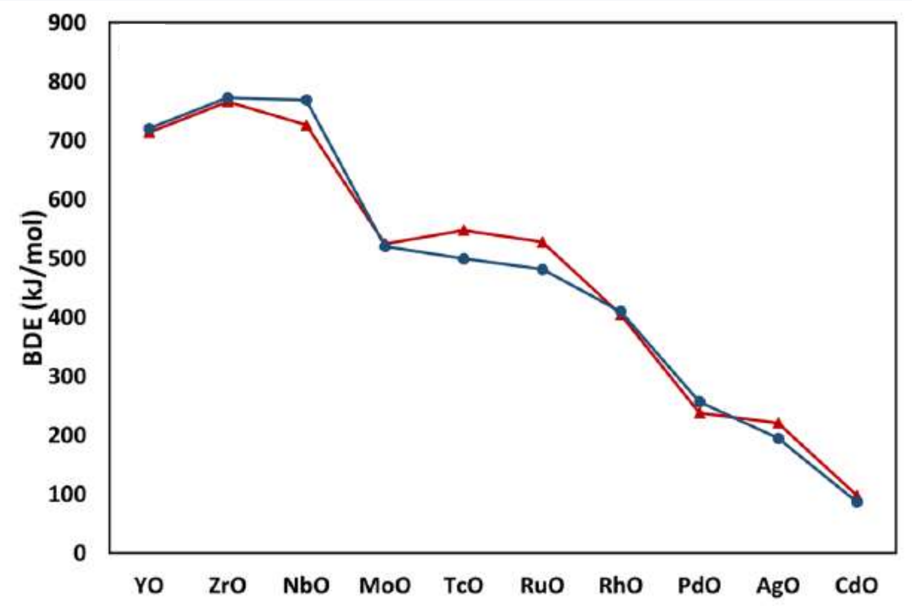
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

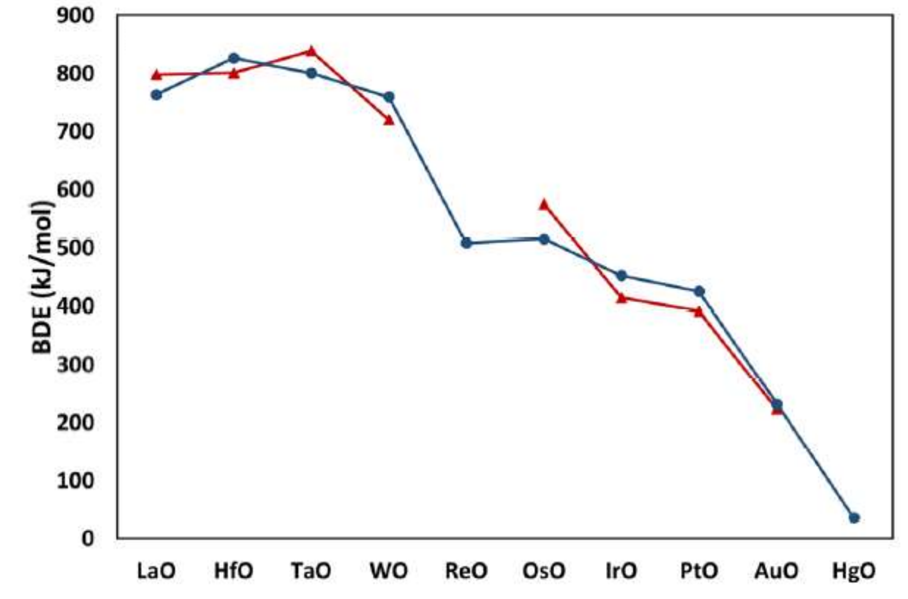
Lanthanides 6	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.0
Actinides 7	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

CRC handbook of chemistry and physics

M-O bond strength (bond dissociation energy)







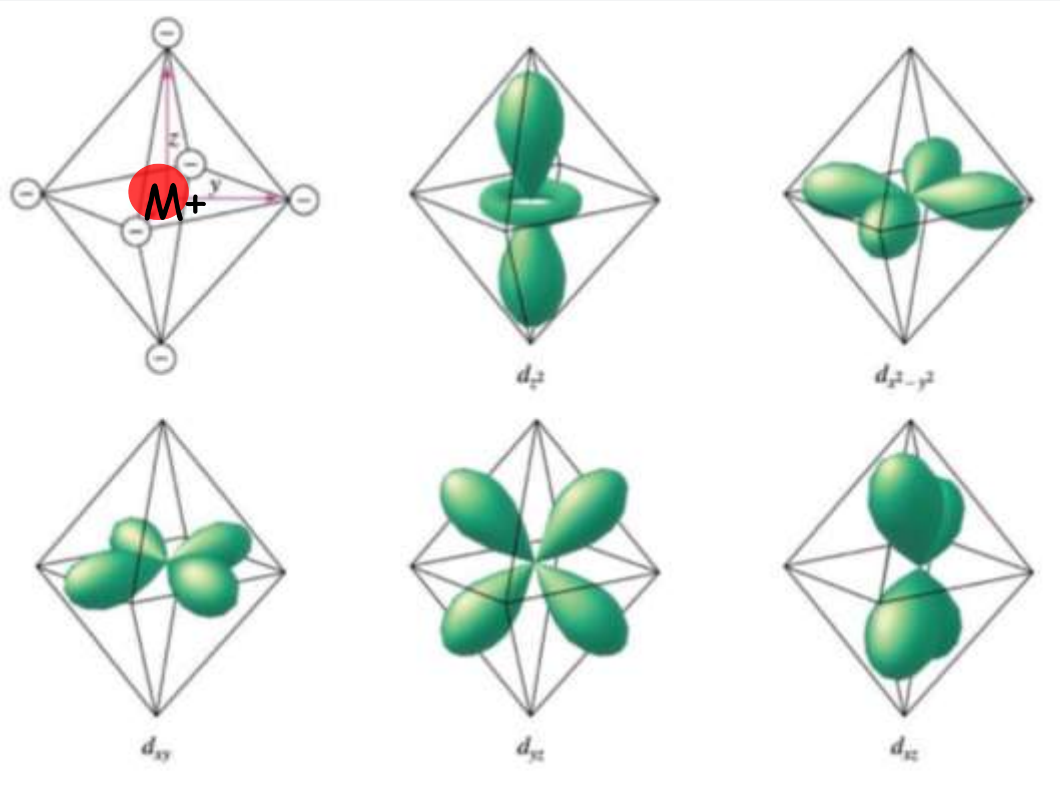
- Increasing the electronegativity towards the right in the transition metal series, M-O strength decreases
- The element with the lowest electronegativity should have the largest interaction with oxygen

Moltved and Kepp, J. Phys. Chem. C 2019, 123, 18432

Crystal field theory

- Crystal field theory: metal ion and set of ligands can be treated as charged particles (neglect the covalent bond defined by valence bond theory, instead, it is simply electrostatic or ionic)

  1) attraction: between positive ion and negative ligand
  2) repulsion: d electrons of metals and surrounding negative ligand

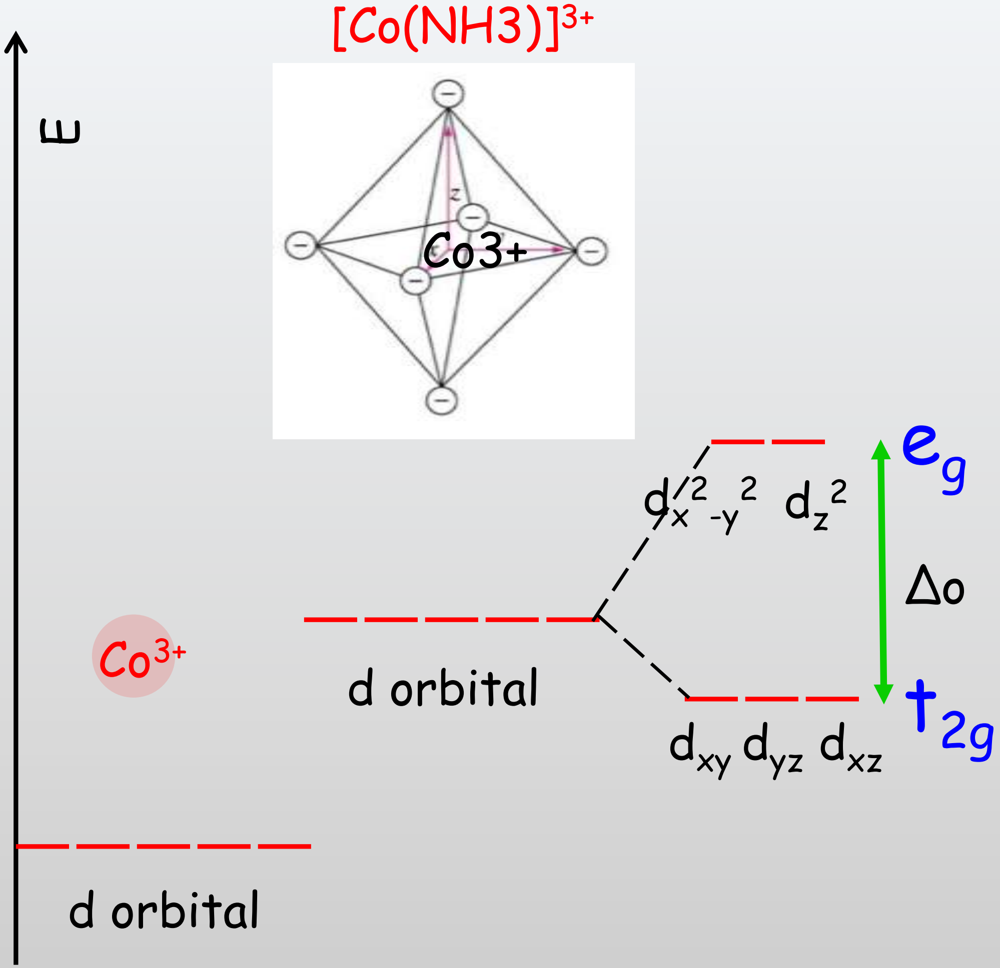


1) Stronger repulsion→ d_{z^2} and $d_{x^2-y^2}$ orbitals are destabilized

2) Less repulsion→ d_{xy}, d_{xz}, d_{yz} are stabilized by the same amount

(Credit of Andrea Snow)

Octahedral crystal field splitting diagram



→ ligand are negative charges can be repulsive to the d orbital

→ the energy levels of metal's d orbital are altered from those in the free metal ions

→ some experience more opposition from d orbital electrons than others because of the geometric structure of molecules

→ such electrostatic environment create a splitting of d orbital

Δo: octahedral crystal field splitting energy

Spectrochemical series

- Ligand determines the splitting energy →Ligands that produce a large splitting are called **strong field** ligands, and those that produce a small splitting are called **weak field** ligands

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < H_2O <$ Pyridine $< NH_3 < NO_2^- < CN^-$

Weak field ligand

Strong field ligand

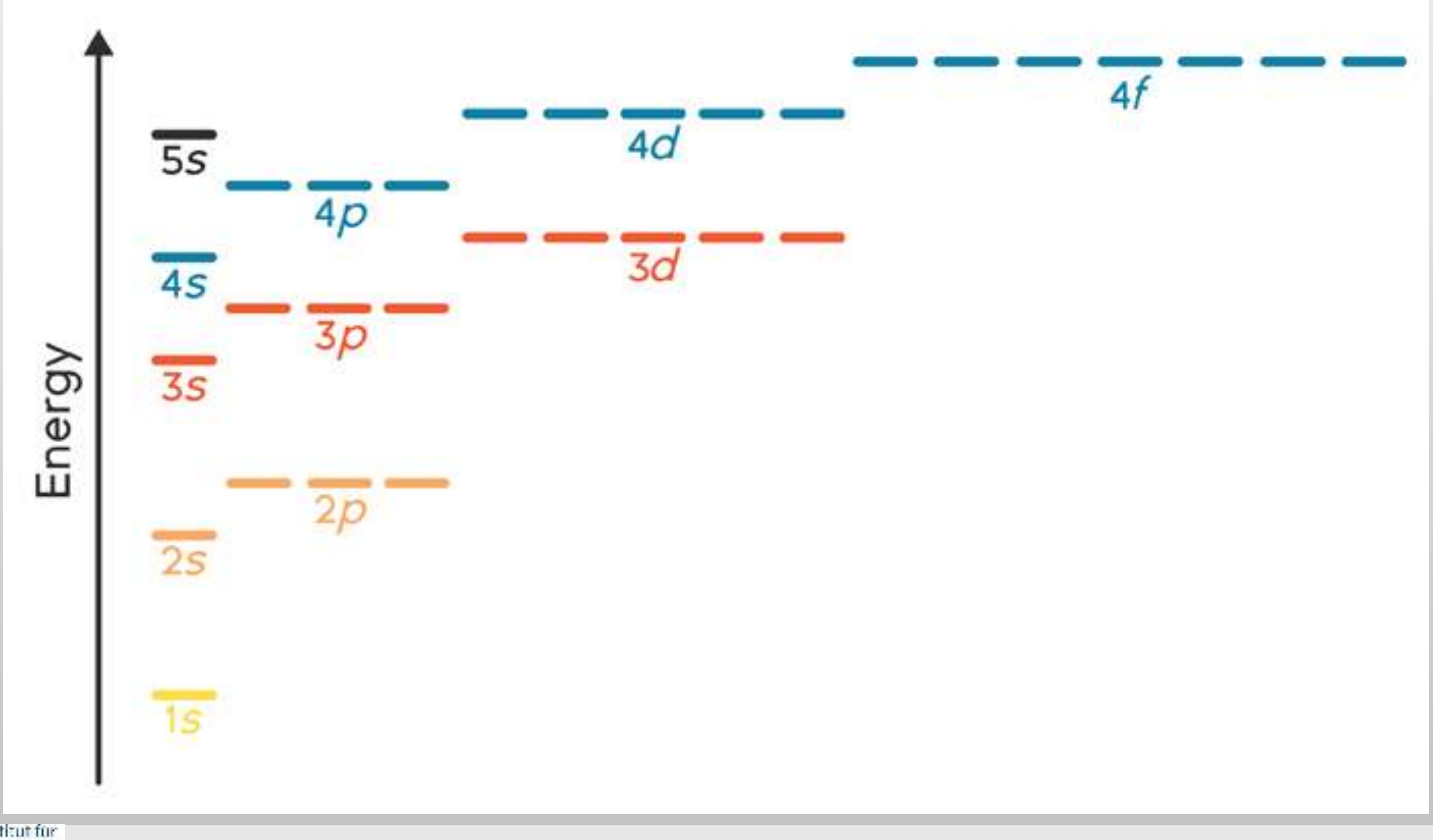
Small field splitting energy Δo

Large field splitting energy Δo

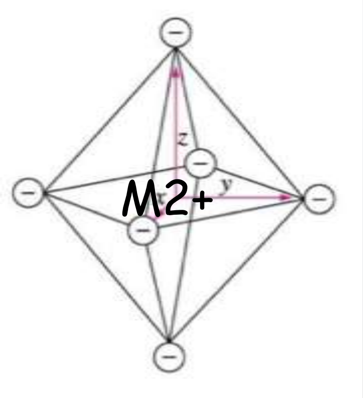
(Courtesy of chem libretexts)

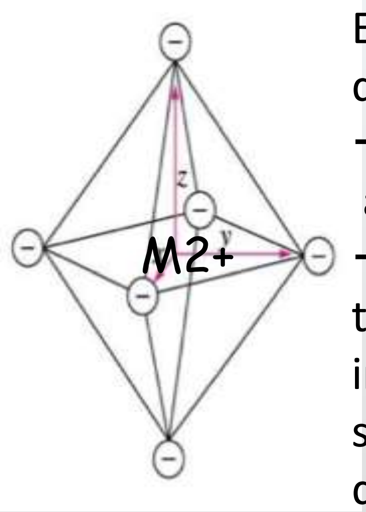
Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Fe3+: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$



Jahn Teller effect

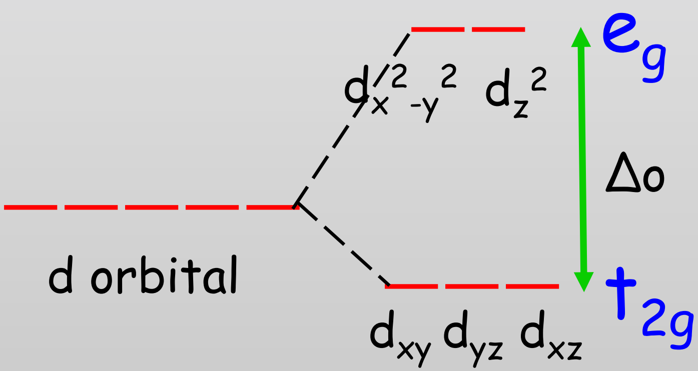


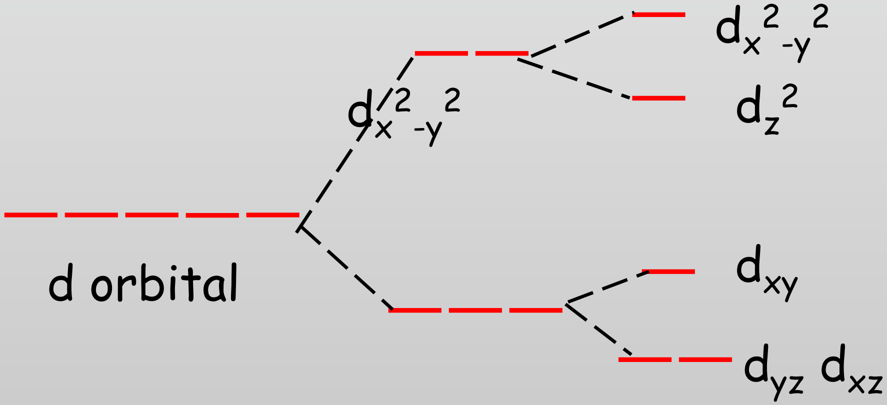


Elongation Jahn-Teller distortion

→ Increase the $d_{x^2-y^2}$ and d_{xy} orbital energy

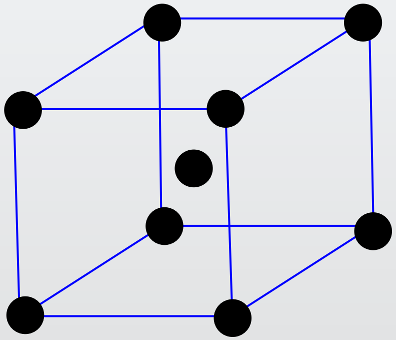
→ Elongation lower the repulsion and increase the complex stability through distortion



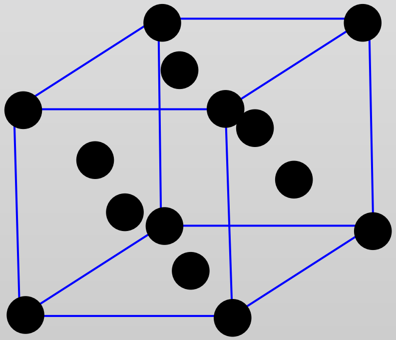


Crystal structure of oxides

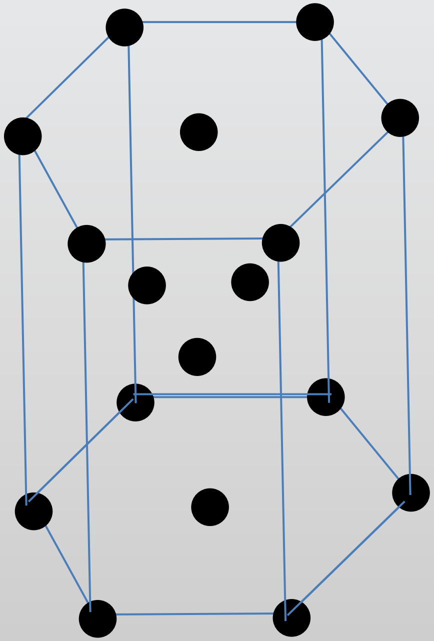
Closed packed sites



Body
centered
cubic (BCC)



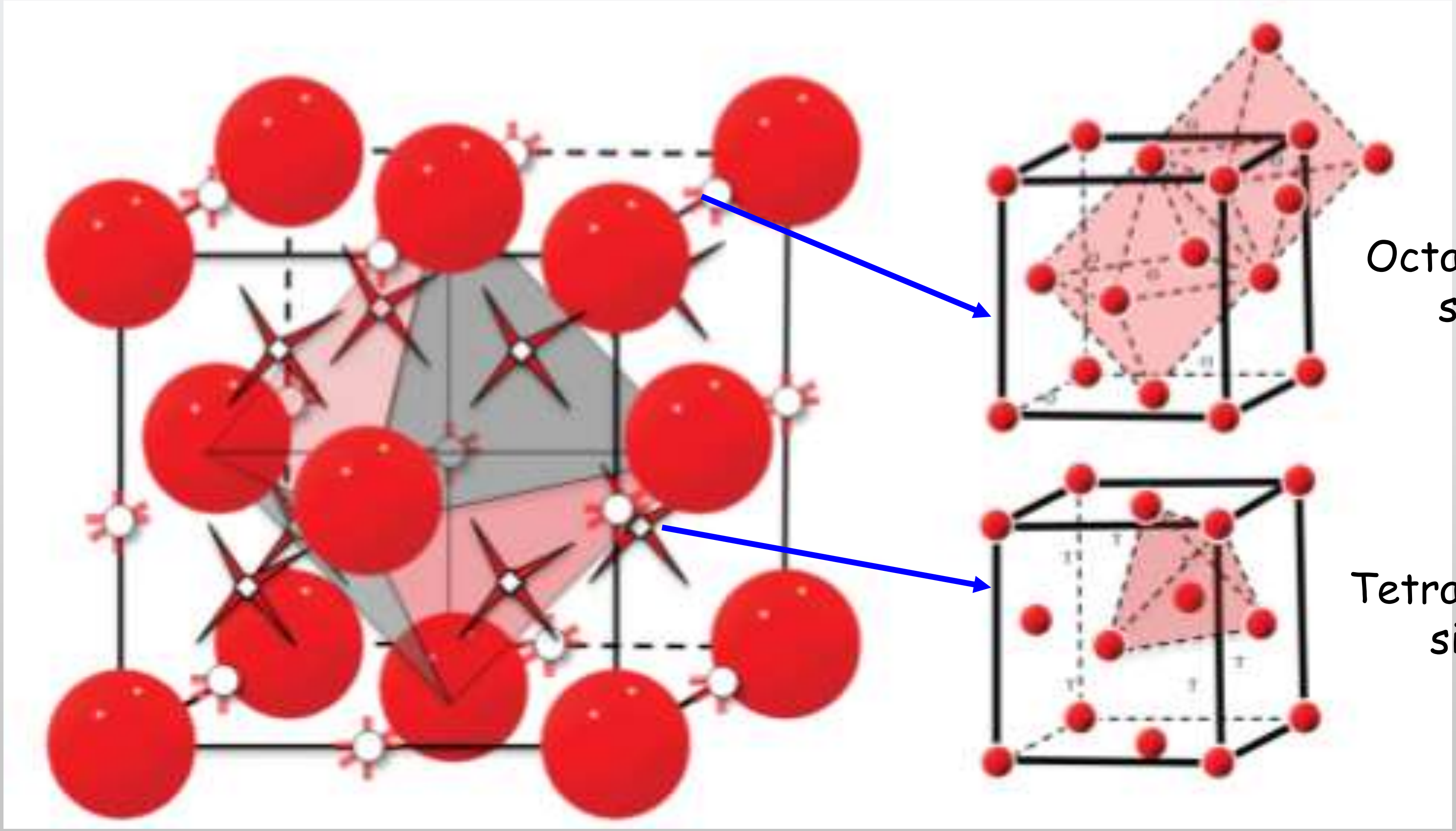
Face
centered
cubic (FCC)



Hexagonal
close
packing
(HCP)

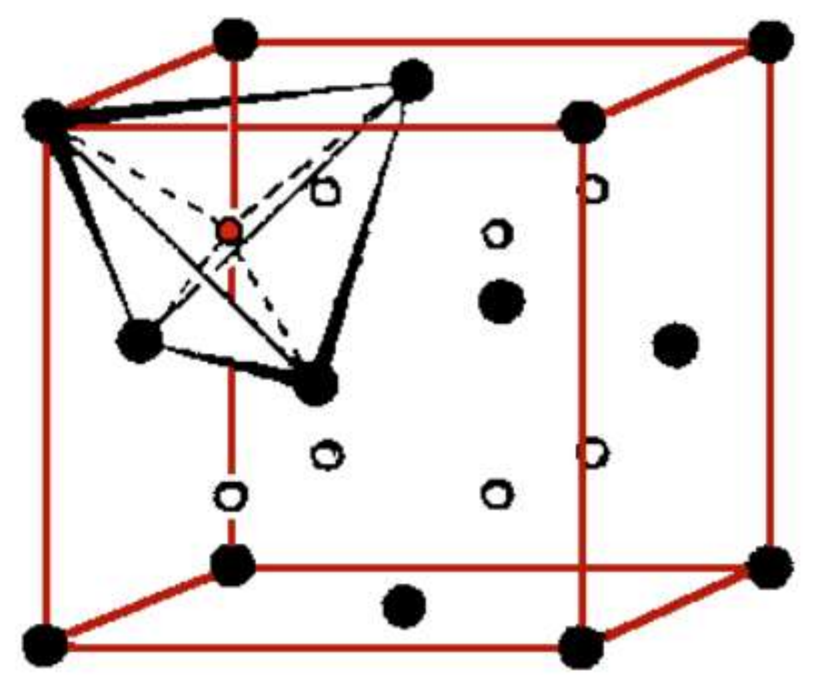
Interstitial sites

Anions: closed packed arrangement
Cations: interstitial sites

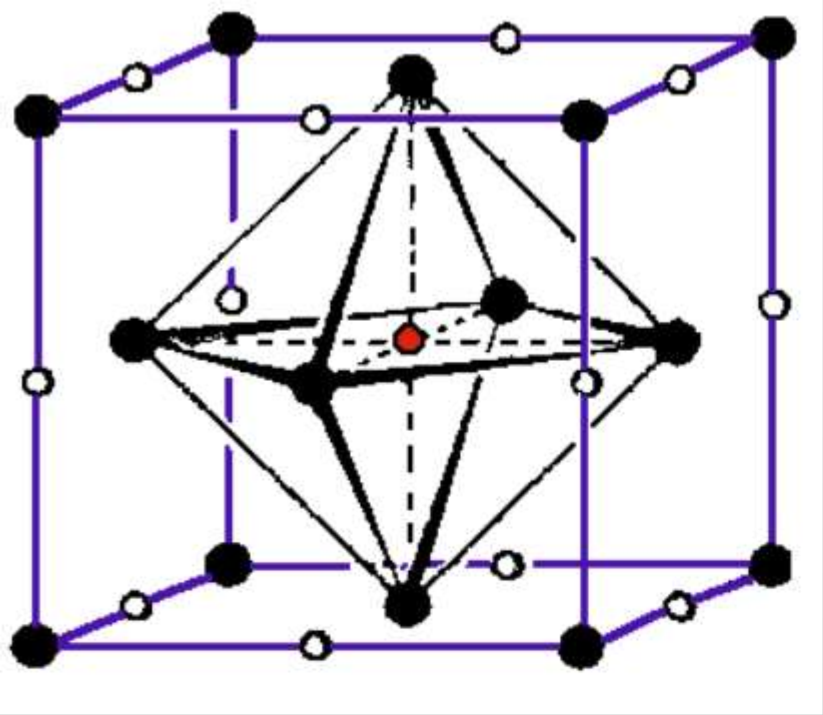


Interstitial sites

FCC contains 8 tetrahedral sites and 4 octahedral sites (12/4 +1)

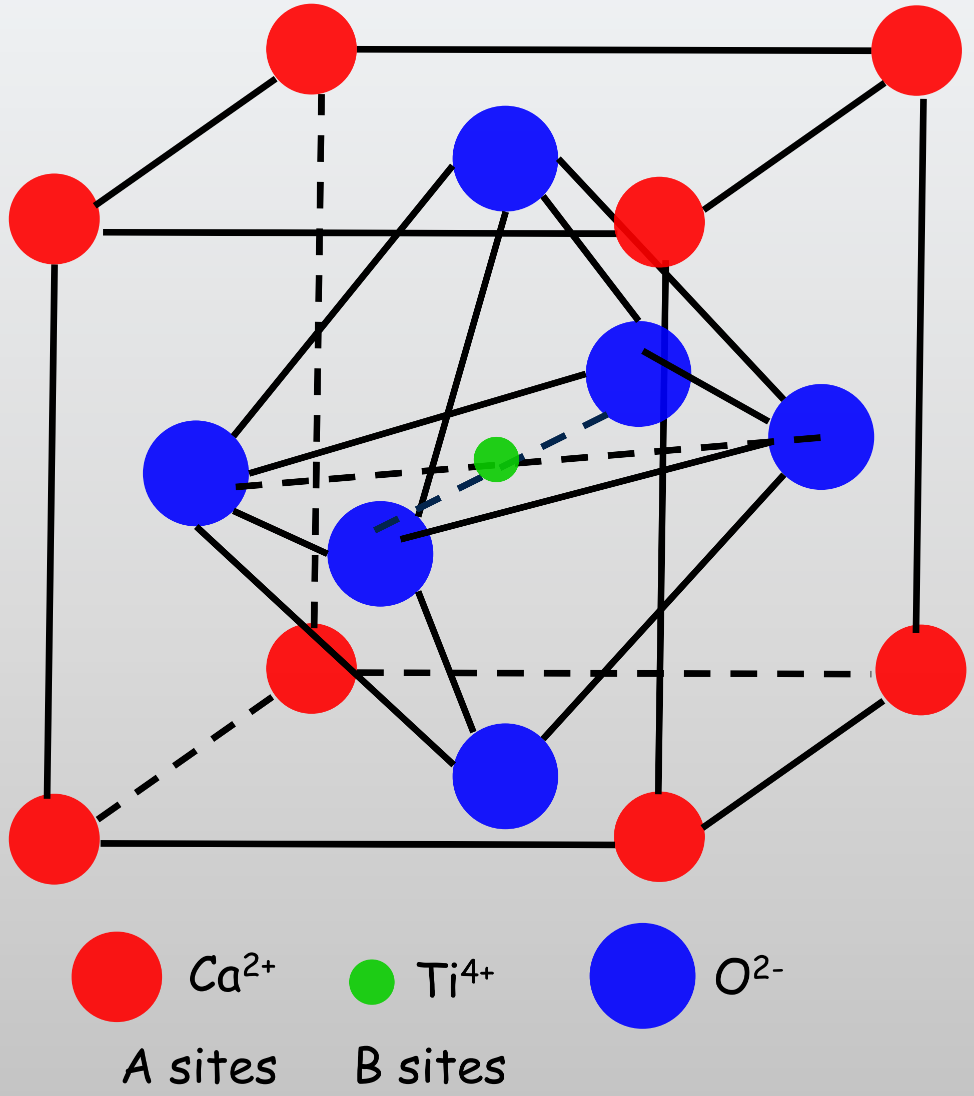


Tetrahedral sites



Octahedral sites

ABO_3 ($LaCoO_3$, $CaTiO_3$ etc)



Anions and A site cations form FCC arrangement

B site occupies the octahedral sites

A site coordination: 12

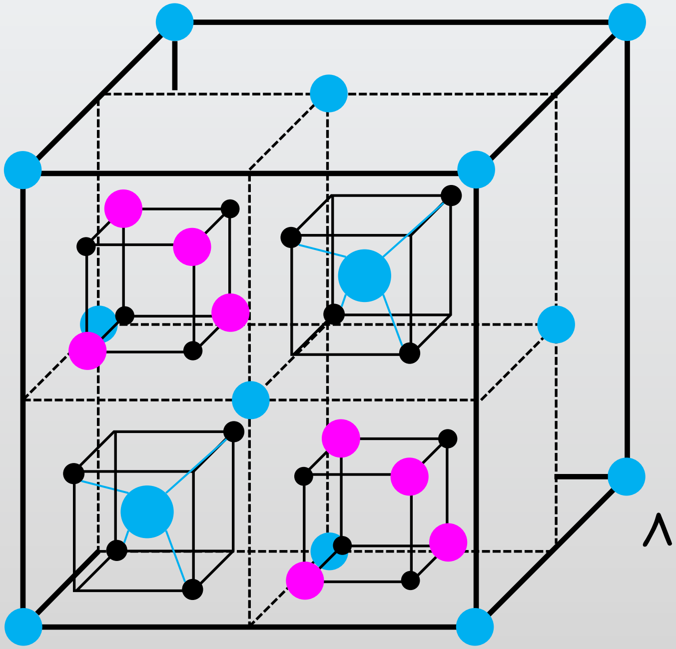
B site coordination: 6

1 out of 4 octahedral sites is filled

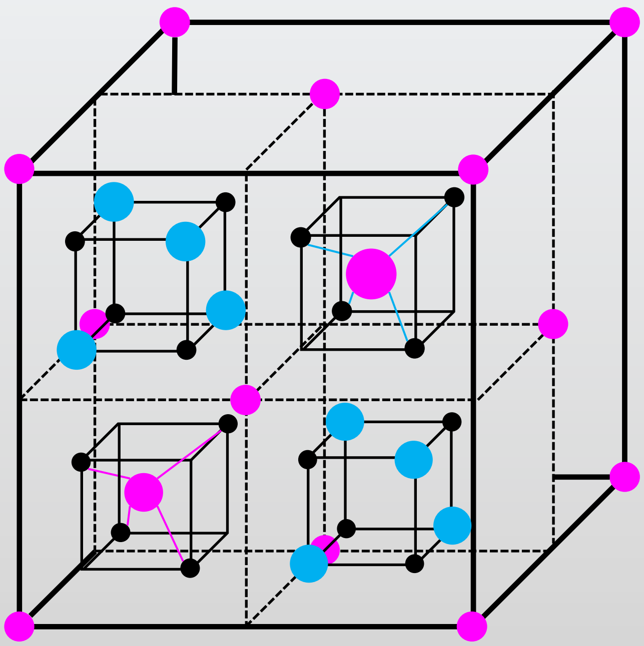
Spinel structure AB_2O_4

Oxygen on the lattice sites, and A and B cations are in the interstitial sites

Normal spinel



Inverse spinel



Intermediate spinel

$(A_{1-\Lambda}B_{\Lambda})[A_{\Lambda}B_{2-\Lambda}]O_4$

Λ is degree of inversion

Normal spinel

$(A^{2+})[B^{3+}_2]O^{2-}_4$

( ): tetrahedral sites

[ ]: octahedral sites

Inverse spinel

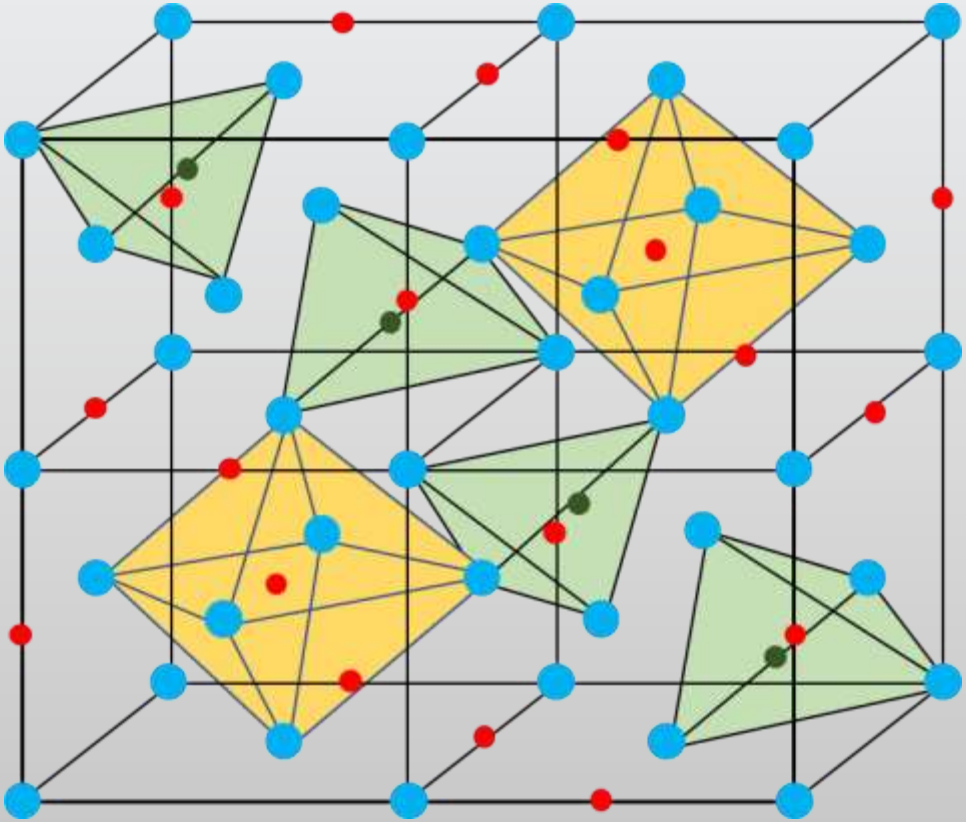
$(B^{3+})[A^{2+}B^{3+}]O^{2-}_4$

A cation is larger than B cation → A goes to larger octahedral sites

Spinel structure AB_2O_4

A cations in 2 tetrahedral sites and B cations 1,5 octahedral sites

A cations in 0 tetrahedral sites and B cations 2,5 octahedral sites



1/8 of the tetrahedral sites of ½ octahedral sites

O^{2-}

B^{3+}

A^{2+}

Defects in oxides

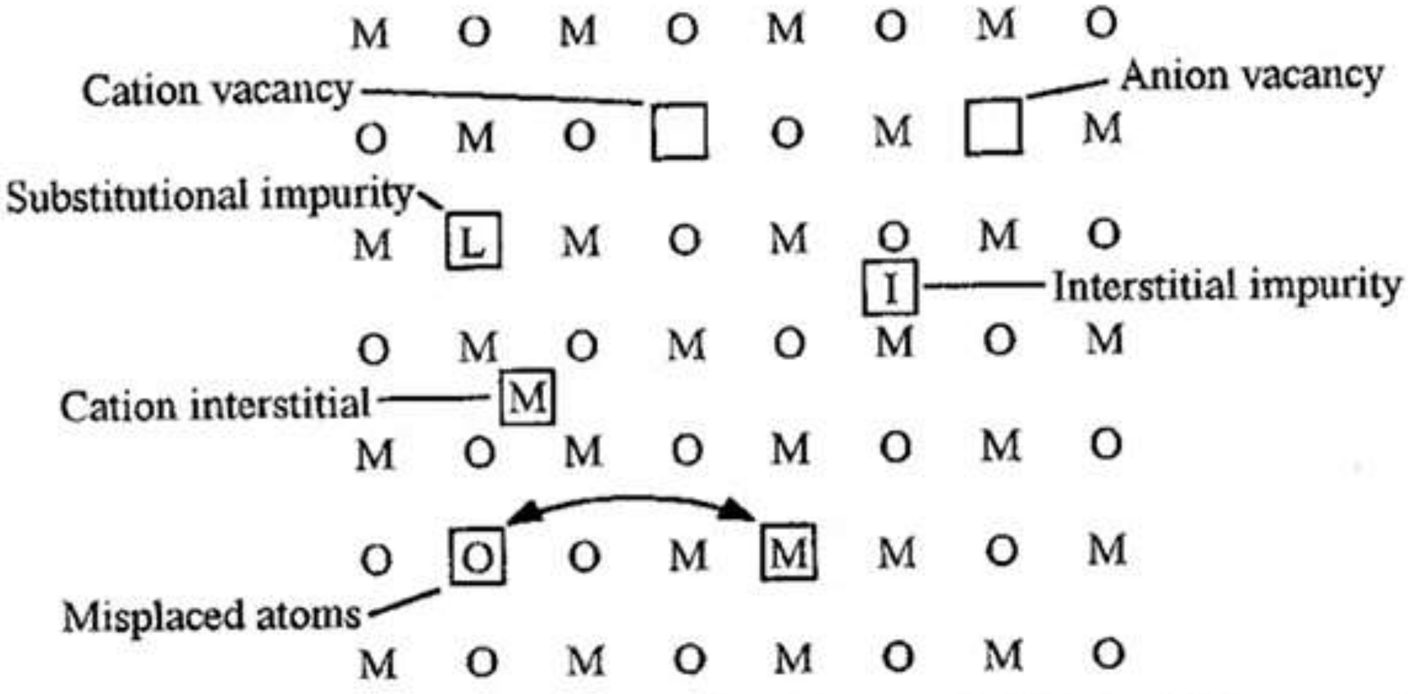
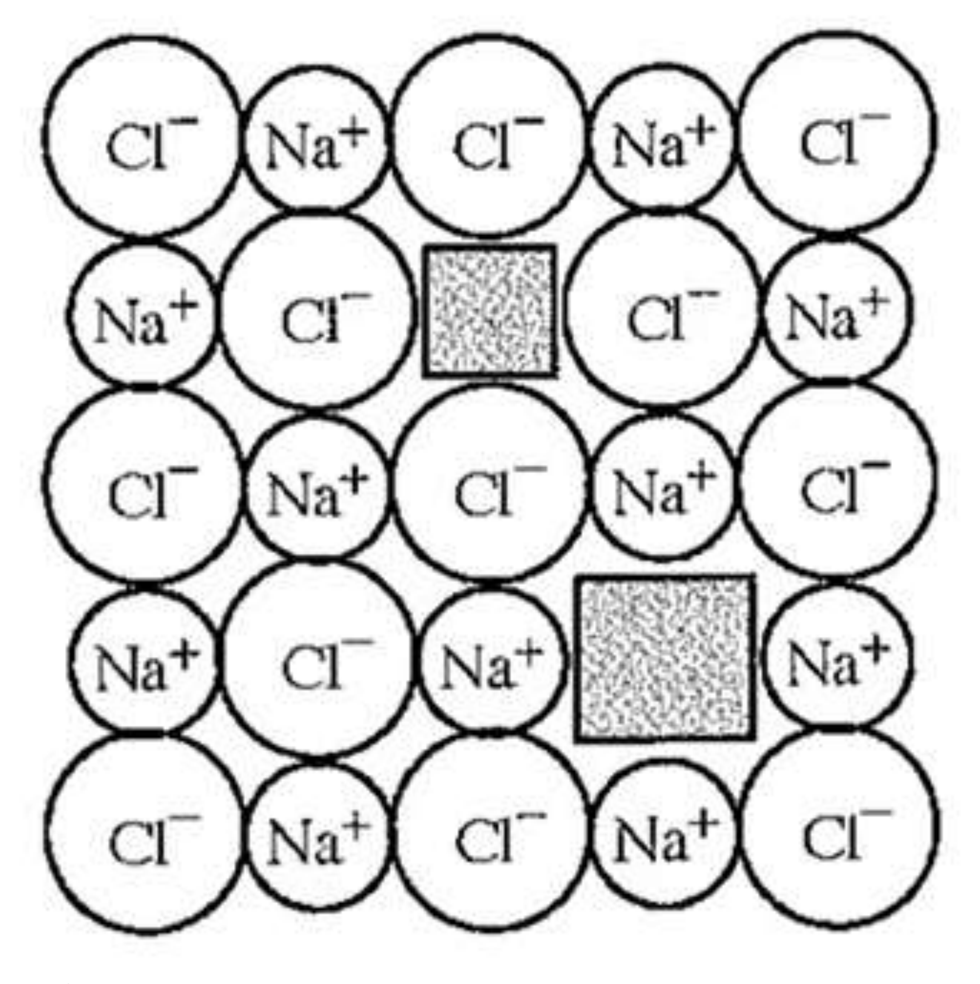


Figure 6.1 Various types of defects typically found in ceramics. Misplaced atoms can only occur in covalent ceramics due to charge considerations.

Charges are associated → neutralized charges

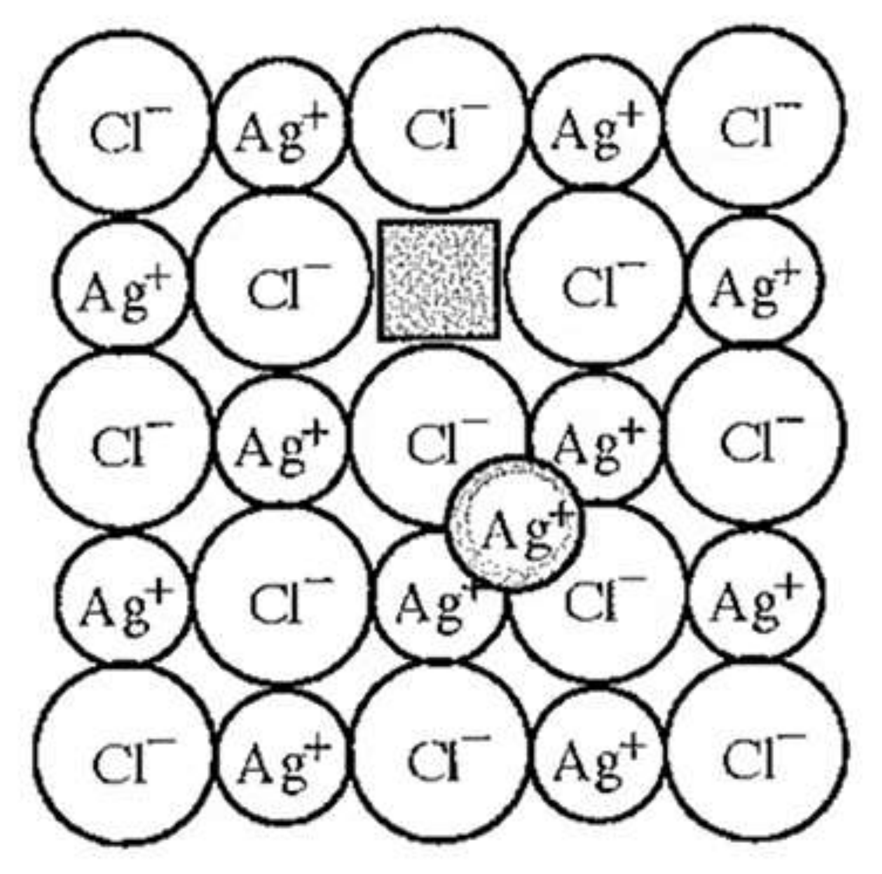
Schottky defects



→ charge-equivalent number of vacancies formed on each sublattice

→ Remove a formular unit (remove +1 and -1 charges, that is charge equilibrium numbers

Frenkel defects



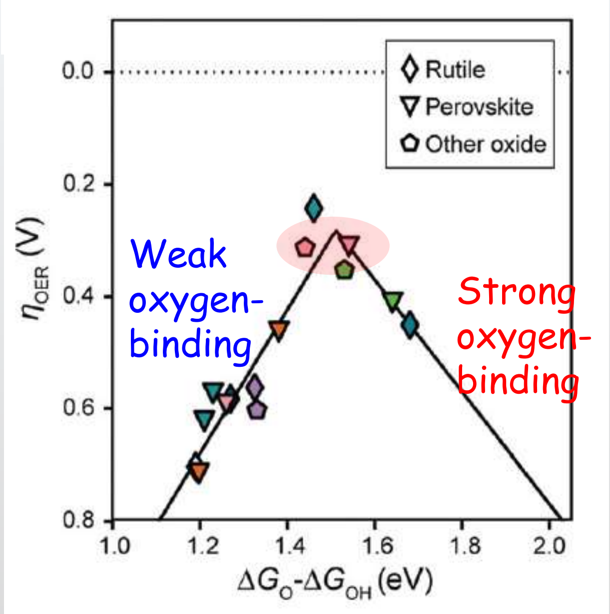
→ Ion vacancy on a regular lattice site migrates to interstitial site

e.g., Ag+ leaves the lattice site and moves to the interstitial site

electrocatalysts' design – descriptors

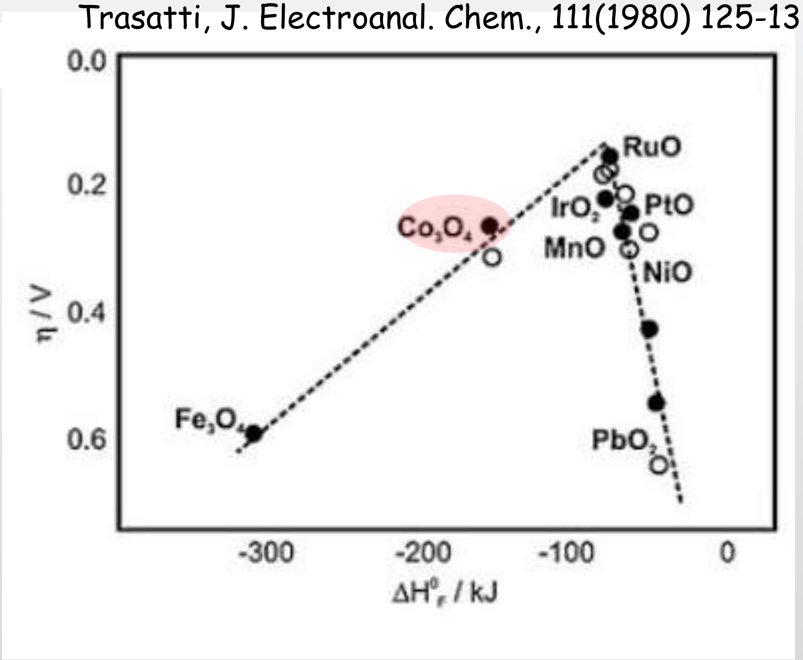
Perovskite ABO_3 & spinel oxides – AB_2O_4

$\Delta G_{O*} - \Delta G_{HO*}$



Enthalpy of lower to higher oxidation oxide

Trasatti, J. Electroanal. Chem., 111(1980) 125-131



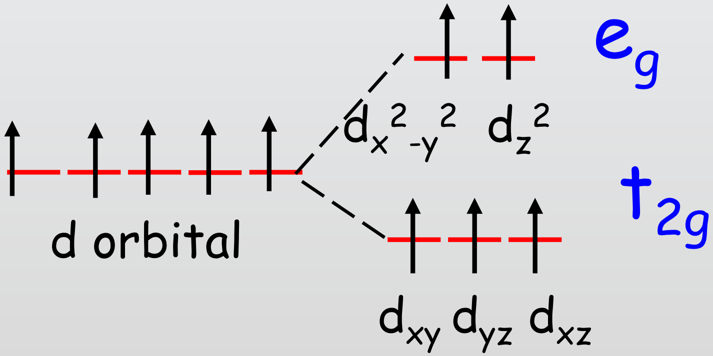
- Spinels and perovskites (ABO_3 , AB_2O_4) are promising

- Design strategies:

1) e_g orbital occupancy → the higher the e_g occupancy, the better OER activity
2) Increasing metal-oxygen covalency → improving OER activity, why?
3) Substitution of foreign elements
4) Tetrahedral and octahedral sites, which is more active for OER?

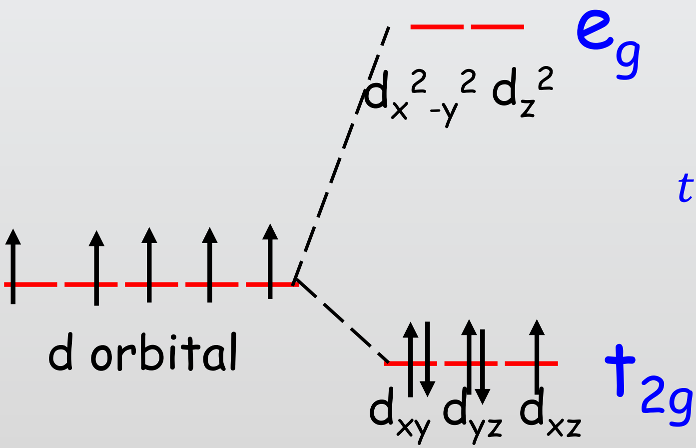
Fe3+: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$

Weak ligand: $[Fe(H_2O)_6]^{3+}$



$t_{2g}^4 e_g^2$

Strong ligand: $[Fe(CN)_6]^{3-}$



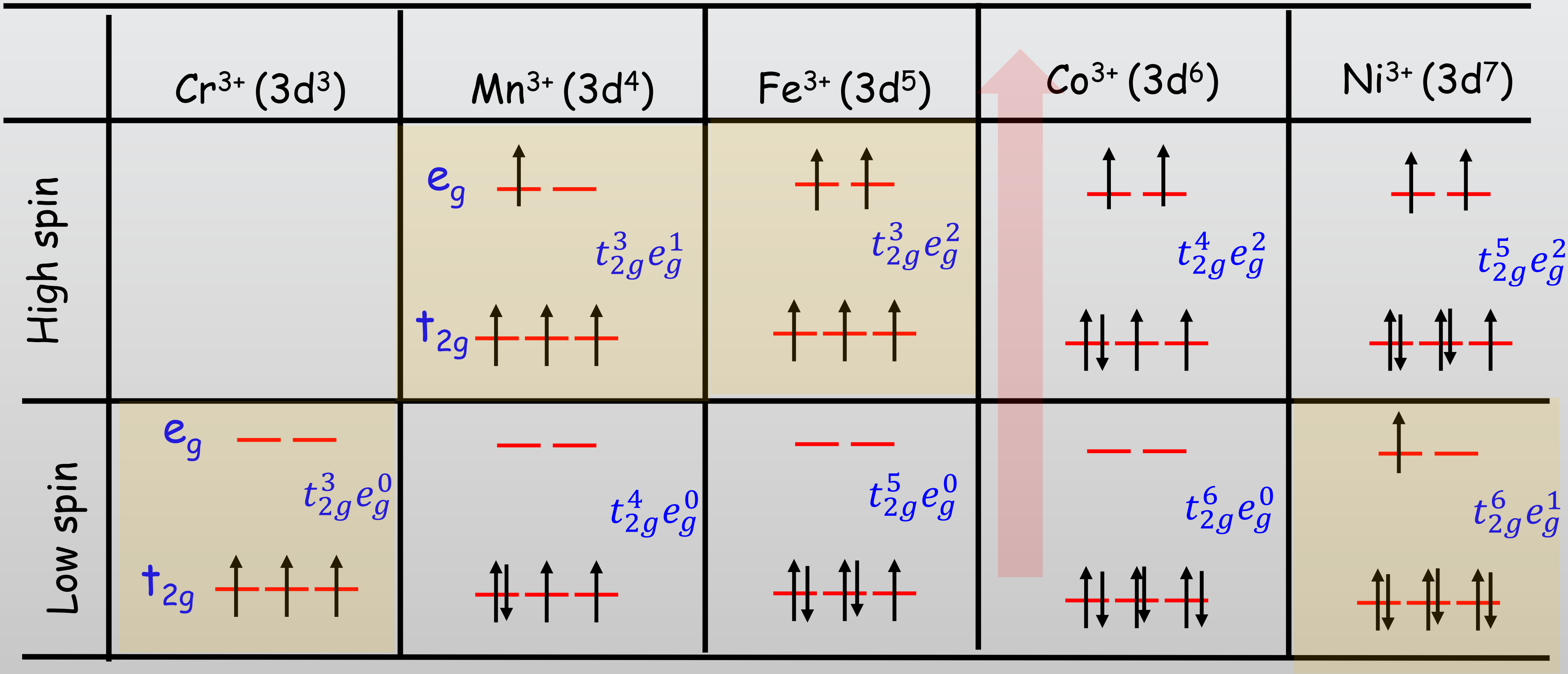
$t_{2g}^6 e_g^0$

Δo < paring energy
(high spin complex → maximum number of unpaired electrons)

Δo > paring energy
(low spin complex → minimum number of unpaired electrons)

e_g orbital occupancy/spin state of M-O oxides

- high spin state → lower the adsorption energy → better OER activity



Doping/strain engineering etc

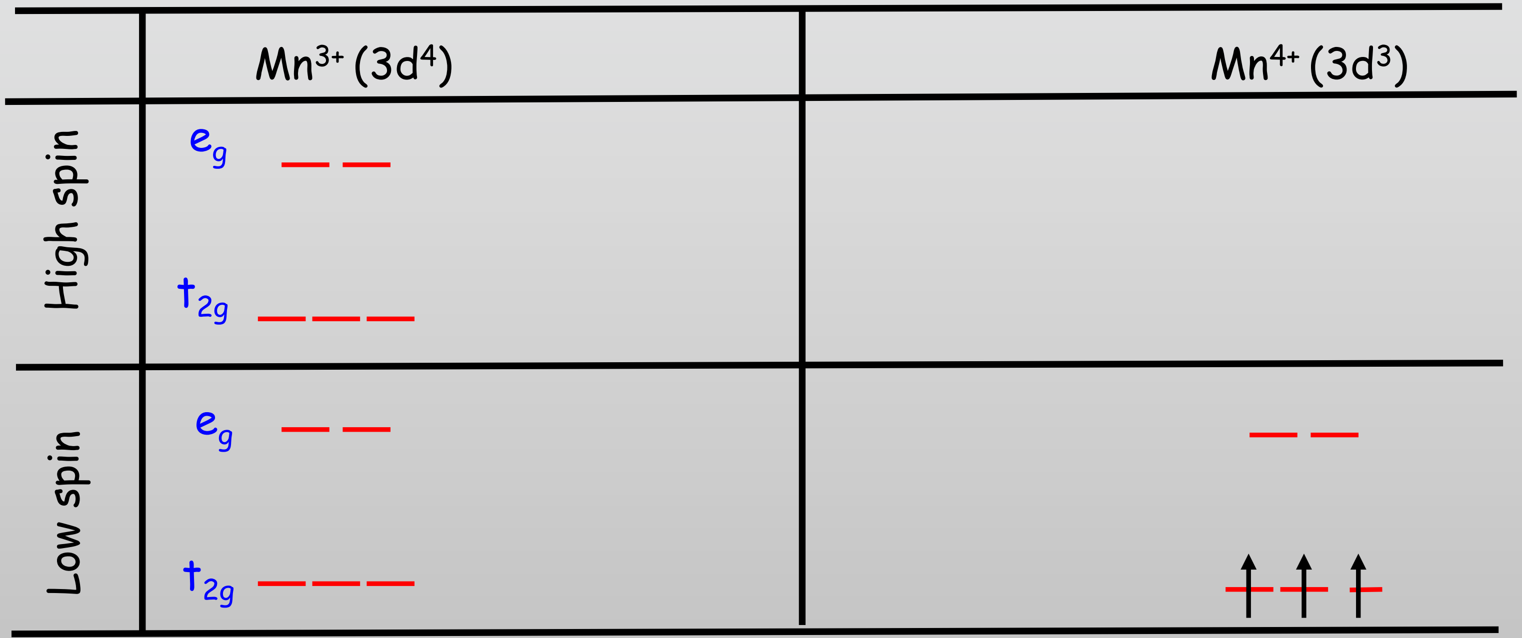
	Cr^{3+} ($3d^3$)	Mn^{3+} ($3d^4$)	Fe^{3+} ($3d^5$)	Co^{3+} ($3d^6$)	Ni^{3+} ($3d^7$)
High spin		$t_{2g}^3e_g^1$	$t_{2g}^3e_g^2$	$t_{2g}^4e_g^2$	$t_{2g}^5e_g^2$
Low spin	$t_{2g}^3e_g^0$	$t_{2g}^4e_g^0$	$t_{2g}^5e_g^0$	$t_{2g}^6e_g^0$	$t_{2g}^6e_g^1$

e_g orbital occupancy

- Substitution with cations with different valences or electronegativities or the creation of oxygen vacancies can effectively tailor the 3d electron occupancy and oxidation state of octahedral metal centers
- E.g., $CaMnO_3$ → $CaMnO_{2.4}$ (removing lattice oxygen) what would change?? What is d coordination of Mn?

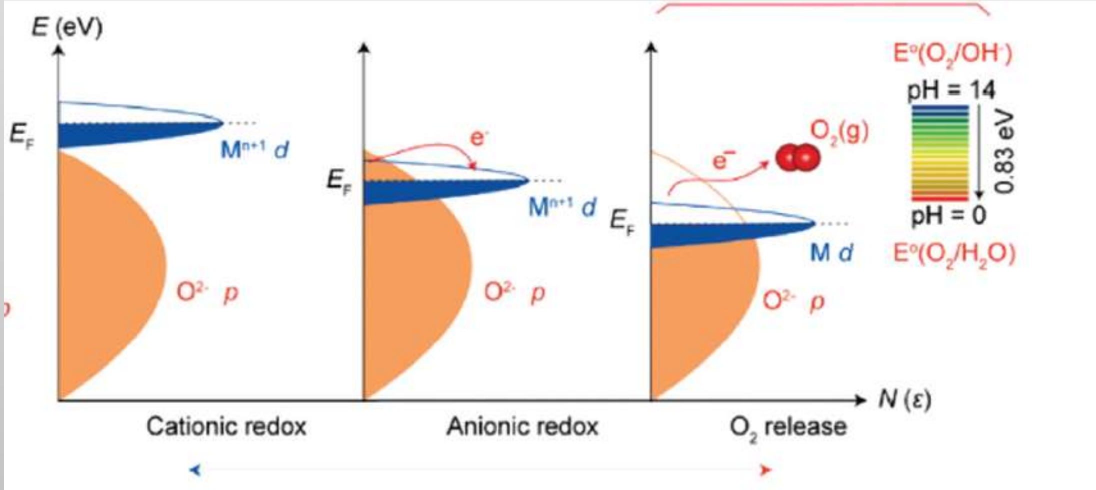
→ changing oxidation state and spin state of Mn from Mn^{4+} ($3d^3$) to high-spin-state Mn^{3+} ($3d^4$)

→ the e_g electron of 1 would decrease adsorption strength for intermediates better OER activity

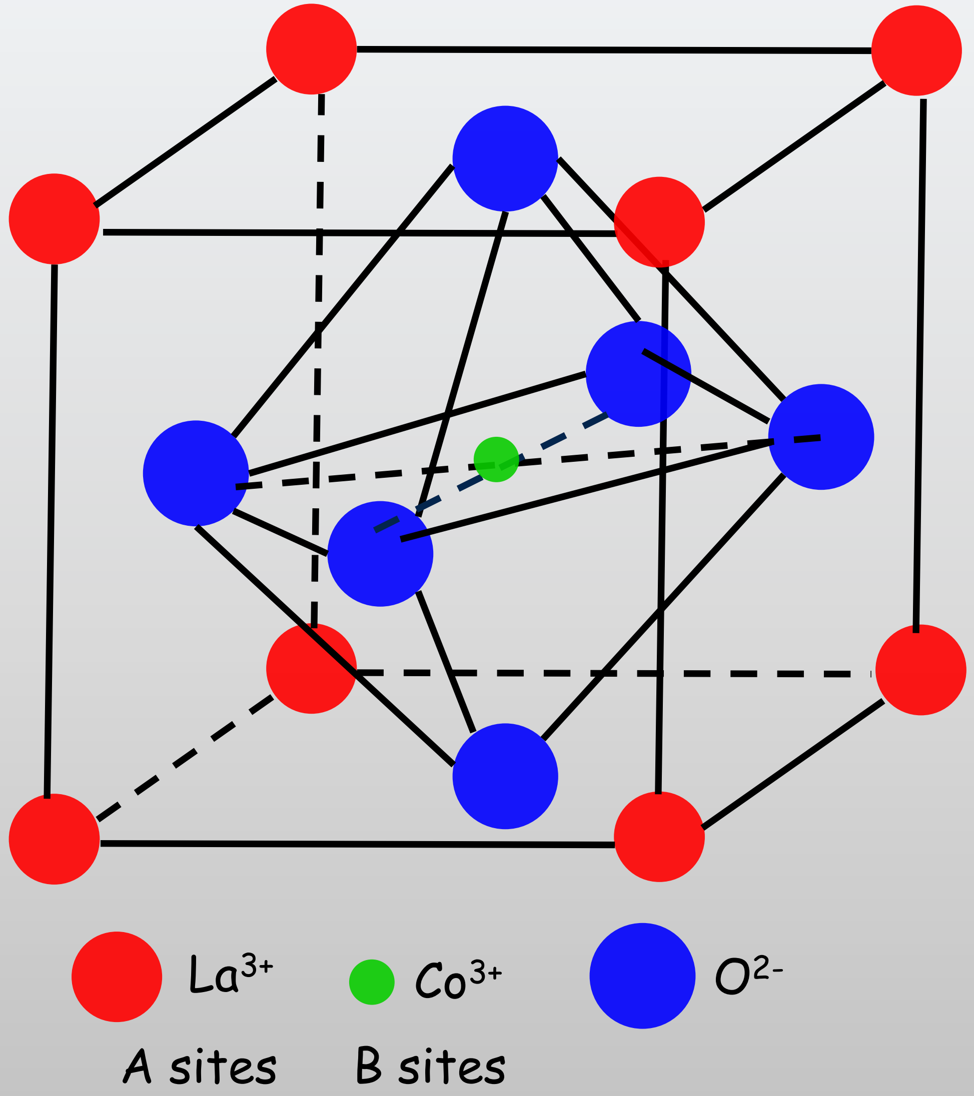


Metal-oxygen covalency

- e_g orbital occupancy of a metal cation is based on the crystal field theory
- Oxides have both ionic and covalent nature of bonding → metal-oxygen covalency descriptor to consider the sharing electrons along the metal-oxygen bond
- Increasing the electronegativity of transition metal typically moves the metal d state close to O 2p state → decreasing the binding dissociation bonds of M-O → improving OER activity



Substitution of foreign elements in perovskites

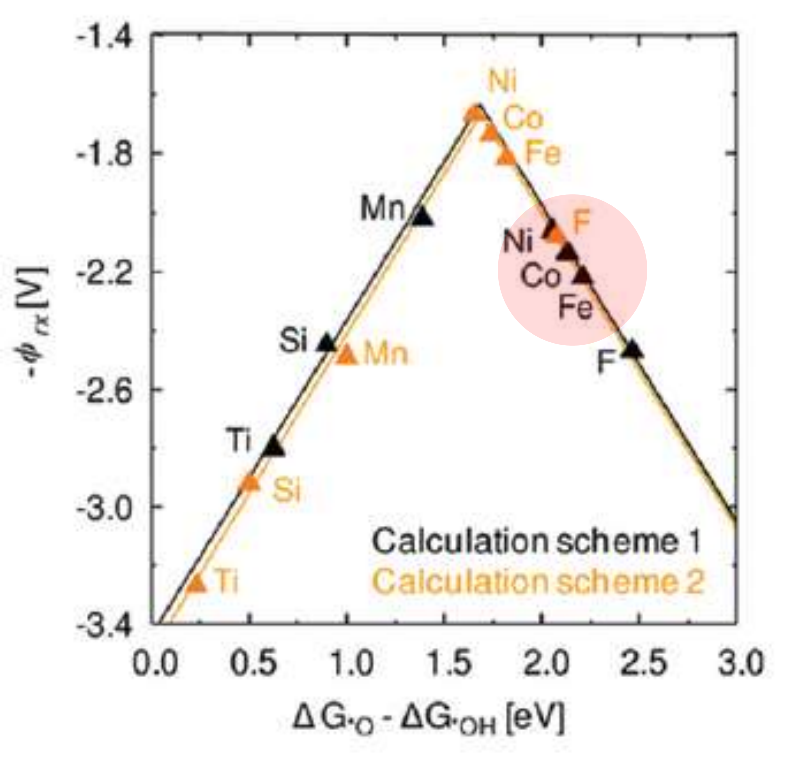


Replace La3+ with Ca2+,
what would change?

→ Oxygen vacancy
→ Electron holes by moving one electron away from Co

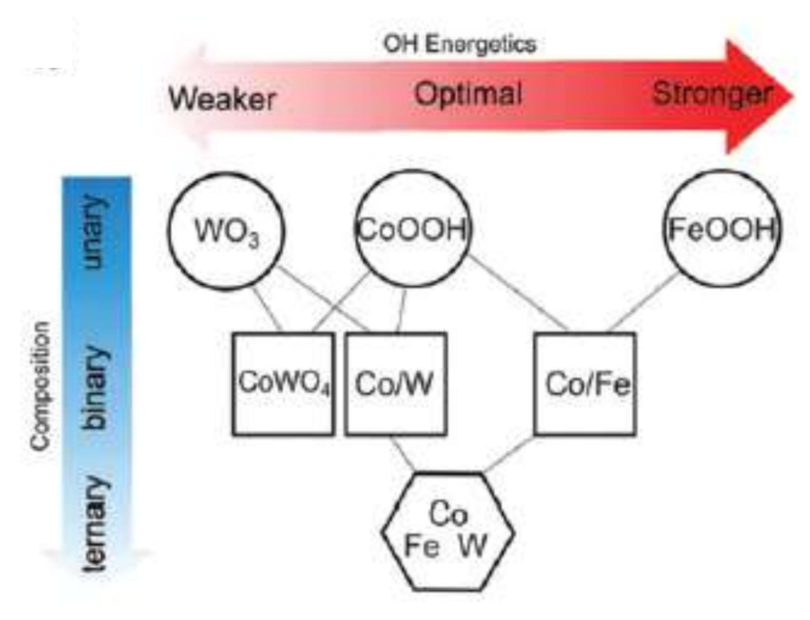
Substitution of foreign elements in spinels

Reaction potential versus binding energy difference of $\Delta G_{O*} - \Delta G_{HO*}$



By replacing Fe with Co or Ni leads to a slightly lower oxygen binding energies

Liao et al. JACS, 2012, 134,13296-13309



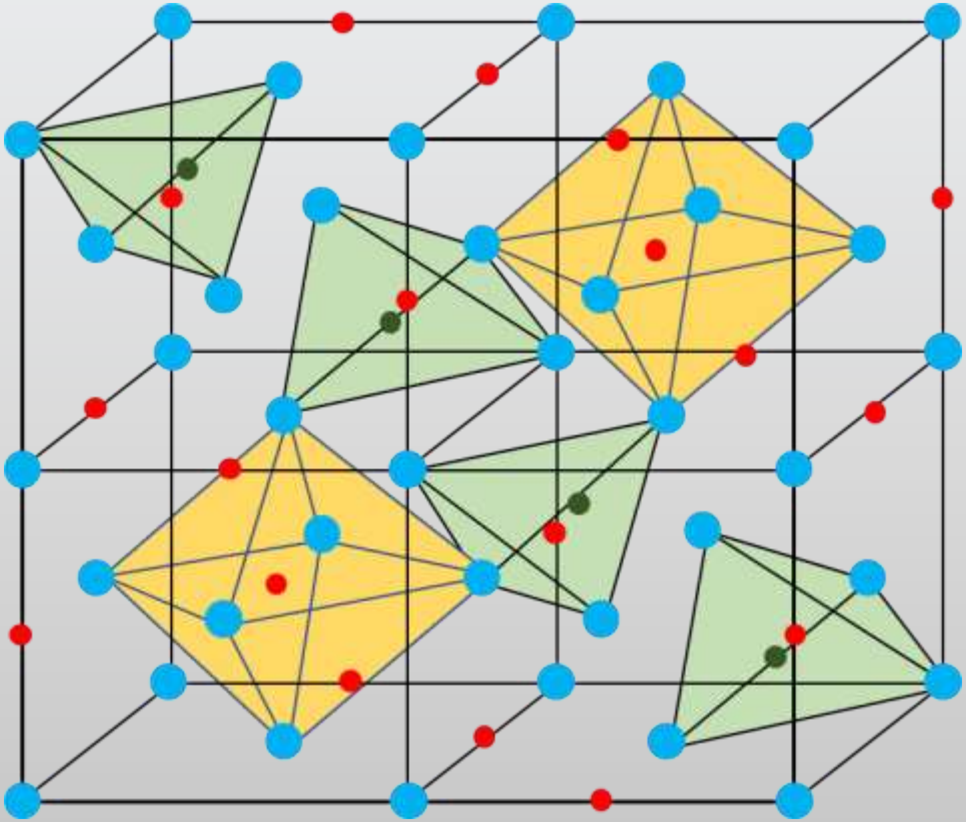
ternary oxyhydroxides with the optimized binding energy

Zhang et al. Science, 2016, 352, 333-337

Tetrahedral or octahedral sites?

A cations in 2 tetrahedral sites and B cations 1,5 octahedral sites

A cations in 0 tetrahedral sites and B cations 2,5 octahedral sites



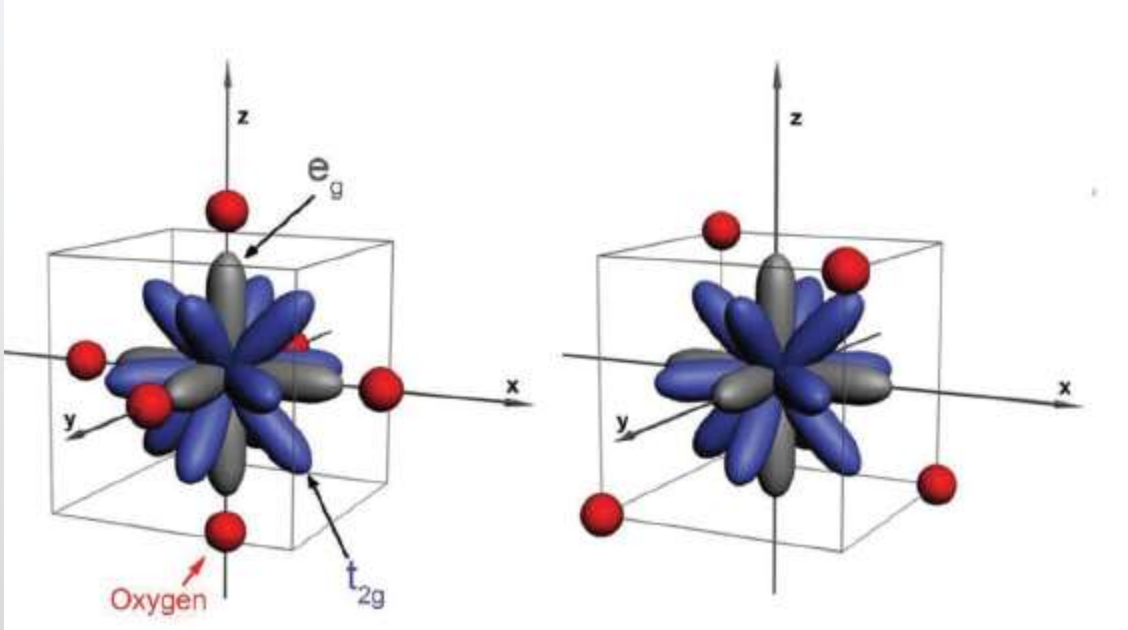
1/8 of the tetrahedral sites of ½ octahedral sites

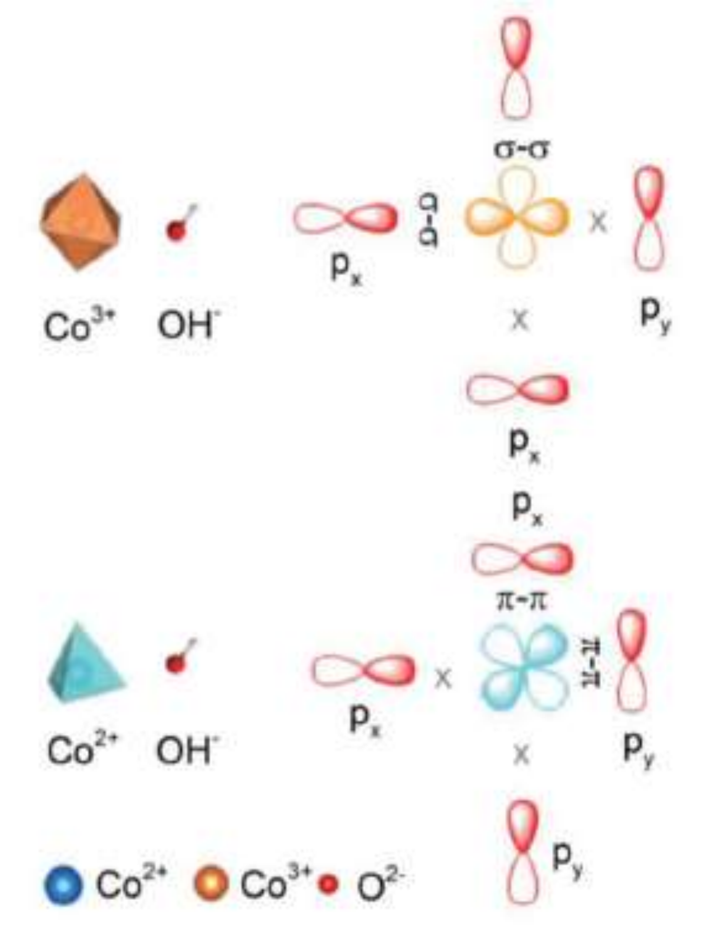
O^{2-}

B^{3+}

A^{2+}

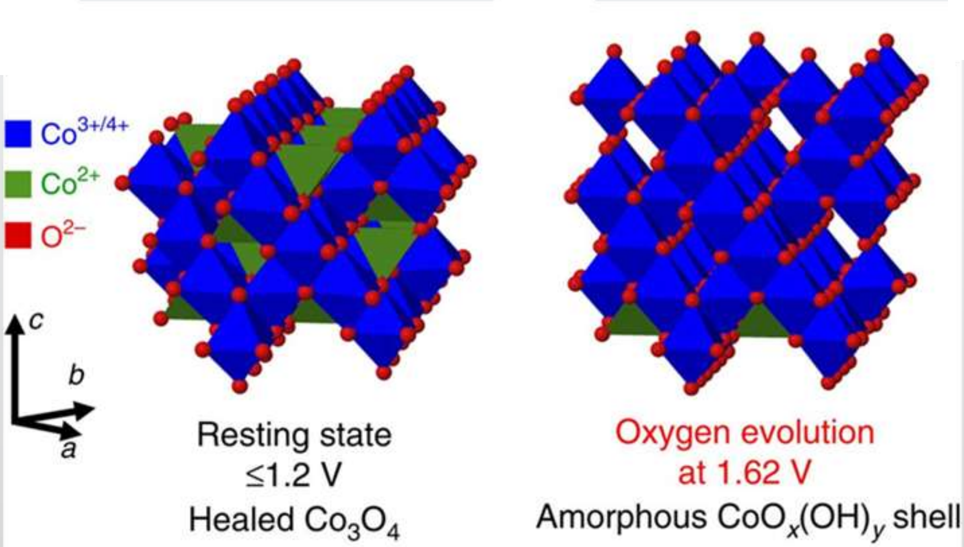
Tetrahedral or octahedral sites

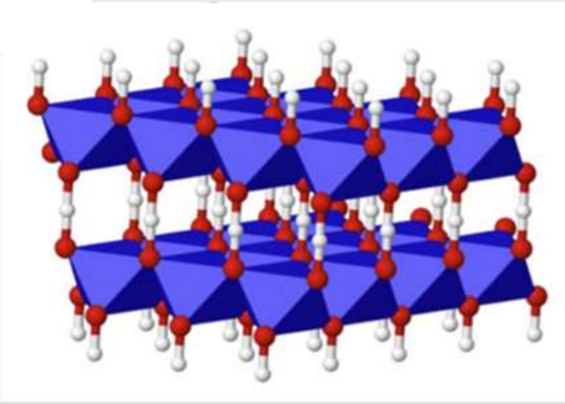




Interaction between the octahedral TM and O is more effective than the tetrahedral TM-O interaction.

Active intermediate species





CoOOH

Co2+ at Tetrahedral sites → active CoOx(OH)y species → OER activity

Reference books

- Fundamental of Ceramics

- Introduction to Ceramics