Legame chimico

LEGAME IONICO

KCl $\quad K(s) + \frac{1}{2}\, Cl_2\,(g) \rightarrow KCl\,(s)$ $\quad$ Tavola Periodica

Lewis: $\quad K\cdot + :\ddot{\underset{\ddot{}}{Cl}}\cdot \rightarrow K^{\oplus}\ :\ddot{\underset{\ddot{}}{Cl}}:^{\ominus}$

1. Formazione degli atomi isolati (cioè gassosi)
2. Formazione degli ioni gassosi

$K\,(g) \rightarrow K^+ + e^-$ $\quad \Delta H = EI = +418$ kJ/mol $\quad$ EI

$Cl\,(g) + e^- \rightarrow Cl^-$ $\quad \Delta H = -AE = -349$ kJ/mol $\quad$ AE

$K\,(g) + Cl\,(g) \rightarrow K^+ + Cl^-$ $\quad \Delta H = +69$ kJ/mol

3. En. potenziale fra gli ioni

$$E_{pot} = 1.39 \cdot 10^3 \frac{Z_{K^+}\, Z_{Cl^-}}{r} \text{ kJ/mol}$$

$= -443$ kJ/mol $\quad$ se r = 3.14 Å (sper)

Ciclo di Born-Haber

Risultato: $\Delta H°_{reaz} = -163$ kJ/mol (calcolo)

sperimentale $\Delta H°_{reaz} = -437$ kJ/mol.

$K(s) + \frac{1}{2} Cl_2(g) \rightarrow KCl(s)$

Spiegazione: reticolo ionico NaCl CaF_2

$\Rightarrow$ interazioni elettrostatiche ottimizzate

Proprietà di solidi ionici $E_{pot} = 1.39 \cdot 10^3 \frac{Z_+ Z_-}{r}$ kJ/mol

- Ordine cristallino 3D solidi ionici
- Elevate proprietà meccaniche: alto modulo
- Relativa fragilità
- Alta T_{fus} . Cfr. NaCl $T_{fus} = 801$ °C ; MgO $T_{fus} = 2800$°C
  Struttura NaCl Raggi ionici
- Conducibilità elettrica solo nel fuso e in sol. acquosa.

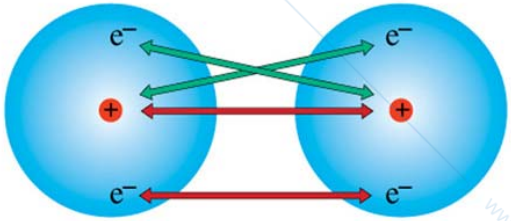
LEGAME COVALENTE

Lewis (1916) :

legame formato da coppie di elettroni condivise fra atomi

Tavola periodica

H· ·H → H–H Ciascun atomo completa il livello (qui $1s^2$)



repulsione

attrazione

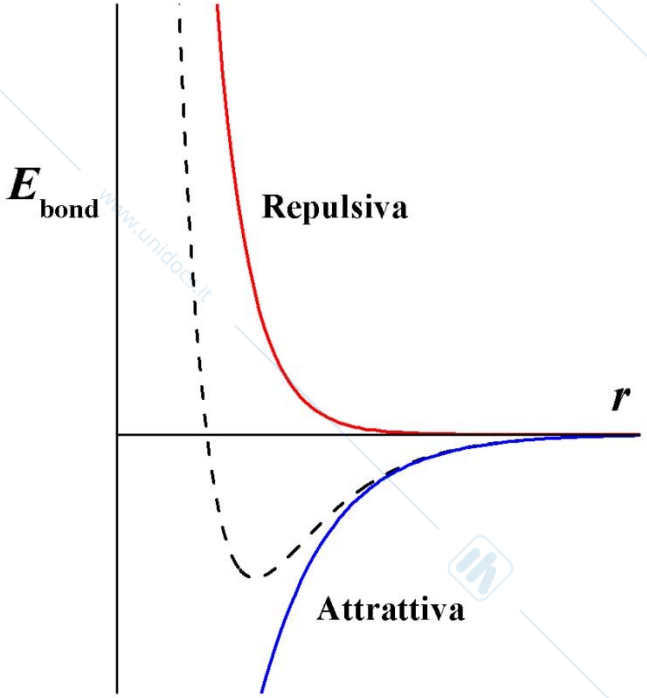


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Tavola Periodica

$H - \overline{\underline{Cl}}|$

I trattini indicano:

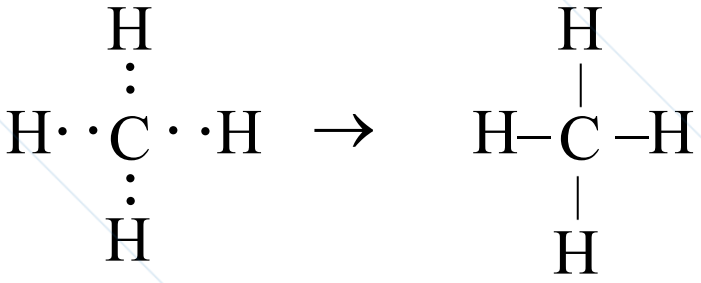
- coppia di elettroni messa in comune
- coppia di elettroni non condivisa = **doppietto**

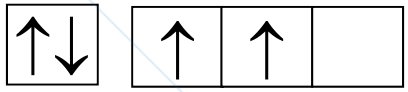
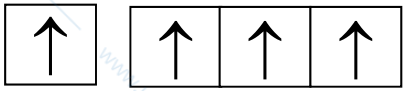
Legami multipli Tavola periodica

- Legame semplice: condivisione 1 coppia e^-
- Legame doppio: condivisione 2 coppie e^-
- Legame triplo: condivisione 3 coppie e^-

Formare il massimo numero di legami per raggiungere lo stato di minimo di energia $\Rightarrow$ tendenza a completare gli orbitali

CH_4 Tavola periodica



Ma … C  → C* 

⇒ 2 legami ⇒ 4 legami

Maggior numero di legami ⇒ minor energia potenziale

⇒ compensa la spesa dell'eccitazione.

STRUTTURE DI LEWIS

Tavola periodica

- atomo centrale
- connessione degli atomi con e^- di valenza per formare il n. max di legami

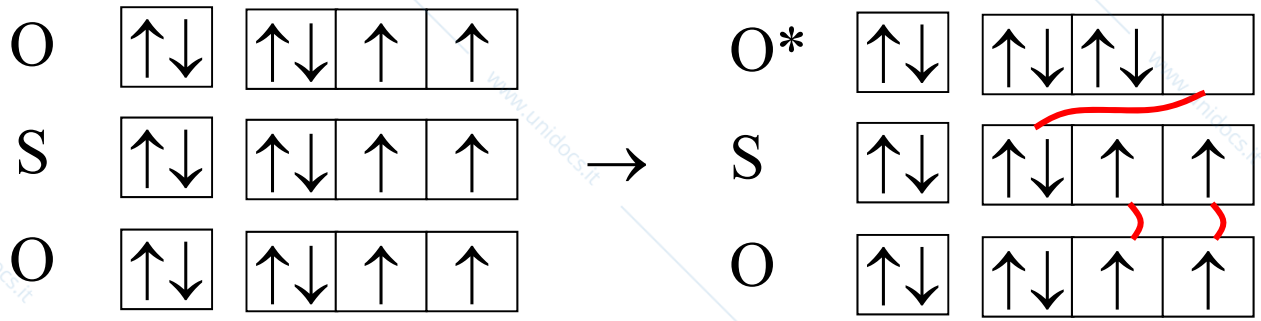
$N + H$ $\quad |\dot{\underset{\cdot}{N}}\cdot \quad H\cdot \quad NH_3 \quad$ H–N(–H)–H

$C + O \quad \cdot\dot{\underset{\cdot}{C}}\cdot \quad |\underline{O}\cdot \quad CO_2 \quad |\underline{O}=C=\underline{O}|$

- Possibilità di legami dativi per formare n. max di legami

$SO_2 \quad S + O \quad |\underline{S}\cdot \quad |\underline{O}\cdot \quad |\underline{O}–\underline{S}–\underline{O}|$ **NO**

$|\underline{O}=S\rightarrow\underline{O}|$ **SI**

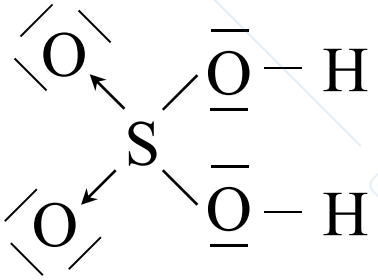


$$|\underline{O}=\overline{S}\rightarrow\underline{\overline{O}}|$$

Nota: SO_3

$$\begin{array}{c} |\overline{O}| \\ \uparrow \\ |\underline{O}=S\rightarrow\underline{\overline{O}}| \end{array}$$

In acqua: $SO_3 + H_2O \rightarrow H_2SO_4$



Energia di legame = en. necessaria per romperlo >0

$Cl_2\ (g) \rightarrow 2\ Cl\ (g)$ $\quad \Delta H = D(Cl\text{-}Cl) = 244$ kJ/mol

Valore medio: $CH_4 \rightarrow C + 4\ H$

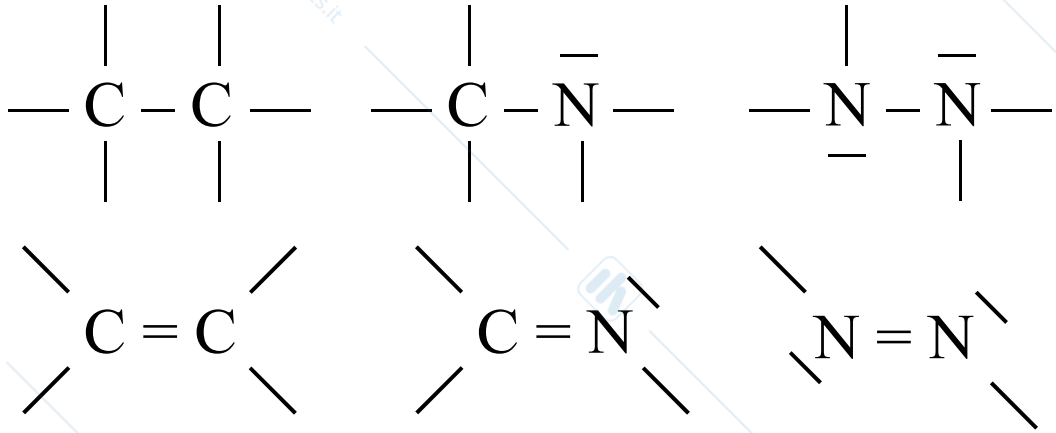
$\Delta H_{tot} = 1660$ kJ/mol $\Rightarrow$ D (C-H) = 415 kJ/mol

Legami multipli sono più forti, es: (in kJ/mol)

- D(C–C) = 348
- D(C=C) = 614
- D(C≡C) = 837

- D(C–N) = 305
- D(C=N) = 615
- D(C≡N) = 891

- D(N–N) = 163
- D(N=N) = 409
- D(N≡N) = 945



Entalpie medie di legame (kJ / mol)

C – H	413
N – H	388
O – H	463
C – C	348
C = C	614
C ≡ C	837
C – O	360
C = O	743
C – N	305
C = N	615
C ≡ N	891

N – N	163
N = N	409
N ≡ N	945
C – F	484
C – Cl	338
C – Br	276
C – I	238
Si – H	323
Si – O	368
Si – Cl	391

Tavola periodica

POLARITA' dei legami

- H-H , Cl-Cl legame covalente puro
- $K^{\oplus}$ $Cl^{\ominus}$ legame ionico
- $^{\delta+}$H-Cl$^{\delta-}$ legame covalente polare Z_{eff}

Momento dipolare μ $^{\delta+}$H-Cl$^{\delta-}$

Elettronegatività

tendenza con cui un atomo attira a sé gli e^- di legame

Scala di Pauling (definita dai dati sperimentali)

L'energia di legame fra due atomi diversi A-B è maggiore della media fra le energie di legame tra gli atomi uguali A-A e B-B.

Motivo: contributo elettrostatico che misura la differenza di elettronegatività EN EI, AE En. legame

Scala di elettronegatività EN

- **Pauling**: se $\Delta = D_{A-B} - \sqrt{D_{A-A} \cdot D_{B-B}}$

  allora $\chi_A - \chi_B \propto \Delta^{1/2}$ con D_{A-B} = en. di legame

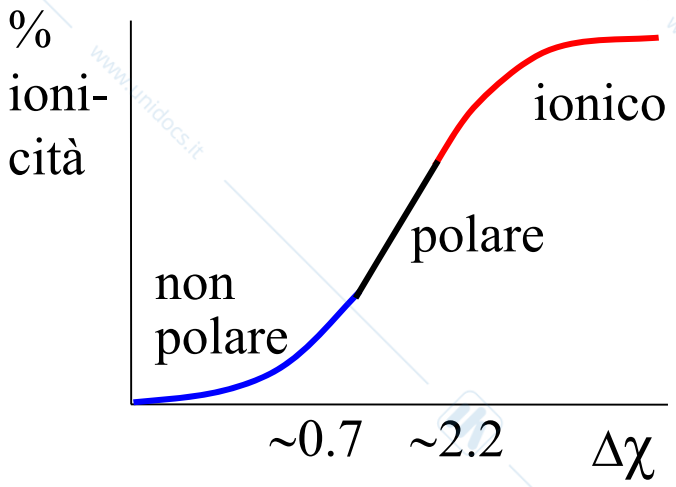
  Richiede la scelta di un valore arbitrario

- **Mulliken**: $\chi_A \propto \frac{1}{2} (EI + AE)$

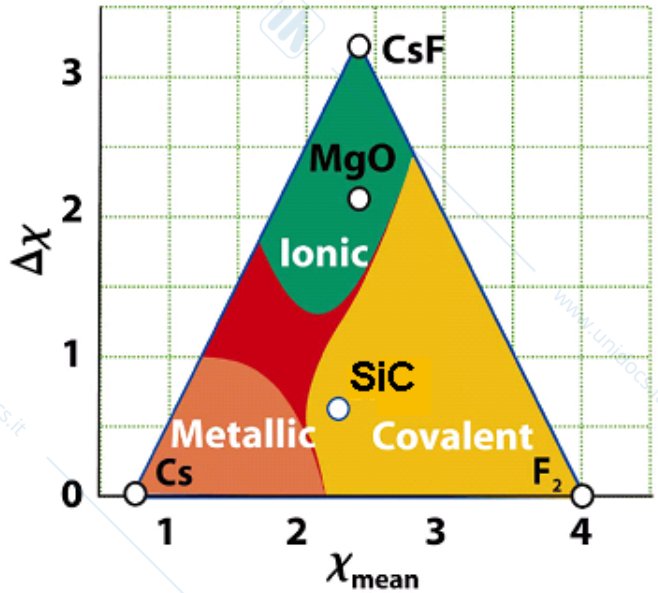
- **Allred – Rochow**: $\chi_A = a \frac{Z_{eff}}{r_{cov}^2} + b$

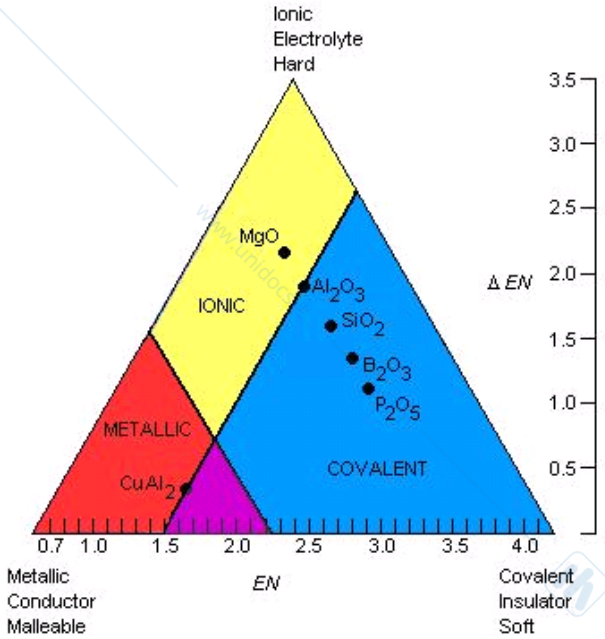
NB: i valori ottenuti sono valori medi!

Diff. di elettronegatività $\Delta\chi$ molto alta
$\Rightarrow$ legame ionico EN



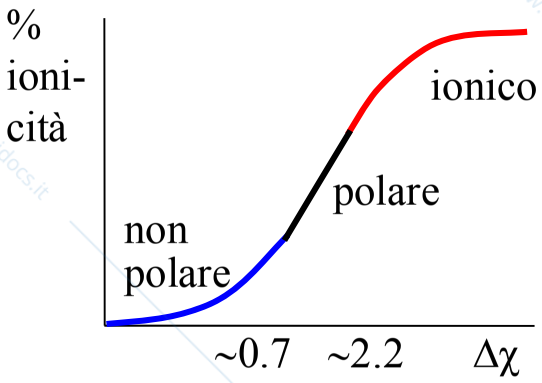
Triangolo di Ketelaar
(o di van Arkel – Ketelaar)

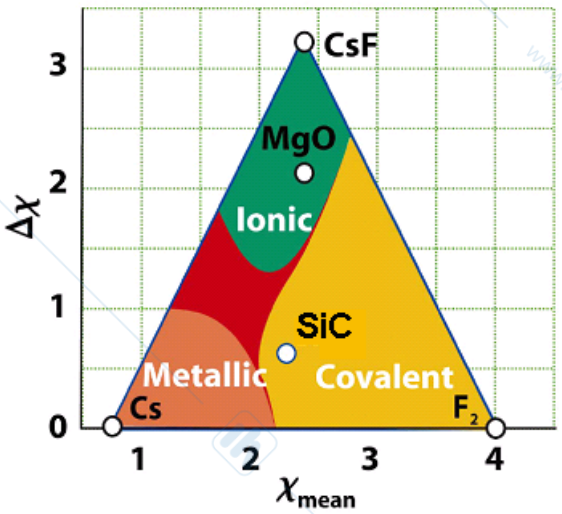


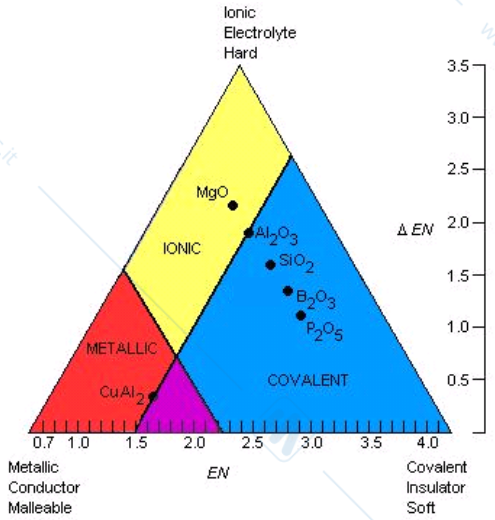


$\Delta\chi$ = diff. di elettronegatività
χ_{mean} = elettronegatività media

EN







Ossidi dei metalli CaO $\Delta\chi = 3.4 - 1.0 = 2.4$, $\chi_{mean} = 2.2$

$Ca^{2+}\ O^{2-} + H_2O \rightarrow Ca(OH)_2 \rightarrow Ca^{2+} + 2\ OH^-$

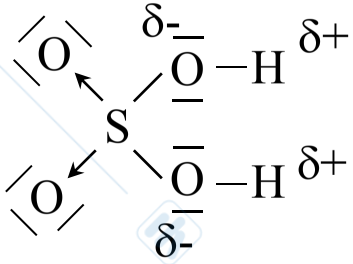
Anche: NaH $\Delta\chi = 2.2 - 0.9 = 1.3$, $\chi_{mean} = 1.55$ $Na^+\ H^-$

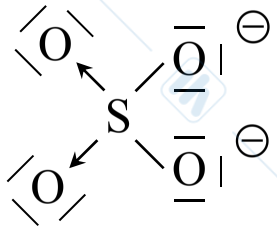
Ossidi di non-metalli

SO_3 $\Delta\chi = 3.4 - 2.6 = 0.8$

$\chi_{mean} = 3$

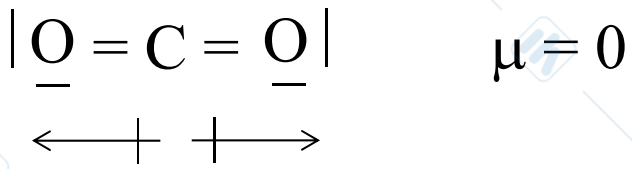
$SO_3 + H_2O \rightarrow H_2SO_4$



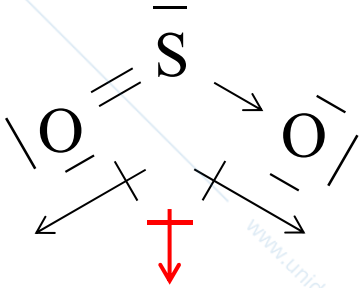


POLARITA' delle molecole

$^{\delta+}H\text{-}Cl^{\delta-}$



$\mu = 0$



$\mu \neq 0$

Descrizione della geometria molecolare

VSEPR Valence Shell Electron Pairs Repulsion

Tavola periodica

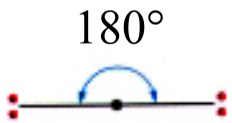
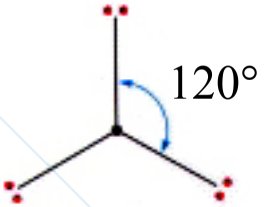
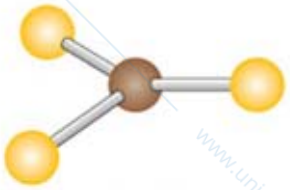
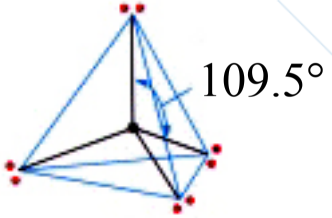
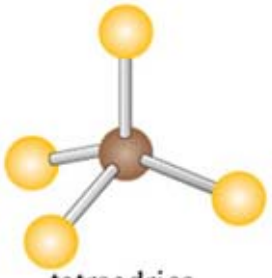
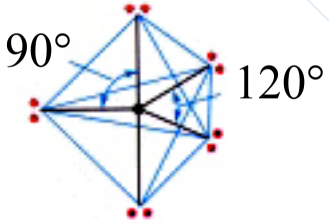
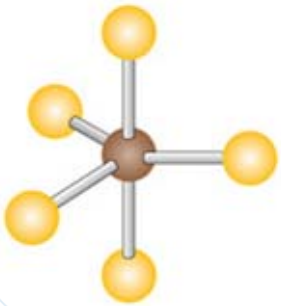
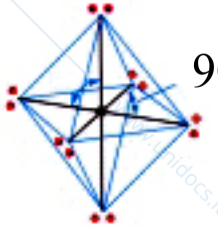
n. coppie	disposizione	geometria	esempio
2		 lineare	$BeCl_2$
3		 trigonale planare	BF_3
4		 tetraedrica	CH_4

Tavola periodica

n. coppie	disposizione	geometria	esempio
5		 trigonale bipiramidale	PCl_5
6		 ottaedrica	SF_6

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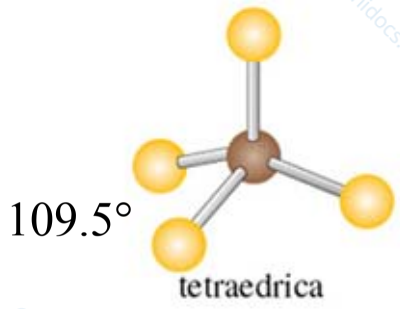
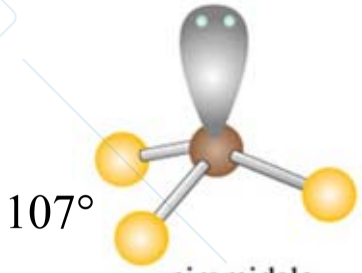
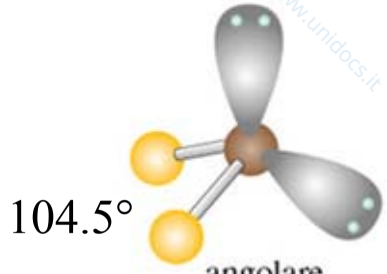
CEA

n. legami	n. doppietti	geometria	esempio
4	0	 tetraedrica	CH_4
3	1	 piramidale	NH_3
2	2	 angolare	H_2O

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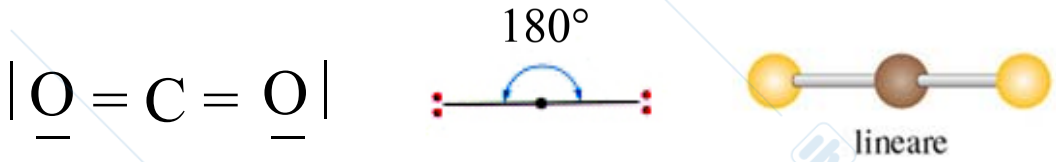
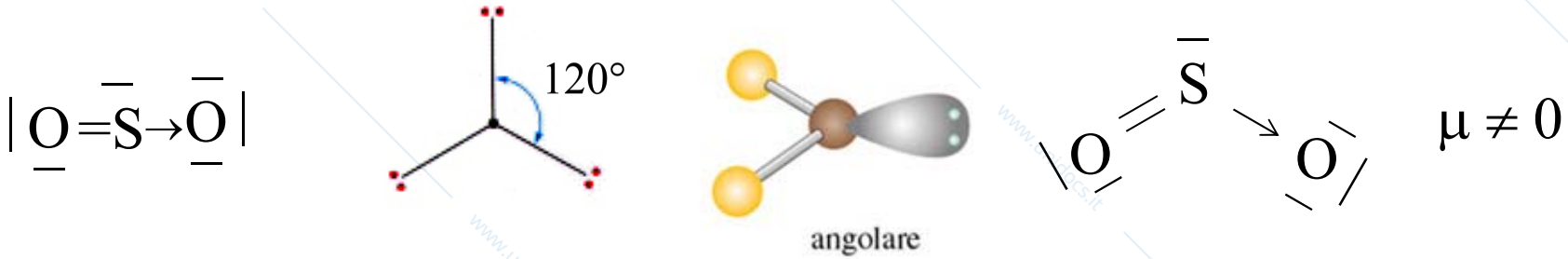
Legami multipli

EN



$\mu = 0$



$\mu \neq 0$

Legame chimico e meccanica quantistica

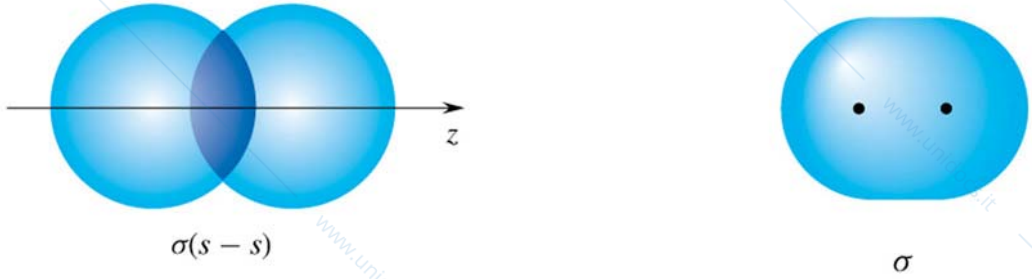
Orbitali Molecolari

Orbitale molecolare = sovrapposizione di orbitali atomici

$H\cdot \quad \cdot H \rightarrow H\text{–}H$ Sovrapposizione degli orbitali 1*s*

Formazione orbitale molecolare **σ**

doppiamente occupato: 2 e^- con spin ↑↓



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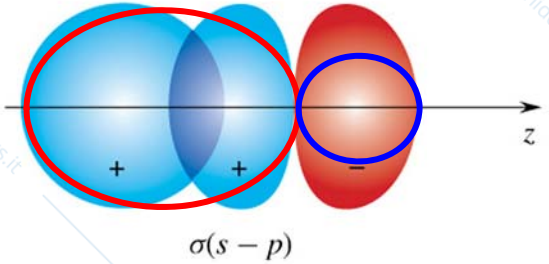
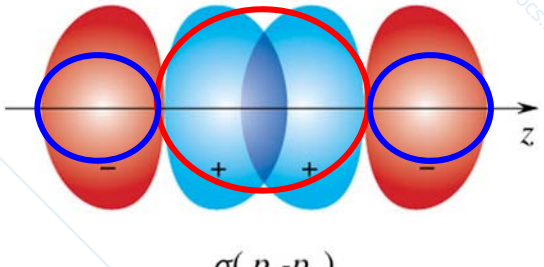
Aumento di densità elettronica fra i nuclei

Funzioni d'onda

Orbitali molecolari σ:



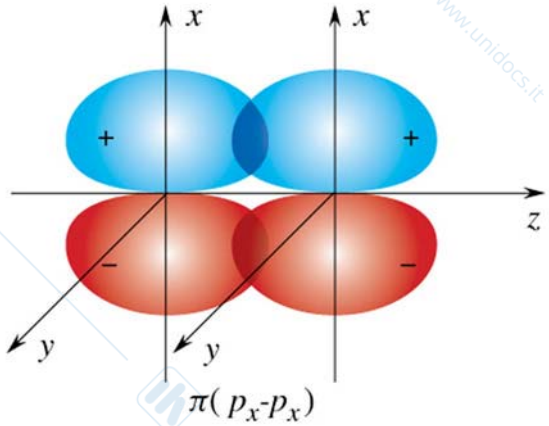
$\sigma(s-p)$



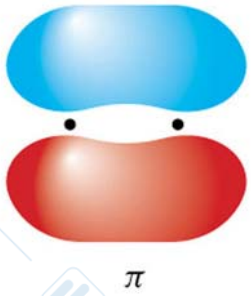
$\sigma(p_z\text{-}p_z)$

Simmetria cilindrica attorno all'asse internucleare

Orbitali molecolari π:



$\pi(p_x\text{-}p_x)$



π

Anti simmetria attorno all'asse internucleare

Diversa simmetria attorno all'asse internucleare

Legami doppi e tripli

Funzioni d'onda

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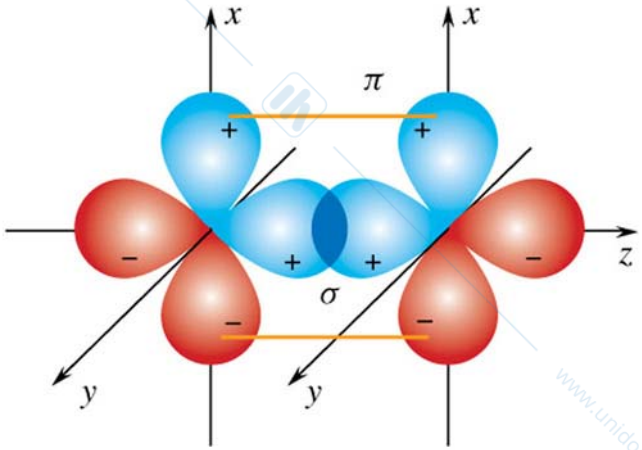

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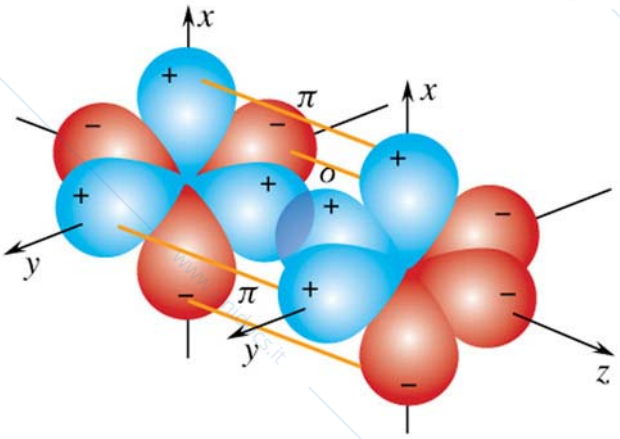

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I legami π hanno energia più alta dei σ (sono più deboli)
cfr orbitali atomici *p* e *s*

In generale:

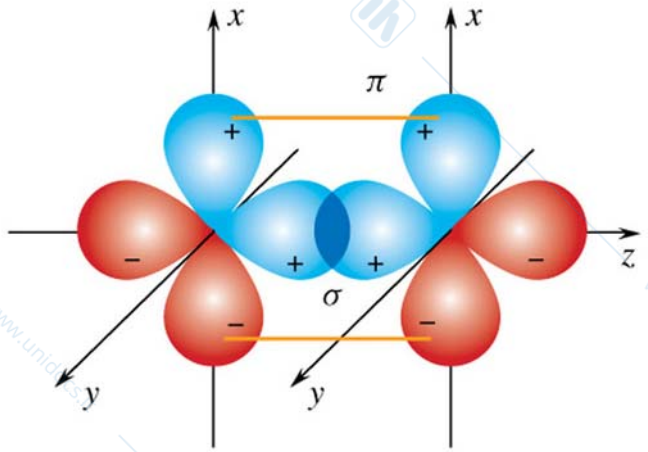
- Legame semplice: condivisione 1 coppia e^- 1 MO σ
- Legame doppio: condivisione 2 coppie e^- 1 MO σ + 1 MO π
- Legame triplo: condivisione 3 coppie e^- 1 MO σ + 2 MO π

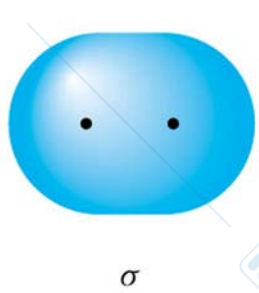
Esempi:

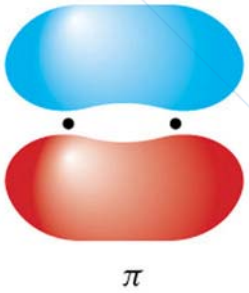
H_2, Cl_2, HCl legame singolo ⇒ 1 MO σ

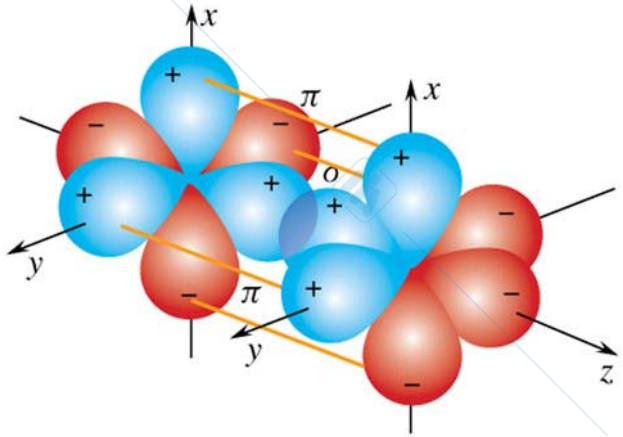
O_2 legame doppio O=O : 1 MO σ + 1 MO π

N_2 legame triplo N≡N : 1 MO σ + 2 MO π

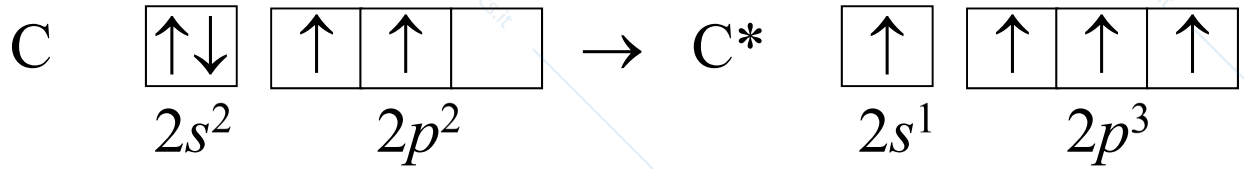








Ibridazione



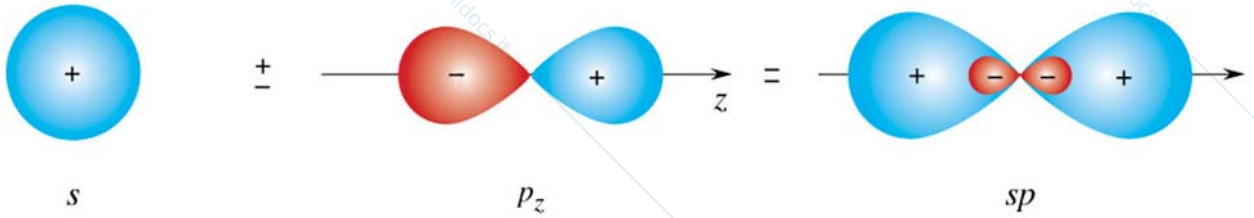
$\Rightarrow$ 2 legami 4 legami non equivalenti

Si possono ibridizzare (mescolare) l'orbitale *s*
e uno o più orbitali *p* $\Rightarrow$ orbitali atomici ibridi

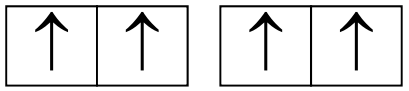
Hanno energia più alta, ma formano legami più forti
(migliore sovrapposizione)

Orbitali atomici ibridi (es.: C)

sp

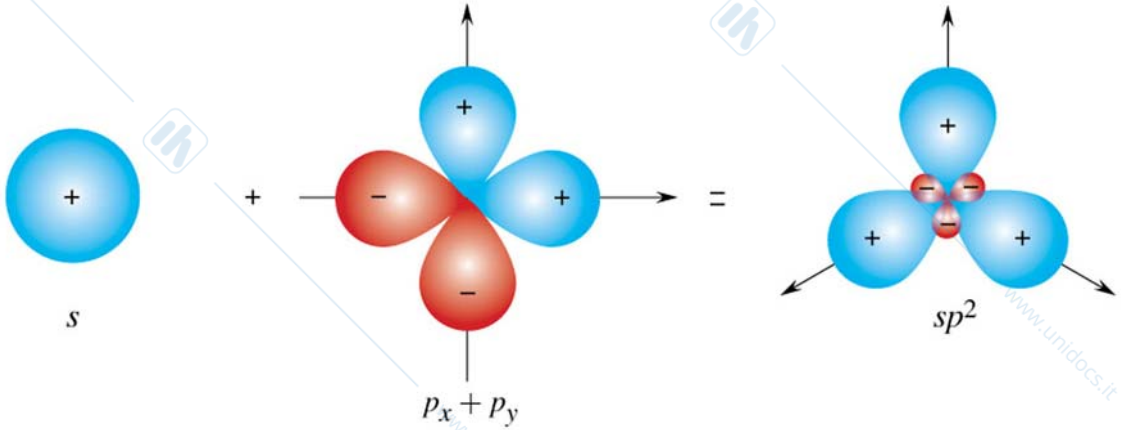


2 orbitali ibridi

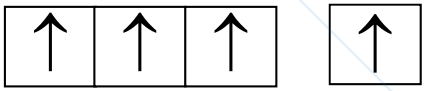


geom. lineare

sp²

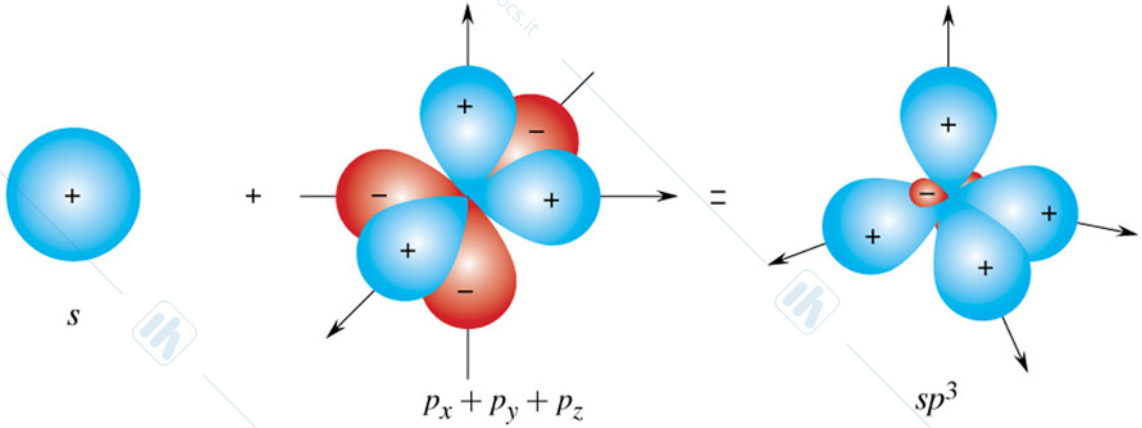


3 orbitali ibridi

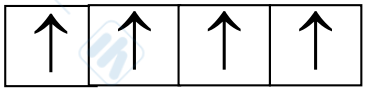


geom. trigonale planare

sp³



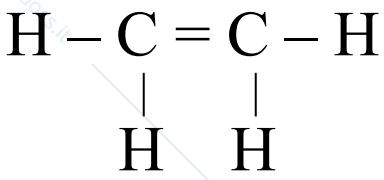
4 orbitali ibridi

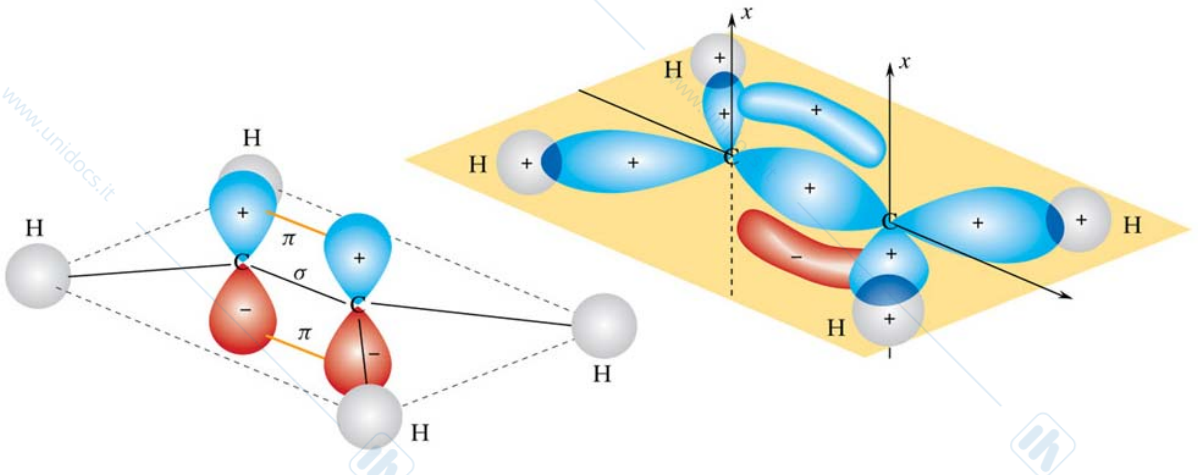


geom. tetraedrica

C_2H_4

sp²

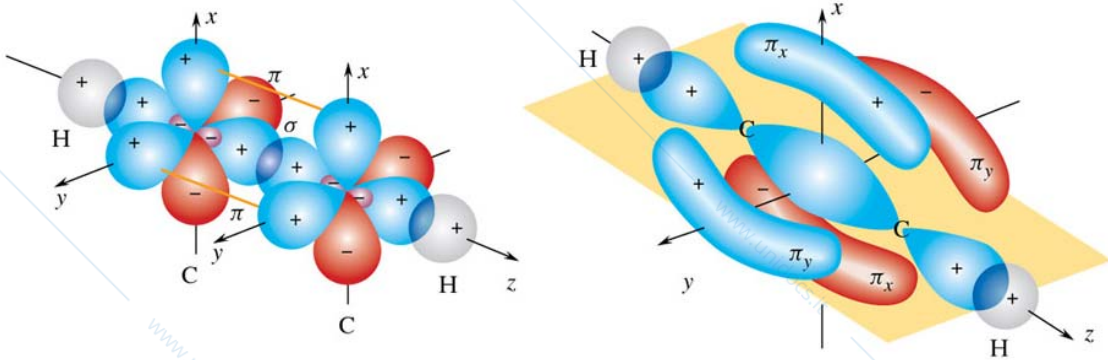




C_2H_2

sp

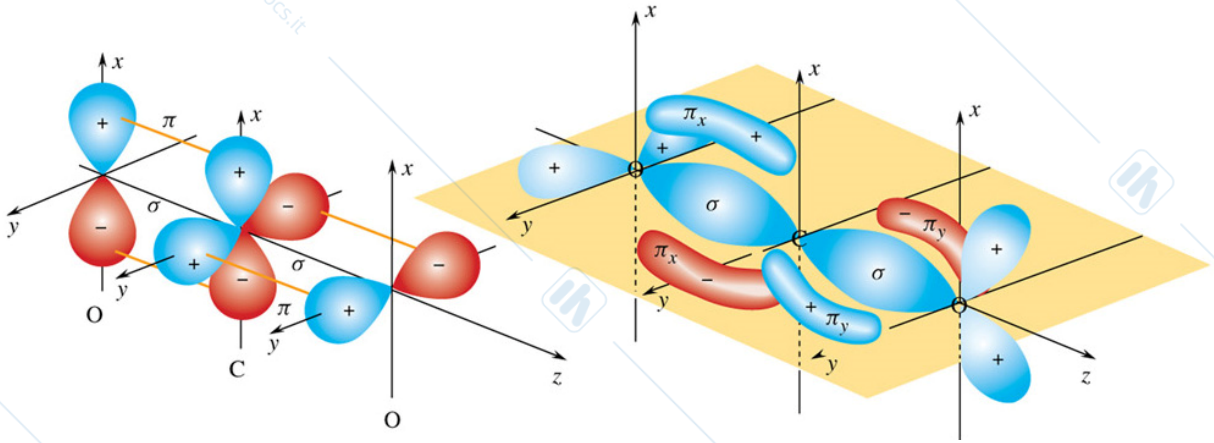
$H – C \equiv C – H$



CO_2

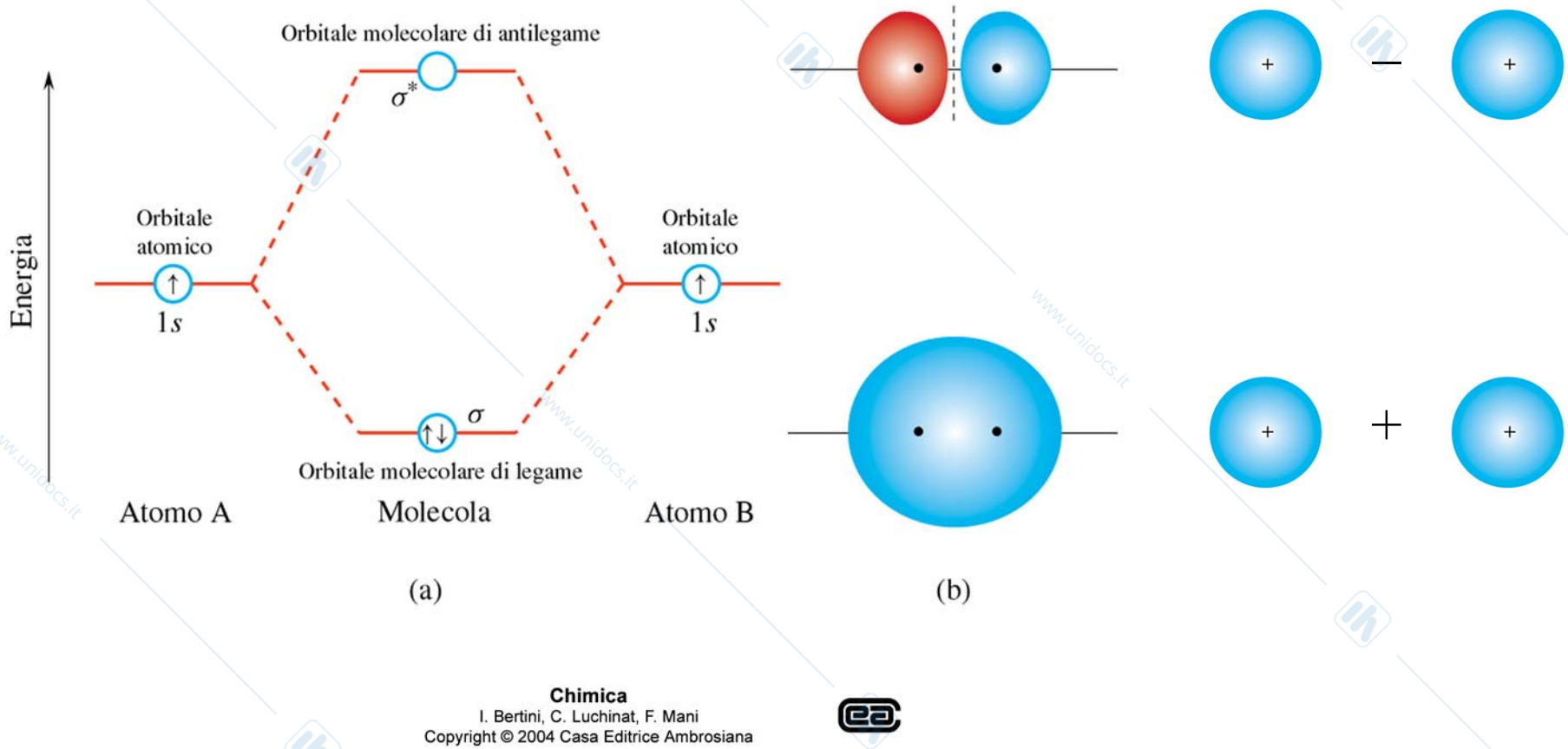
sp

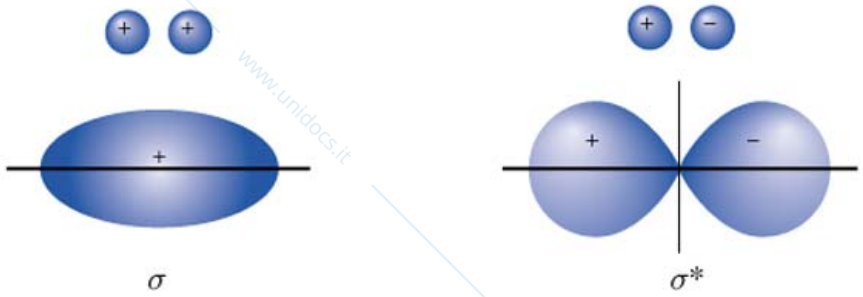
$|\underline{O} = C = \underline{O}|$



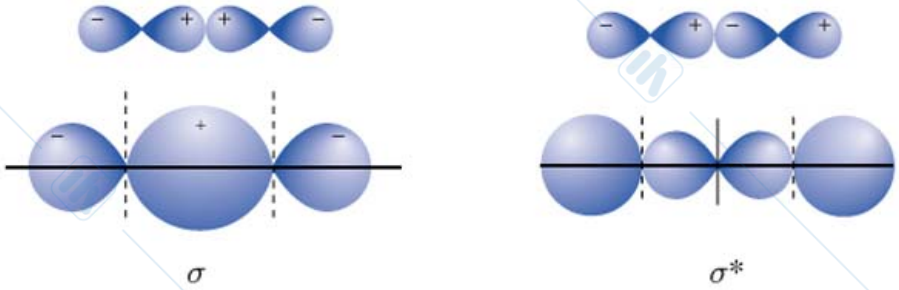
Orbitali antileganti e stati eccitati

Esistono orbitali vuoti nello stato fondamentale
che possono essere occupati negli stati eccitati



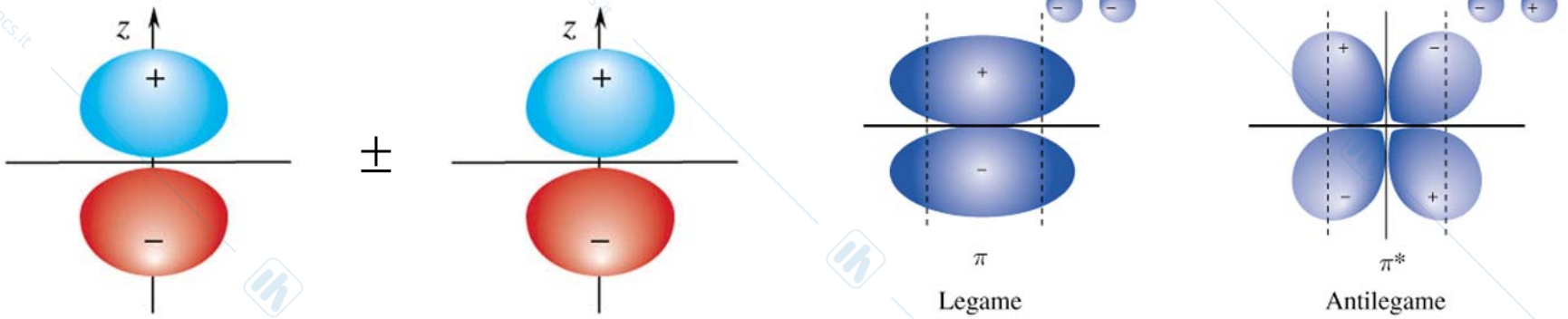


$\sigma(s-s)$



$\sigma(p_z-p_z)$

Analogo per π e π*

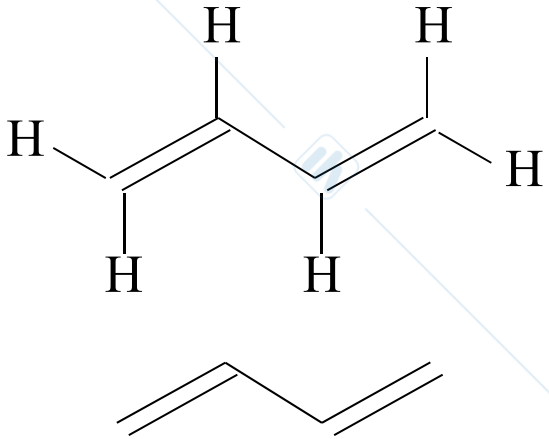


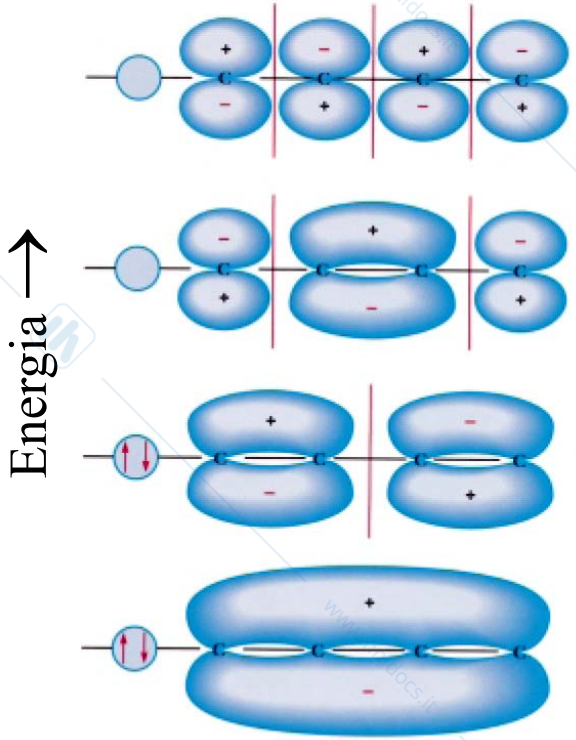
Orbitali delocalizzati per elettroni π

$CH_2 = CH - CH = CH_2$

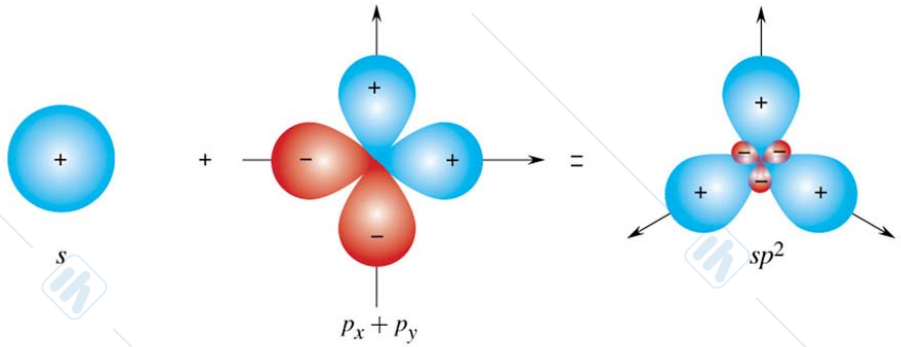
C_4H_6

butadiene



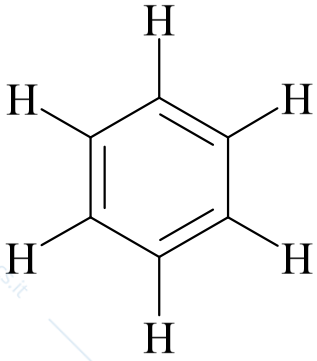


sp²

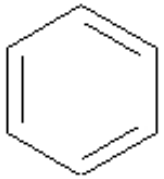


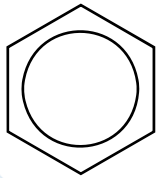
3 orbitali ibridi

geom. trigonale planare

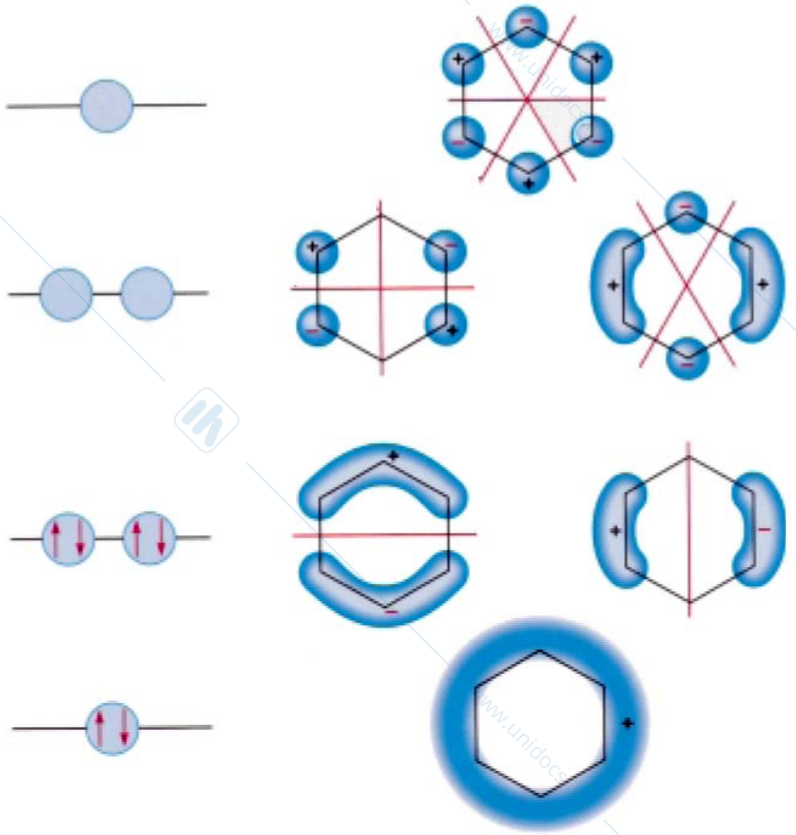


C_6H_6
benzene

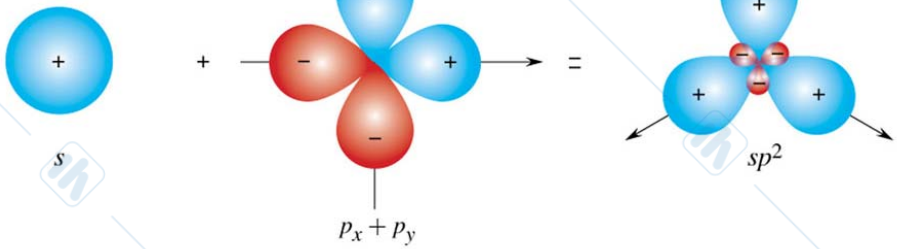




Energia →



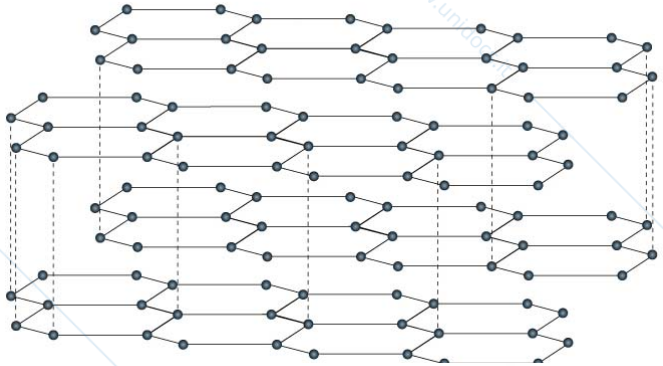
sp²



3 orbitali ibridi

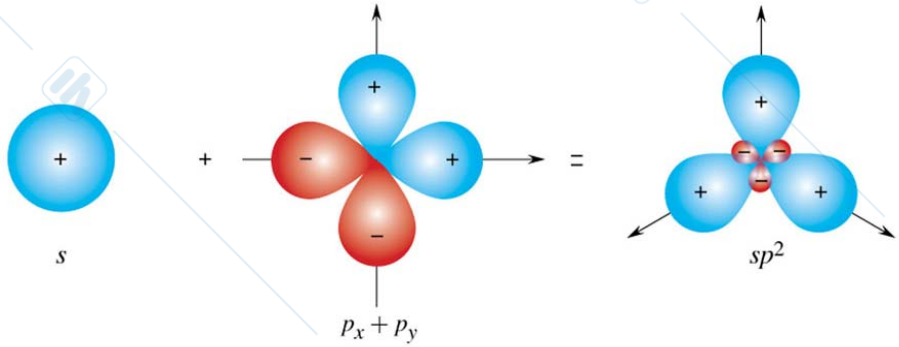
geom. trigonale
planare

Orbitali delocalizzati - elettroni mobili

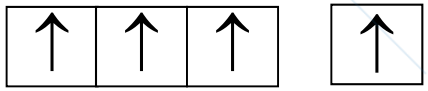


grafite

sp^2



3 orbitali ibridi



geom. trigonale planare

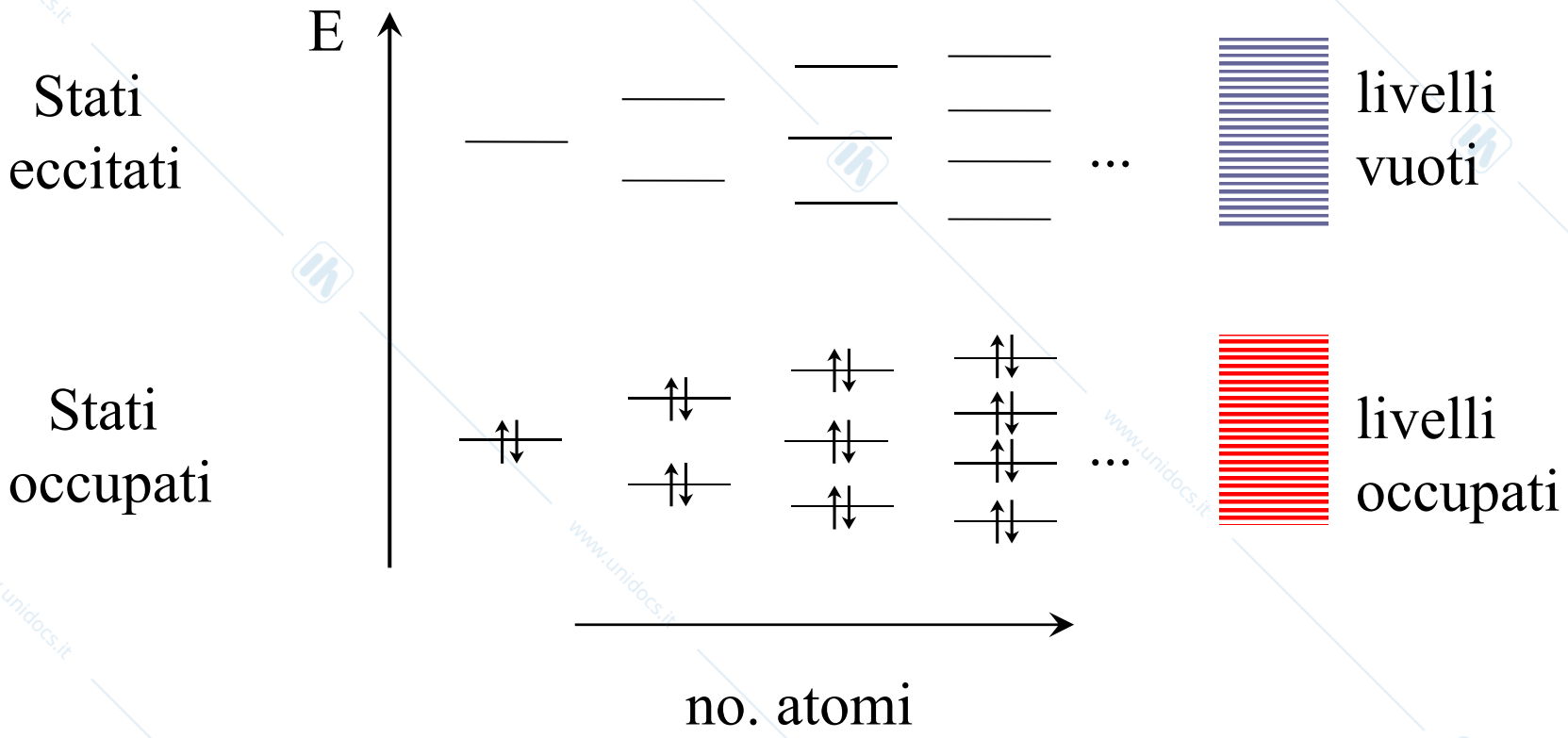
Metalli

Tavola periodica EI

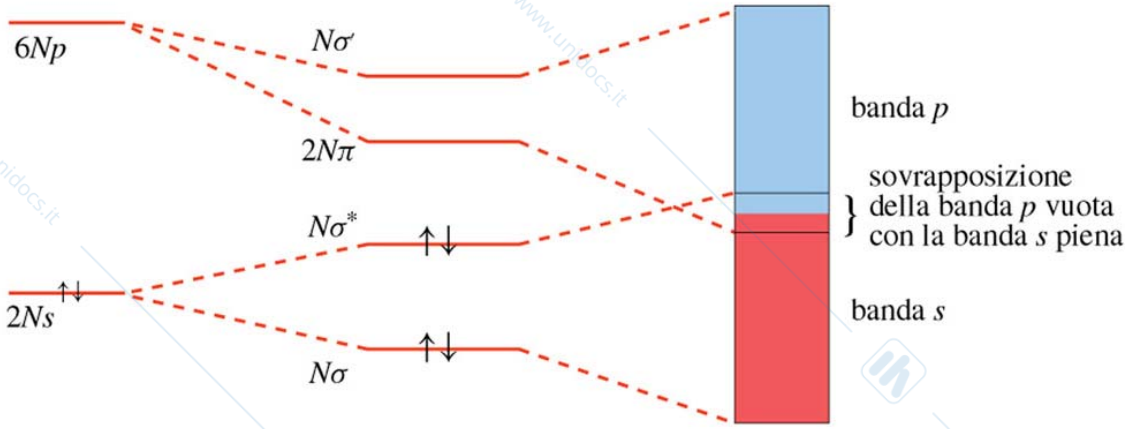
Struttura ordinata, cationi in un mare di e^- Metalli Solidi ionici

- Conducibilità elettrica e termica
- Duttilità e malleabilità

Modello a bande dei metalli



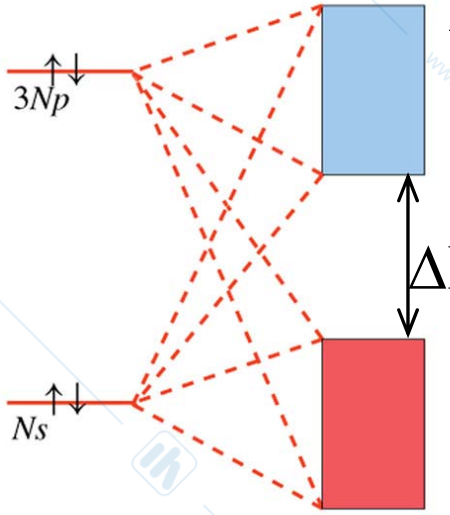
Metalli



banda di conduzione

banda di valenza

Materiali isolanti ($\Delta E >> RT$) e semiconduttori ($\Delta E \sim RT$) quando $T \cong T_{ambiente}$

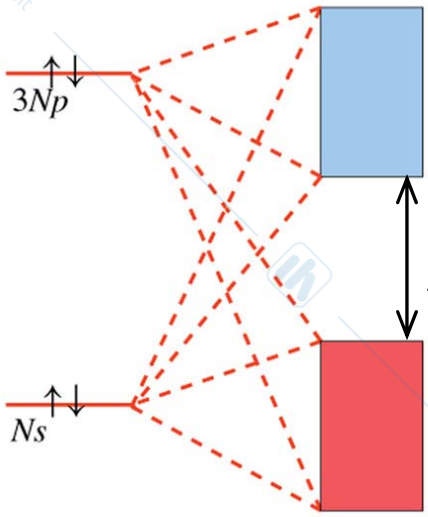


banda di conduzione

banda di valenza

Drogaggio dei semiconduttori

Semiconduttore puro



banda di conduzione

ΔE

banda di valenza

Semiconduttore drogato

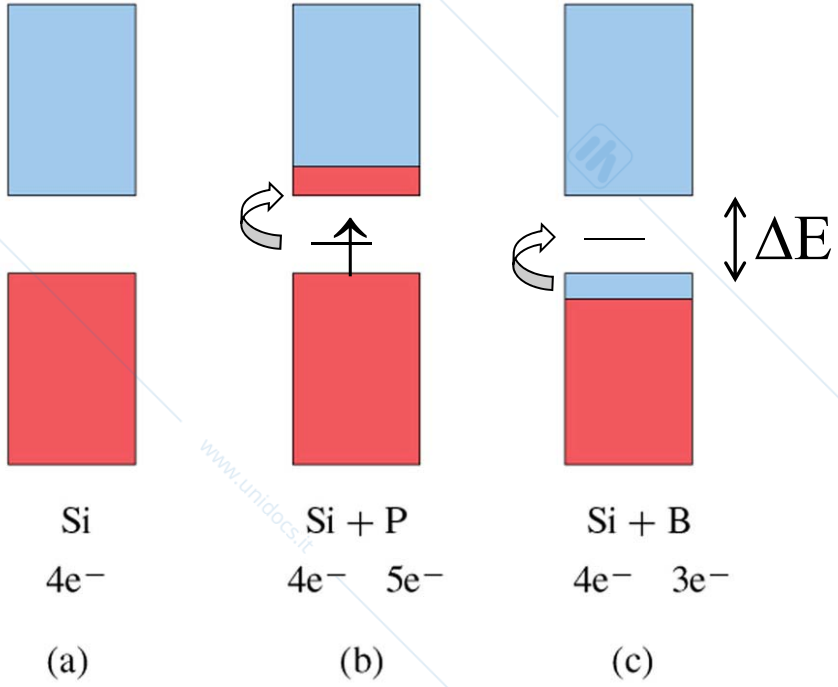


Tavola periodica

(b) drogaggio di tipo *n* = e⁻ aggiunti

(c) drogaggio di tipo *p* = lacune per e⁻ sottratti