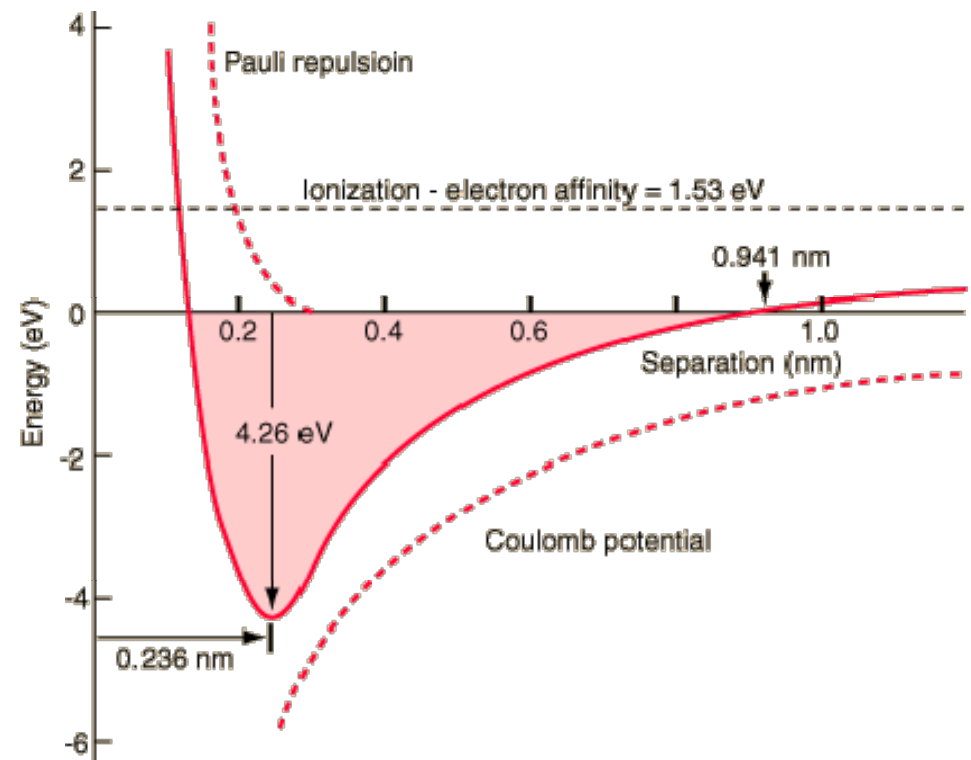
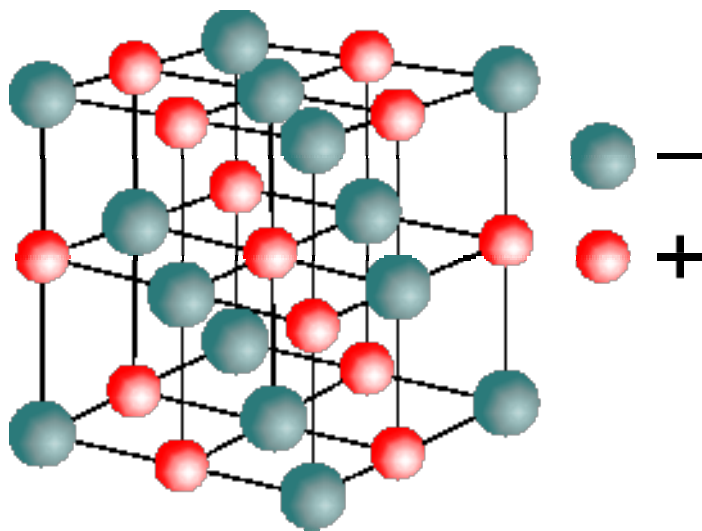


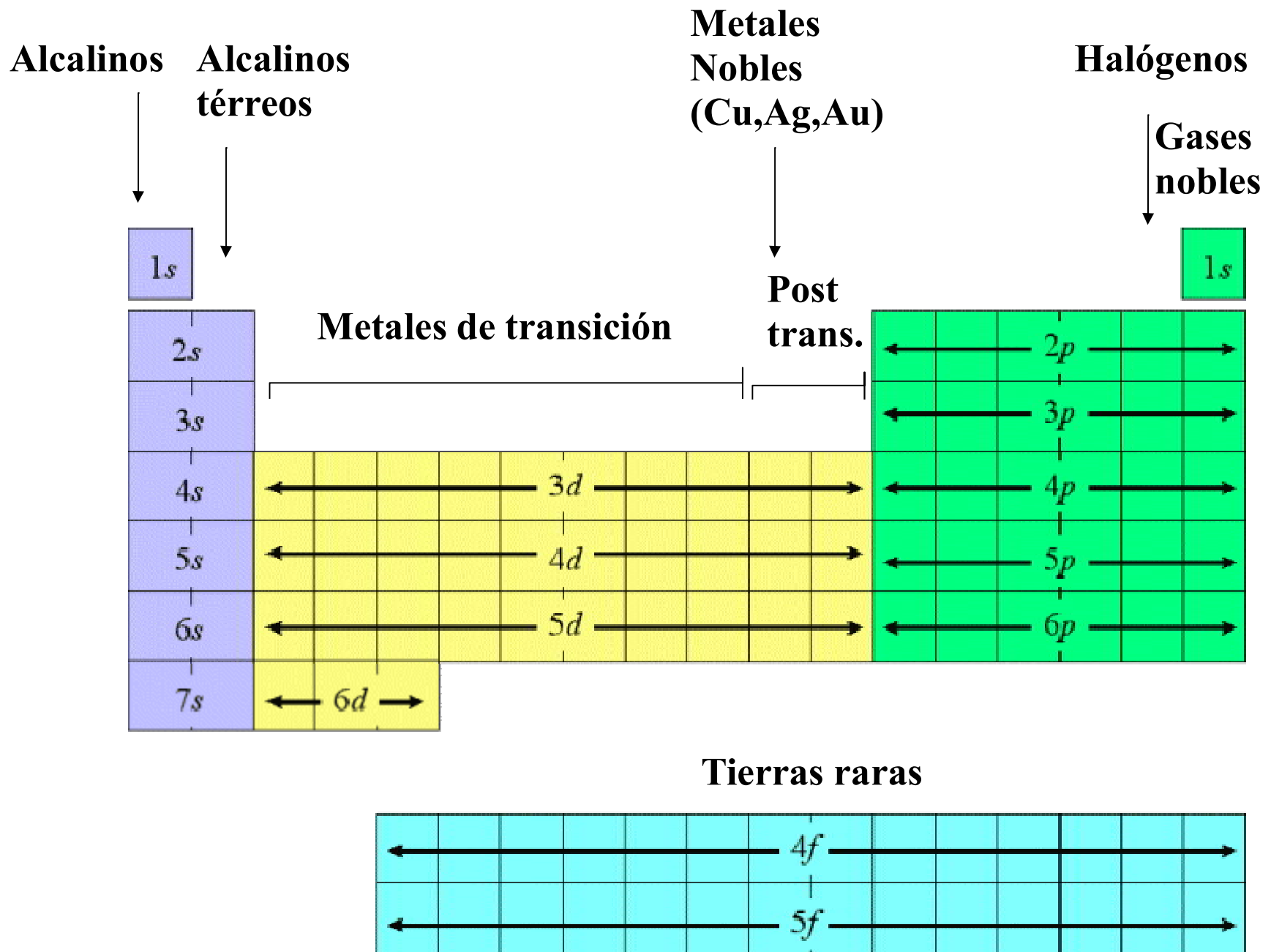
Capítulo 3: Energía de cohesión en cristales



Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States

The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters *s*, *p*, *d*, . . . signify electrons having orbital angular momentum 0, 1, 2, . . . in units \hbar ; the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

H ¹																	He ²
1s																	1s ²
Li ³	Be ⁴											B ⁵	C ⁶	N ⁷	O ⁸	F ⁹	Ne ¹⁰
2s	2s ²											2s ² 2p	2s ² 2p ²	2s ² 2p ³	2s ² 2p ⁴	2s ² 2p ⁵	2s ² 2p ⁶
Na ¹¹	Mg ¹²											Al ¹³	Si ¹⁴	P ¹⁵	S ¹⁶	Cl ¹⁷	Ar ¹⁸
3s	3s ²											3s ² 3p	3s ² 3p ²	3s ² 3p ³	3s ² 3p ⁴	3s ² 3p ⁵	3s ² 3p ⁶
K ¹⁹	Ca ²⁰	Sc ²¹	Ti ²²	V ²³	Cr ²⁴	Mn ²⁵	Fe ²⁶	Co ²⁷	Ni ²⁸	Cu ²⁹	Zn ³⁰	Ga ³¹	Ge ³²	As ³³	Se ³⁴	Br ³⁵	Kr ³⁶
4s	4s ²	3d 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁵ 4s	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ¹⁰ 4s	3d ¹⁰ 4s ²	4s ² 4p	4s ² 4p ²	4s ² 4p ³	4s ² 4p ⁴	4s ² 4p ⁵	4s ² 4p ⁶
Rb ³⁷	Sr ³⁸	Y ³⁹	Zr ⁴⁰	Nb ⁴¹	Mo ⁴²	Tc ⁴³	Ru ⁴⁴	Rh ⁴⁵	Pd ⁴⁶	Ag ⁴⁷	Cd ⁴⁸	In ⁴⁹	Sn ⁵⁰	Sb ⁵¹	Te ⁵²	I ⁵³	Xe ⁵⁴
5s	5s ²	4d 5s ²	4d ² 5s ²	4d ⁴ 5s	4d ⁵ 5s	4d ⁶ 5s	4d ⁷ 5s	4d ⁸ 5s	4d ¹⁰ -	4d ¹⁰ 5s	4d ¹⁰ 5s ²	5s ² 5p	5s ² 5p ²	5s ² 5p ³	5s ² 5p ⁴	5s ² 5p ⁵	5s ² 5p ⁶
Cs ⁵⁵	Ba ⁵⁶	La ⁵⁷	Hf ⁷²	Ta ⁷³	W ⁷⁴	Re ⁷⁵	Os ⁷⁶	Ir ⁷⁷	Pt ⁷⁸	Au ⁷⁹	Hg ⁸⁰	Tl ⁸¹	Pb ⁸²	Bi ⁸³	Po ⁸⁴	At ⁸⁵	Rn ⁸⁶
6s	6s ²	5d 6s ²	4f ¹⁴ 5d ² 6s ²	5d ³ 6s ²	5d ⁴ 6s ²	5d ⁵ 6s ²	5d ⁶ 6s ²	5d ⁹ -	5d ⁹ 6s	5d ¹⁰ 6s	5d ¹⁰ 6s ²	6s ² 6p	6s ² 6p ²	6s ² 6p ³	6s ² 6p ⁴	6s ² 6p ⁵	6s ² 6p ⁶
Fr ⁸⁷	Ra ⁸⁸	Ac ⁸⁹															
7s	7s ²	6d 7s ²	Ce ⁵⁸ 4f ² 6s ²	Pr ⁵⁹ 4f ³ 6s ²	Nd ⁶⁰ 4f ⁴ 6s ²	Pm ⁶¹ 4f ⁶ 6s ²	Sm ⁶² 4f ⁶ 6s ²	Eu ⁶³ 4f ⁷ 6s ²	Gd ⁶⁴ 4f ⁷ 5d 6s ²	Tb ⁶⁵ 4f ⁸ 5d 6s ²	Dy ⁶⁶ 4f ¹⁰ 6s ²	Ho ⁶⁷ 4f ¹¹ 6s ²	Er ⁶⁸ 4f ¹² 6s ²	Tm ⁶⁹ 4f ¹³ 6s ²	Yb ⁷⁰ 4f ¹⁴ 6s ²	Lu ⁷¹ 4f ¹⁴ 5d 6s ²	
			Th ⁹⁰ -	Pa ⁹¹ 5f ² 6d 7s ²	U ⁹² 5f ³ 6d 7s ²	Np ⁹³ 5f ⁵ 7s ²	Pu ⁹⁴ 5f ⁶ 7s ²	Am ⁹⁵ 5f ⁷ 7s ²	Cm ⁹⁶ 5f ⁷ 6d 7s ²	Bk ⁹⁷	Cf ⁹⁸	Es ⁹⁹	Fm ¹⁰⁰	Md ¹⁰¹	No ¹⁰²	Lr ¹⁰³	



Clasificación:

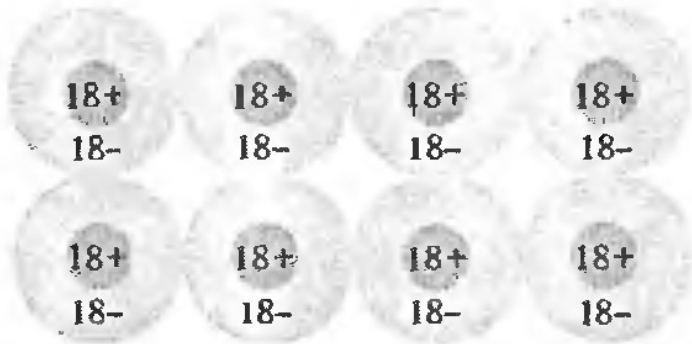
- Basada en las propiedades de conducción: $\left\{ \begin{array}{l} \text{Metales} \\ \text{Aisladores} \\ \text{Semiconductores} \end{array} \right.$
- Basada en la configuración de electrones de valencia

Tipos de uniones

Elementos $\left\{ \begin{array}{l} \text{Metálica} \\ \text{Covalente} \\ \text{Van der Waals} \end{array} \right\}$ Molecular

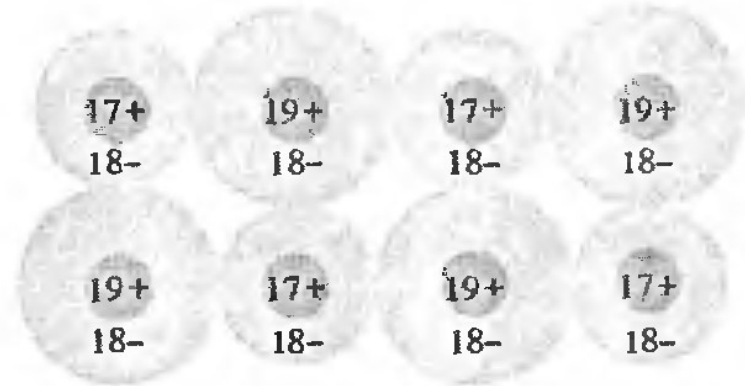
Compuestos \longrightarrow Las mismas + iónica

Ar

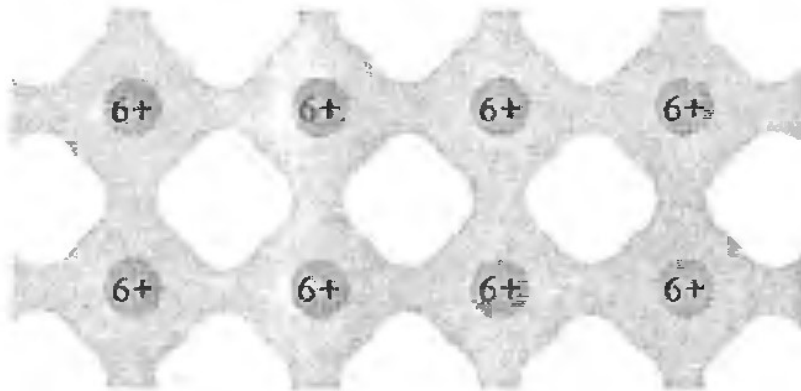


Molecular
(a)

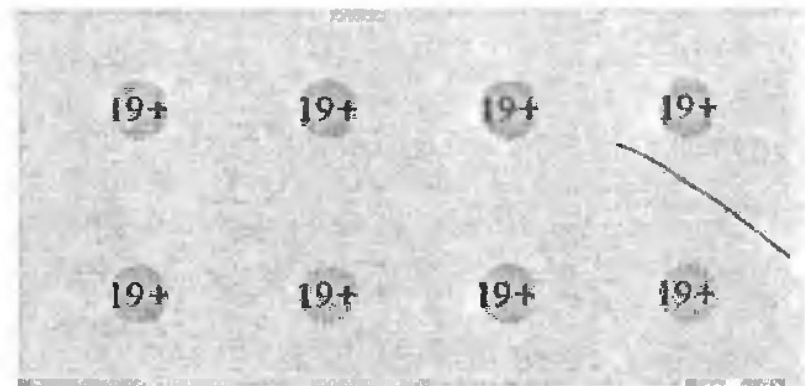
ClK



Ionic
(b)



Covalent
(c)



Metallic
(d)

C

K

Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

Cov. +
vdW

Covalente

unión metálica

Crystal structure.
a lattice parameter, in Å
c lattice parameter, in Å

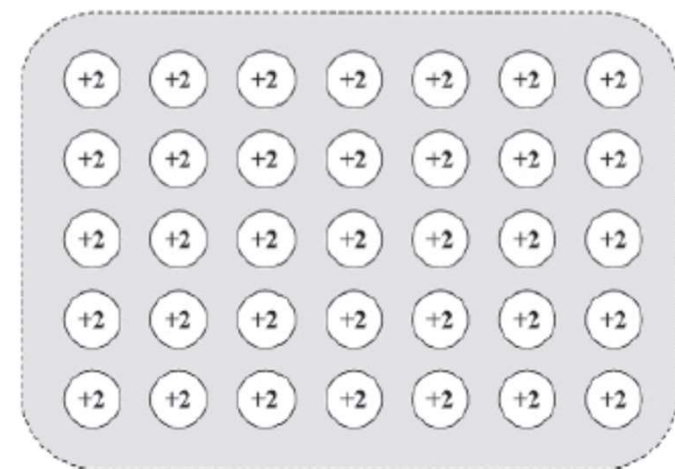
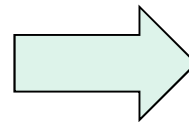
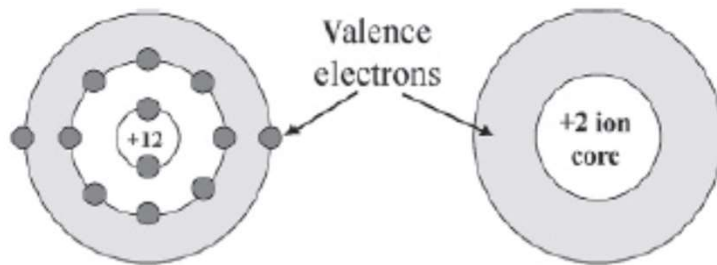
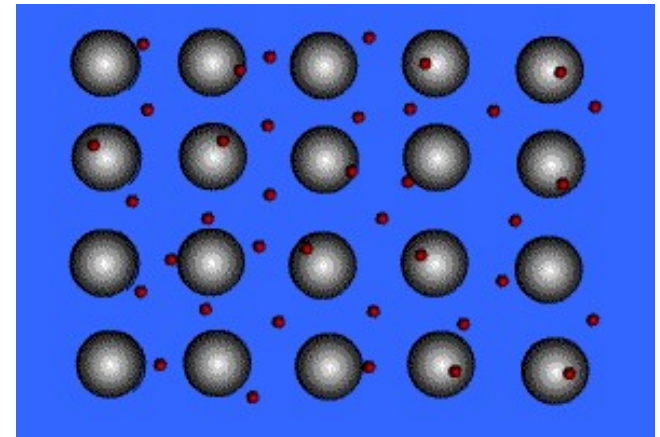
H¹ 4K hcp 3.75 6.12																	He⁴ 2K hcp 3.57 5.83						
Li 78K bcc 3.491	Be hcp 2.27 3.59																	B rhomb. 3.567	C diamond 5.66 (N ₂)	N 20K cubic 5.66 (N ₂)	O complex (O ₂)	F	Ne 4K fcc 4.46
Na 5K bcc 4.225	Mg hcp 3.21 5.21																	Al fcc 4.05	Si diamond 5.430	P complex	S complex	Cl complex (Cl ₂)	Ar 4K fcc 5.31
K 5K bcc 5.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br ₂)	Kr 4K fcc 5.64						
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn (α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I ₂)	Xe 4K fcc 6.13						
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77 ABAC	Hf hcp 3.19 5.05	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At —	Rn —						
Fr —	Ra —	Ac fcc 5.31																					
			Ce fcc 5.16	Pr hex. 3.67 ABAC	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55							
			Th fcc 5.08	Pa tetr. 3.92 3.24	U complex	Np complex	Pu complex	Am hex. 3.64 ABAC	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —							

Metálica

Los electrones se mueven libremente a través del material

Table 19.4
IONIC RADII COMPARED WITH HALF THE NEAREST-NEIGHBOR DISTANCES IN METALS

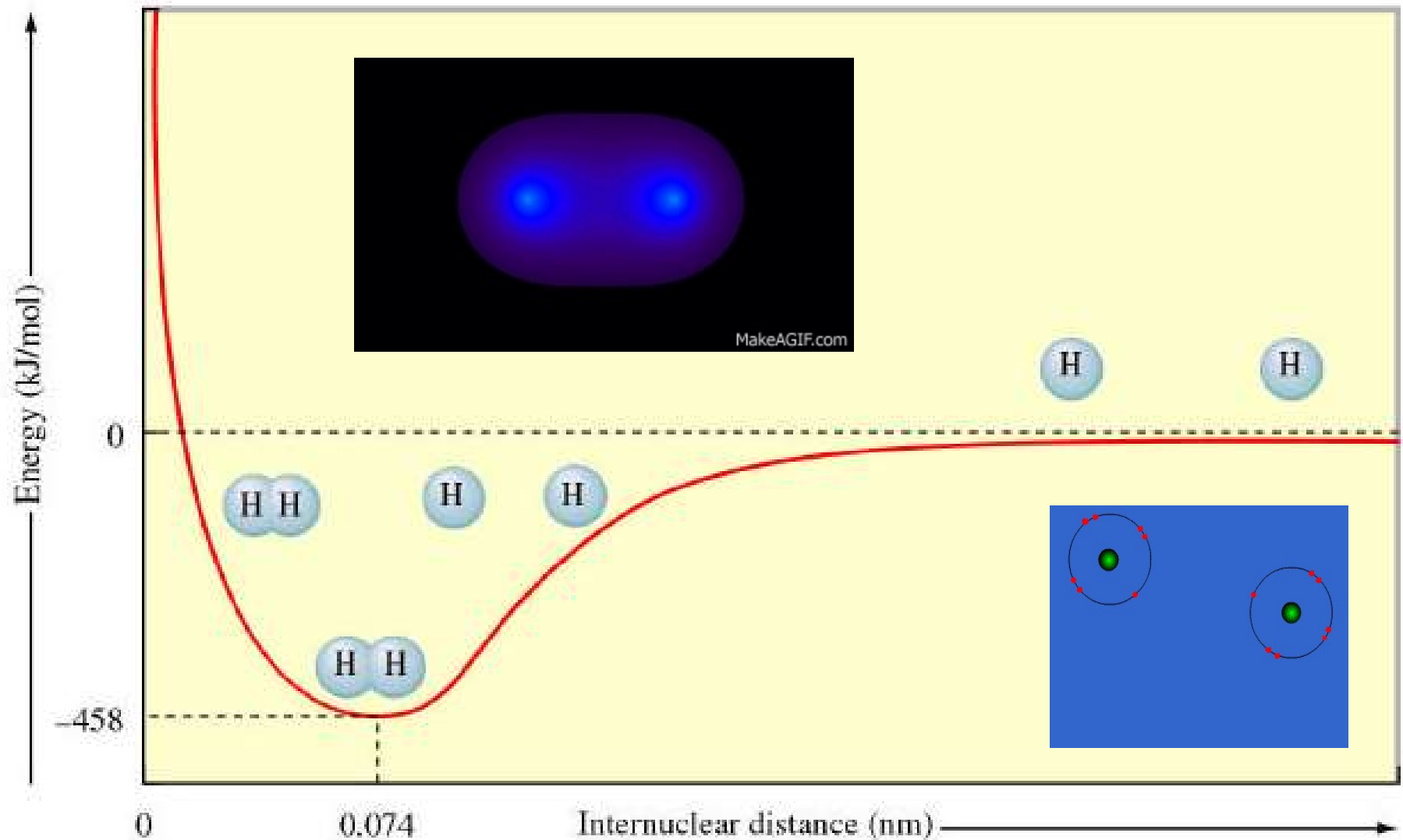
METAL	SINGLY IONIZED IONIC RADIUS, r_{ion} (Å)	NEAREST-NEIGHBOR HALF DISTANCE IN METAL, r_{met} (Å)	$r_{\text{met}}/r_{\text{ion}}$
Li	0.60	1.51	2.52
Na	0.95	1.83	1.93
K	1.33	2.26	1.70
Rb	1.48	2.42	1.64
Cs	1.69	2.62	1.55
Cu	0.96	1.28	1.33
Ag	1.26	1.45	1.15
Au	1.37	1.44	1.05



Modelo: Gas de electrones

Covalente

Densidad electrónica localizada entre átomos vecinos formando “bonds”



Estructura de diamante

Ej.: C, Si, Ge

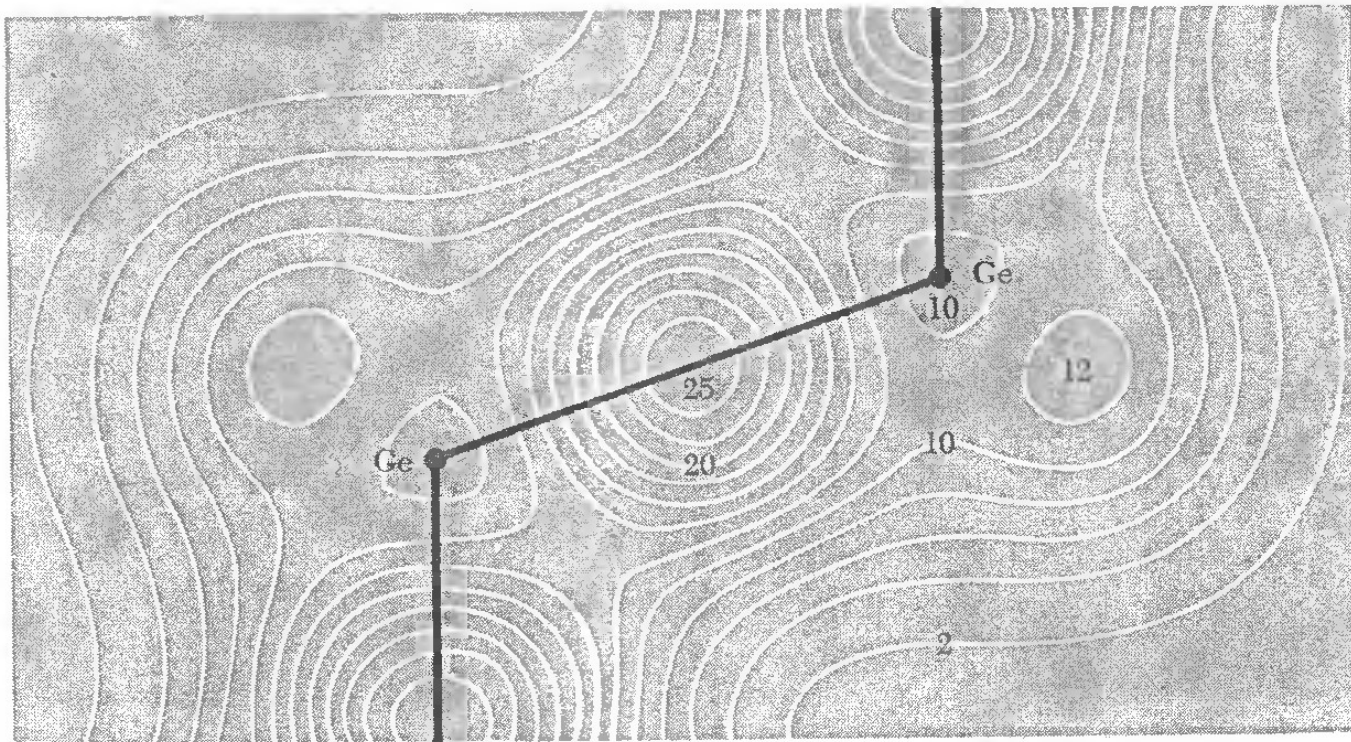
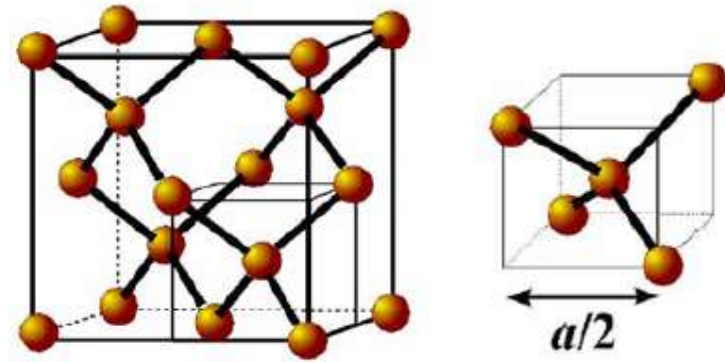
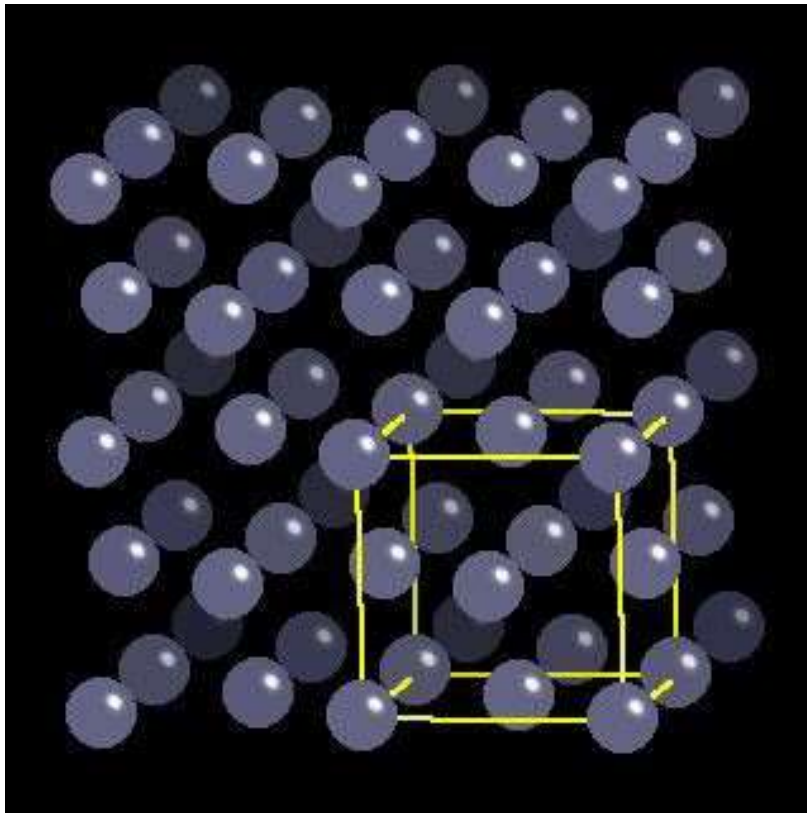


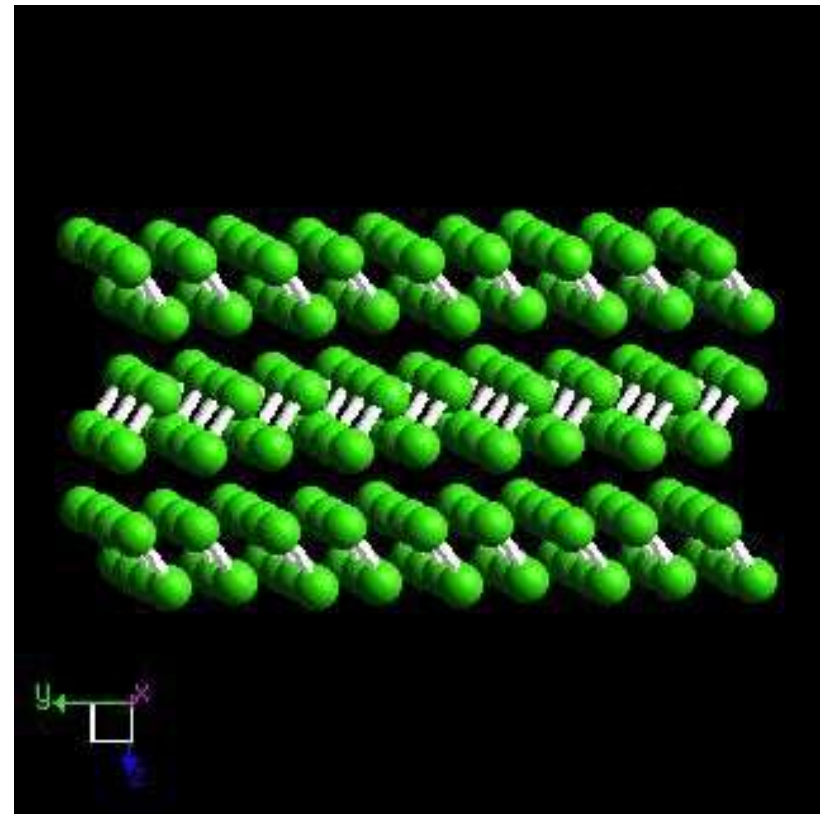
Figure 11 Calculated valence electron concentration in germanium. The numbers on the contours give the electron concentration per primitive cell, with four valence electrons per atom (eight electrons per primitive cell). Note the high concentration midway along the Ge-Ge bond, as we expect for covalent bonding. (After J. R. Chelikowsky and M. L. Cohen.)

Molecular

Densidad electrónica localizada alrededor de los átomos. Se mantienen las características atómicas o moleculares.

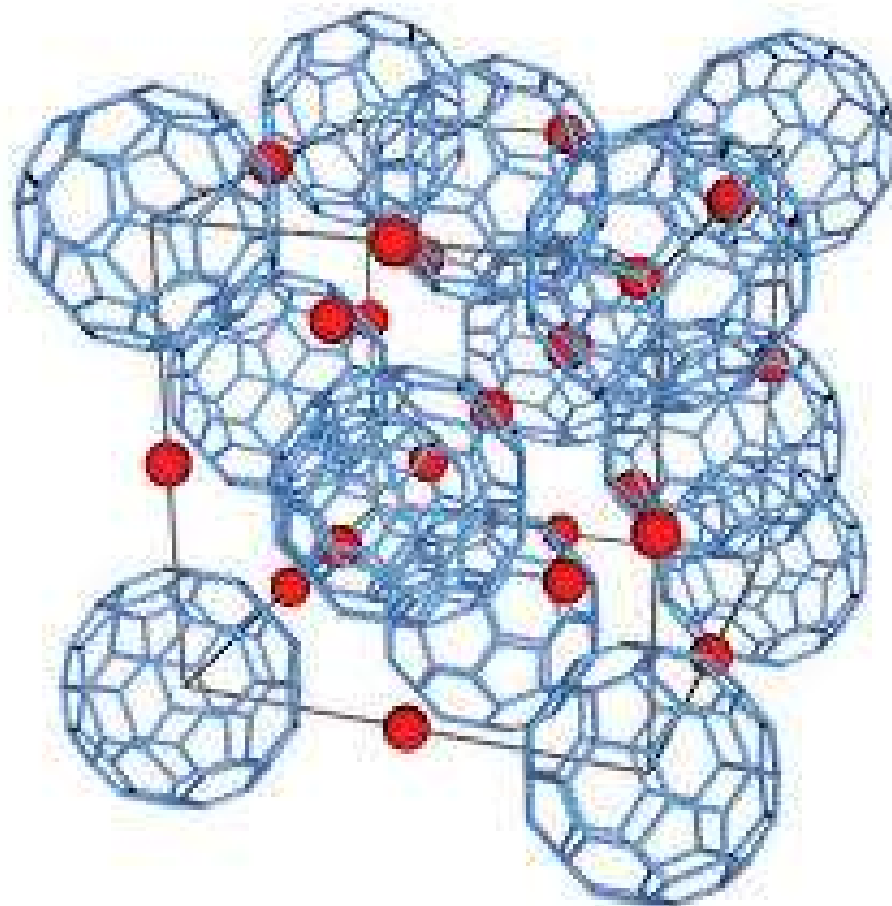
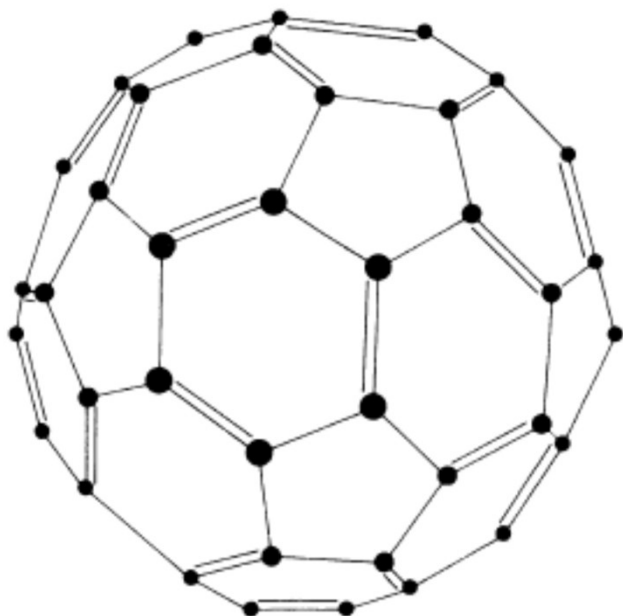


Gases Nobles (fcc)



**Cristal de cloro
(ortorrómbico)**

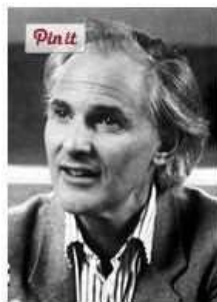
Fulerenos (C_{60} : Buckyballs)



The Nobel Prize in Chemistry 1996



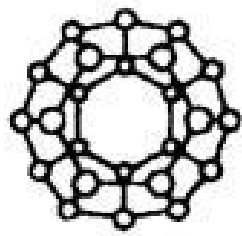
Robert F. Curl Jr.
Prize share: 1/3



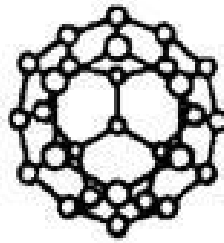
Sir Harold W. Kroto
Prize share: 1/3



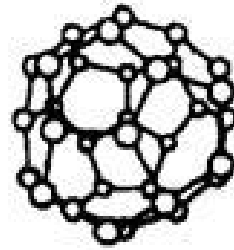
Richard E. Smalley
Prize share: 1/3



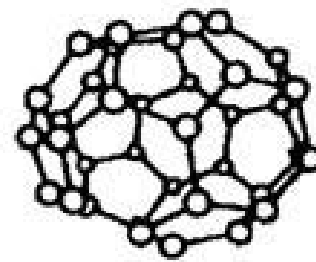
C₂₄



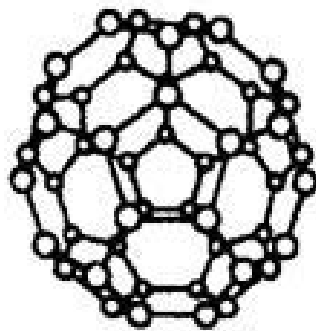
C₂₈



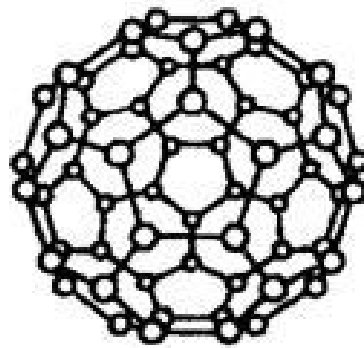
C₃₂



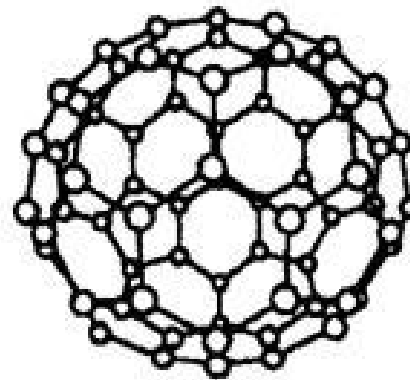
C₃₆



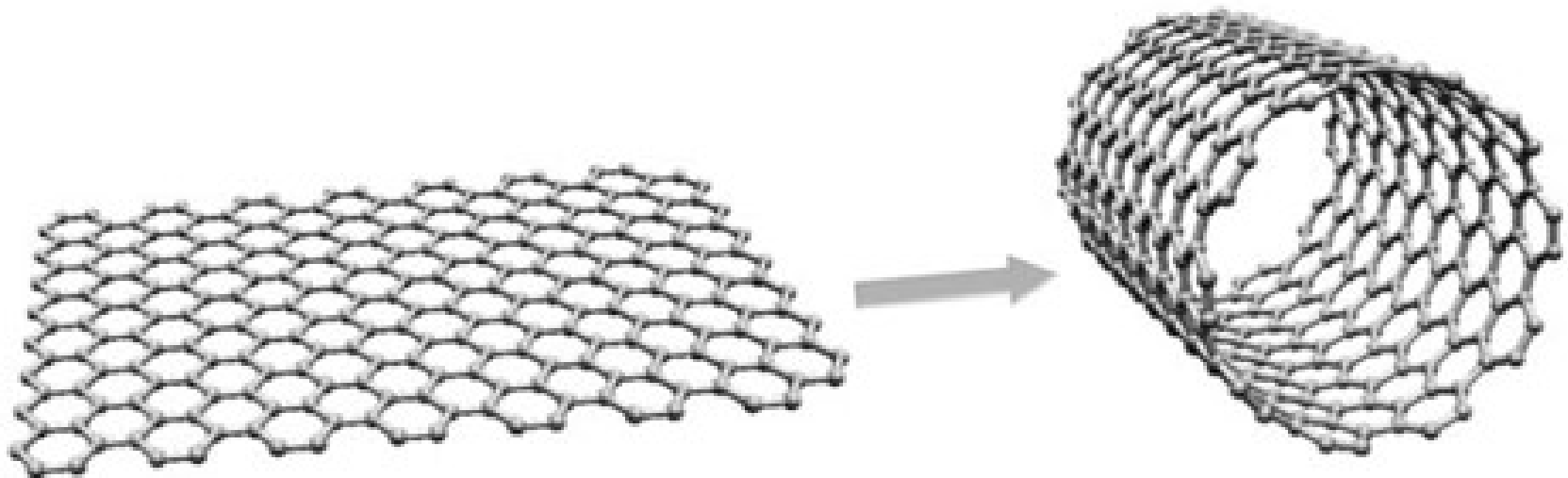
C₅₀



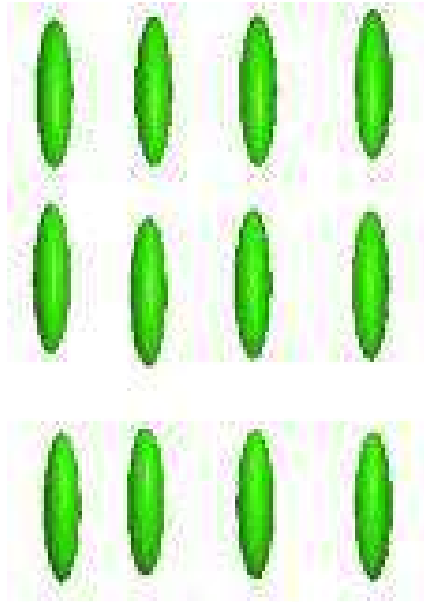
C₆₀



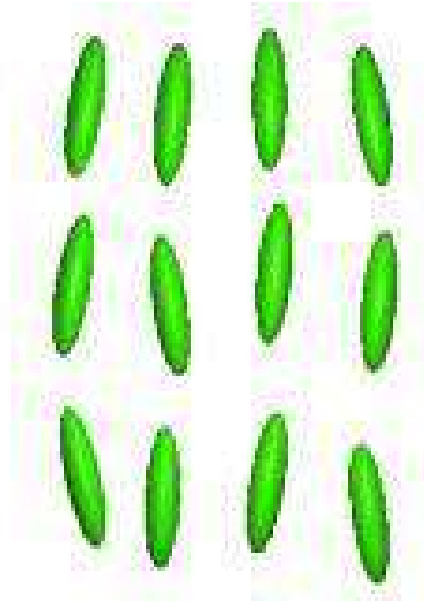
C₇₀



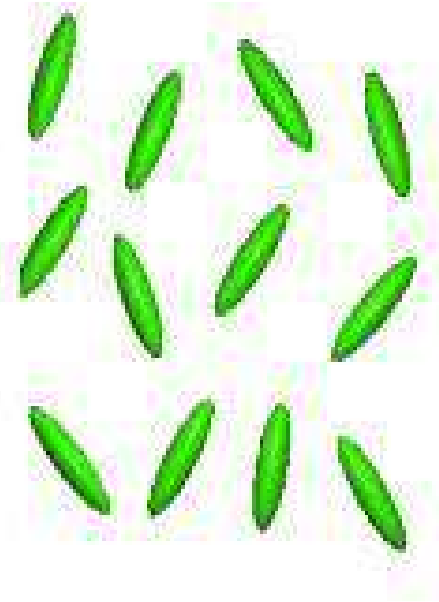
Moléculas muy anisotrópicas



Solid



Liquid Crystal



Liquid



F. Reinitzer



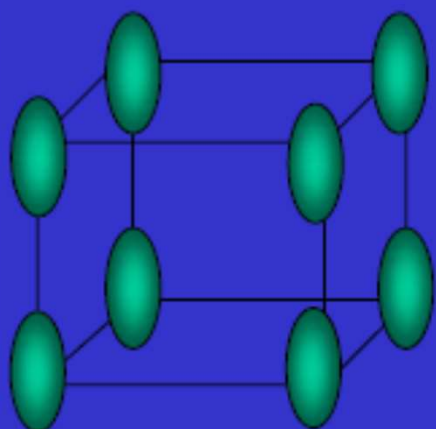
Otto Lehmann

**Presencia de dos puntos de fusión
en un éster derivado del colesterol**

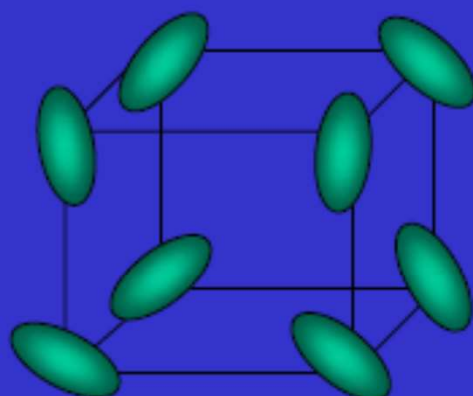
Nuevo estado de la materia

CRISTAL PLÁSTICO

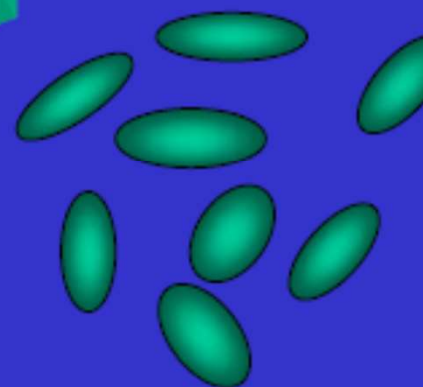
CRISTAL



Transición



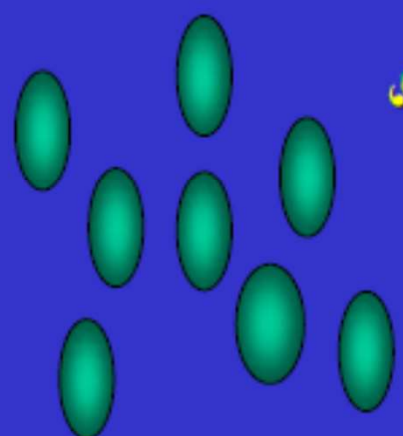
Fusión



LÍQUIDO

Fusión

1ª fusión

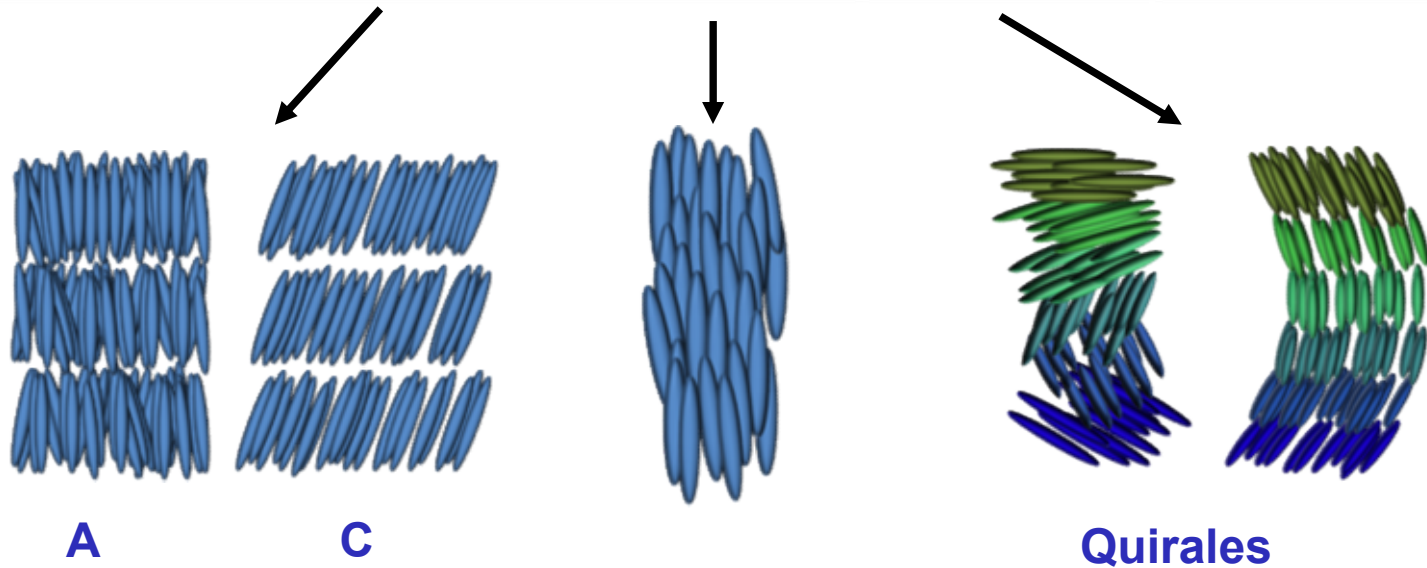
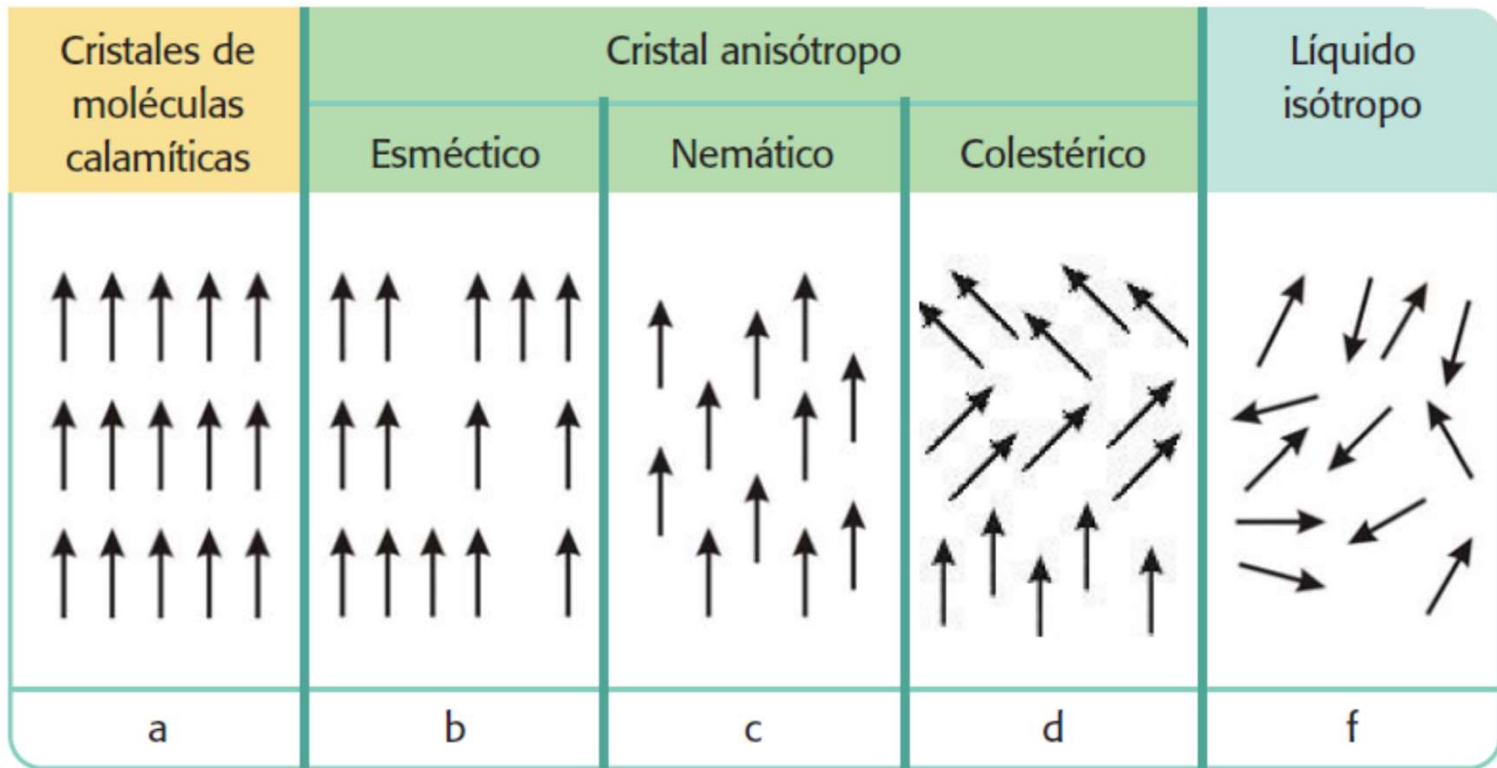


“Clearing”

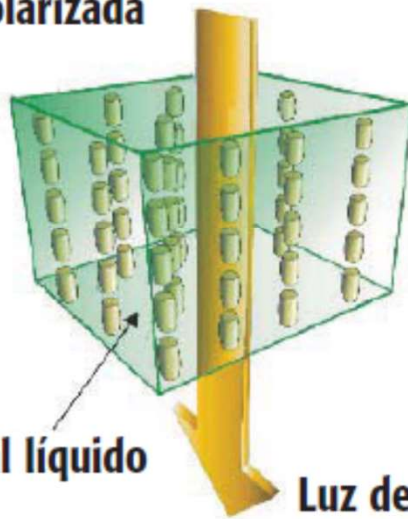
CRISTAL LÍQUIDO

Volver al Índice





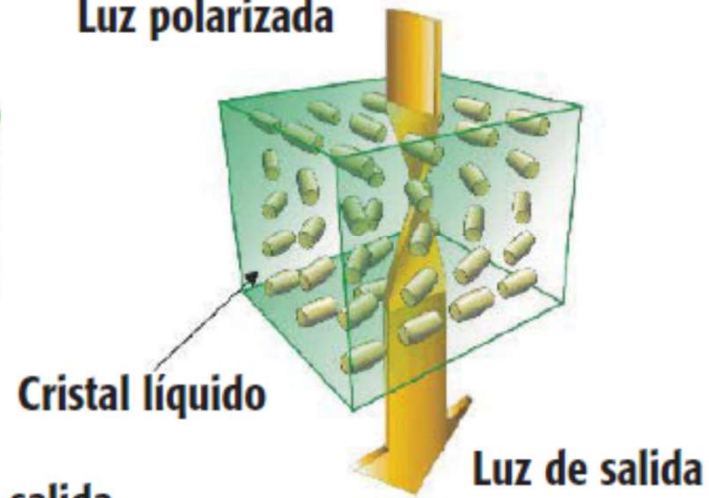
Luz polarizada



Cristal líquido

Luz de salida

Luz polarizada

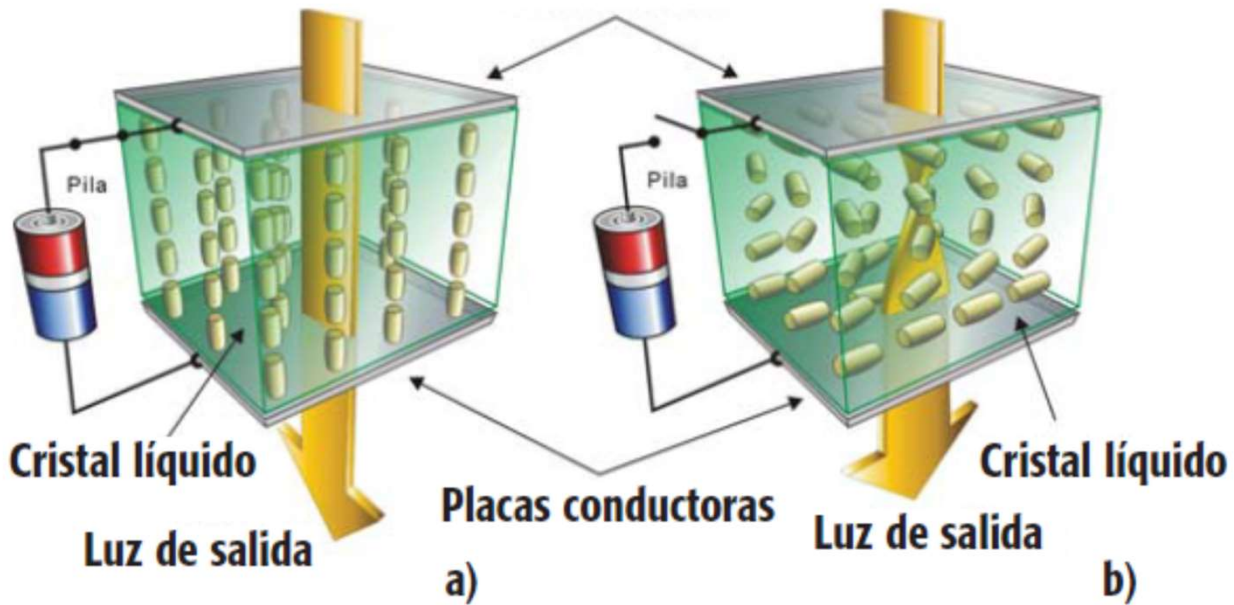


Luz de salida

Luz polarizada

Placas conductoras

Luz polarizada



Cristal líquido

Luz de salida

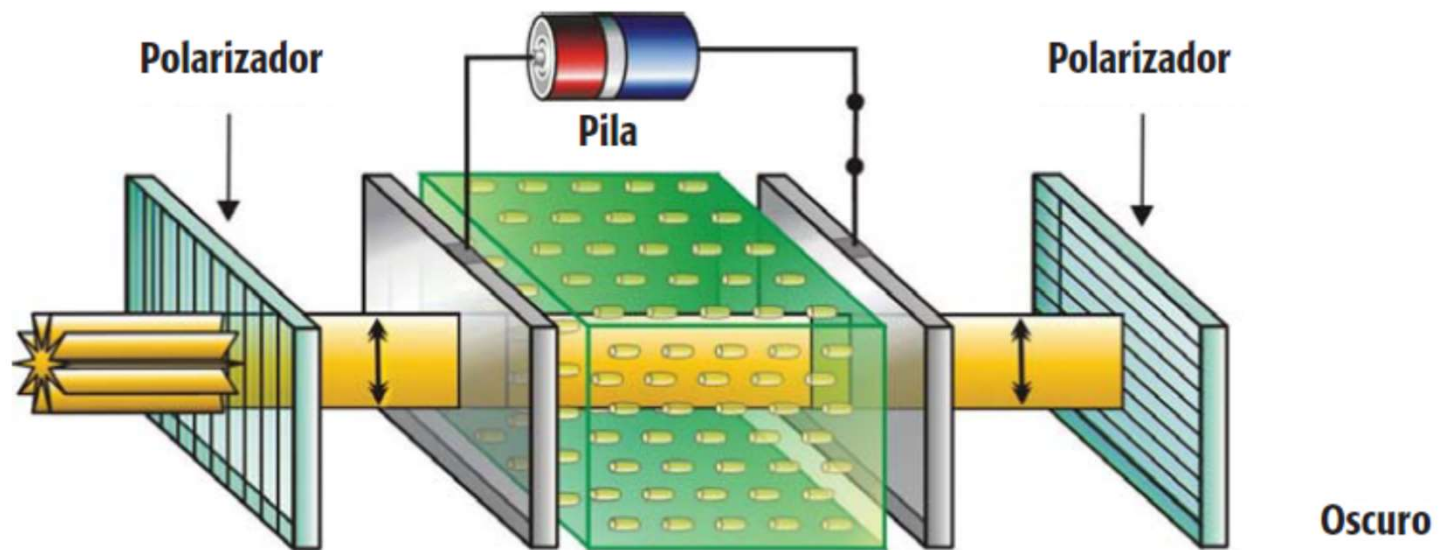
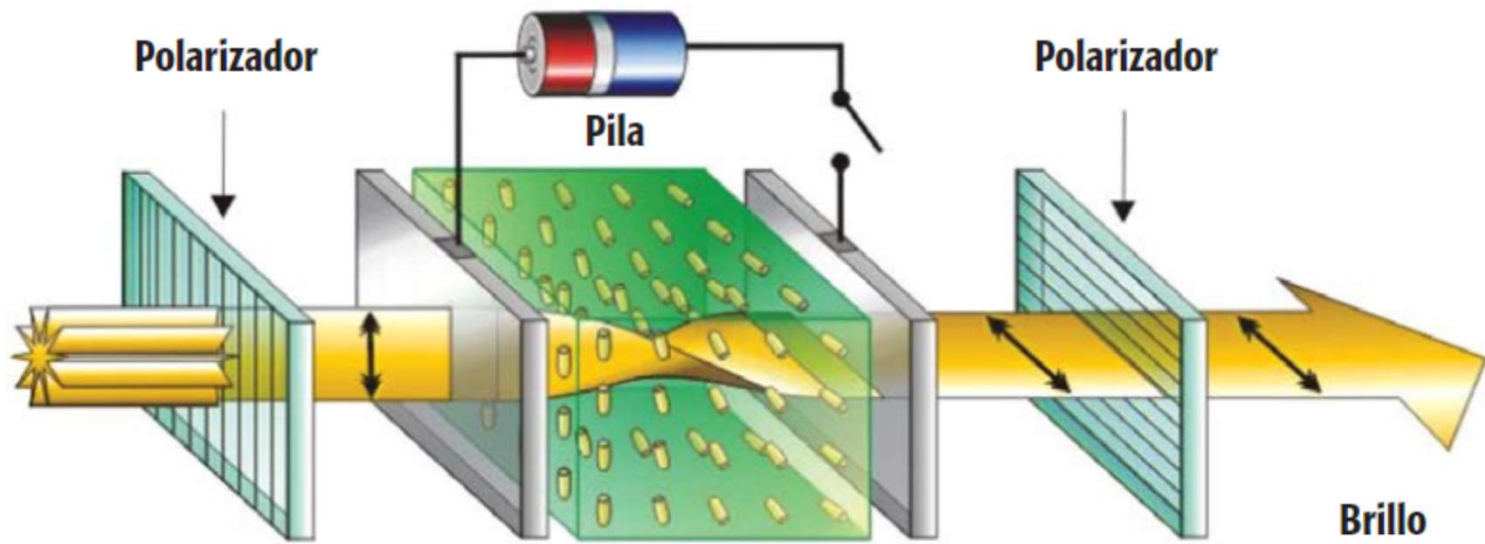
Placas conductoras

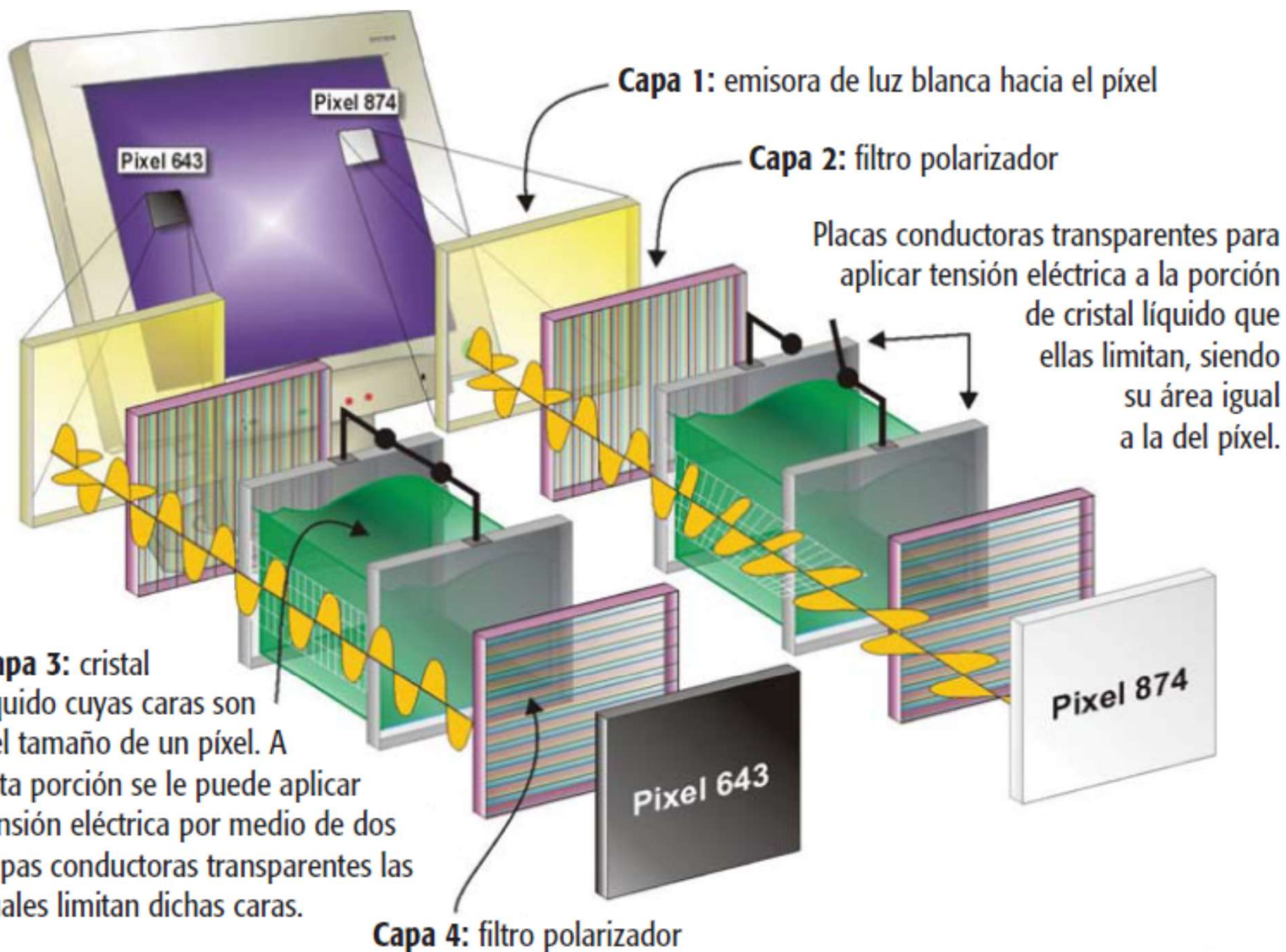
a)

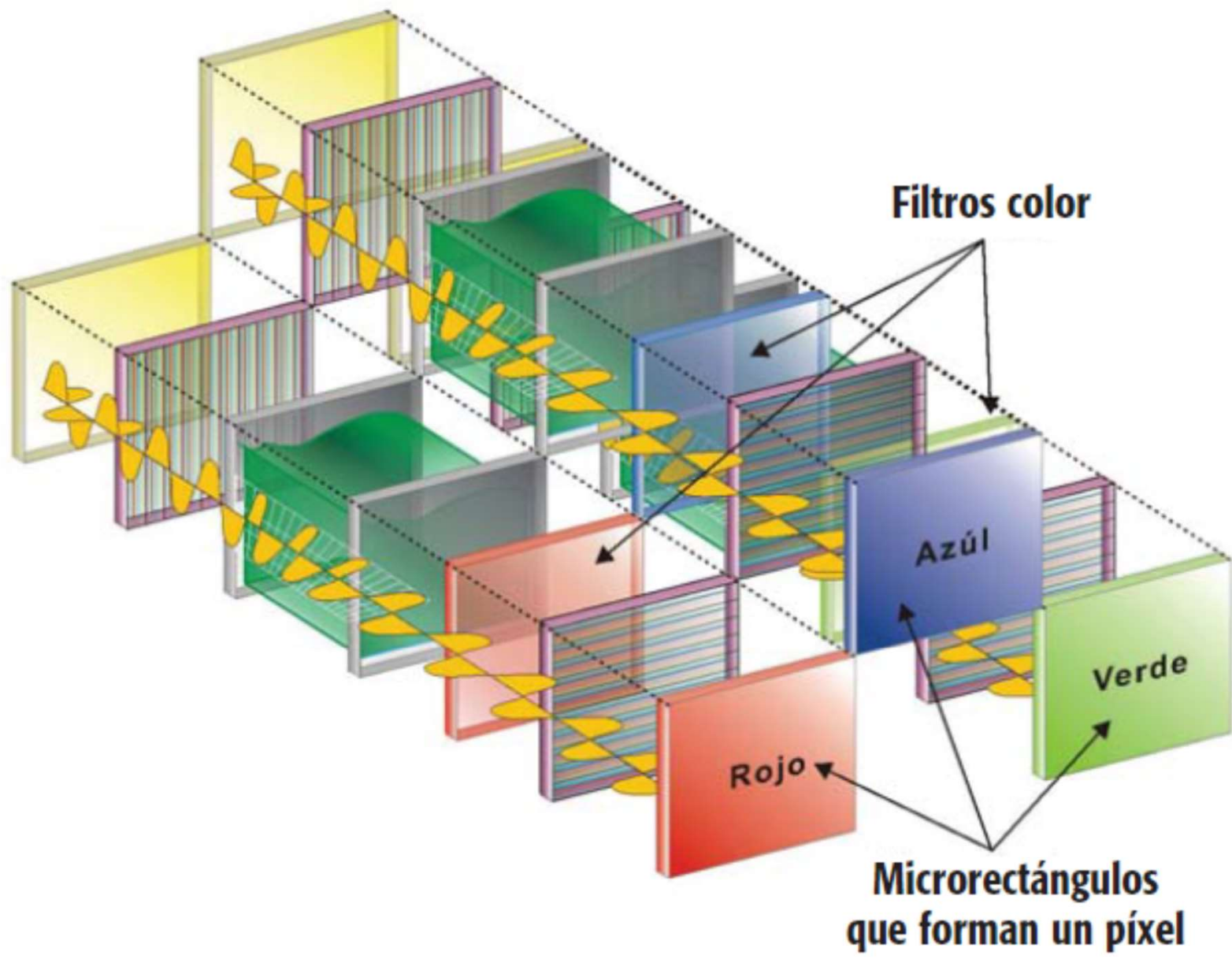
Cristal líquido

Luz de salida

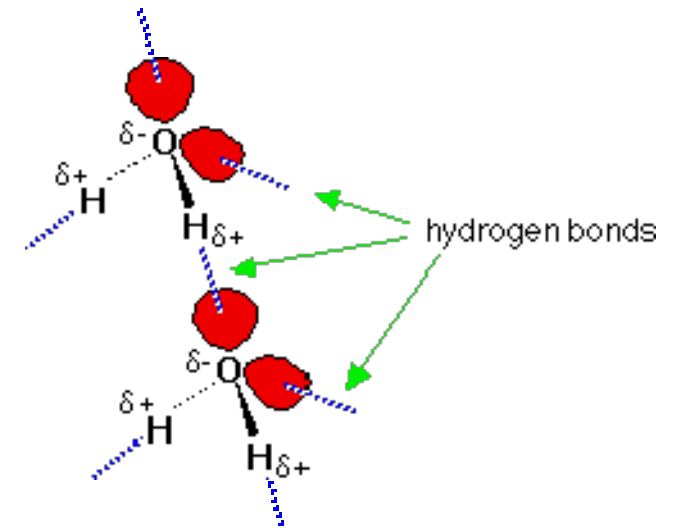
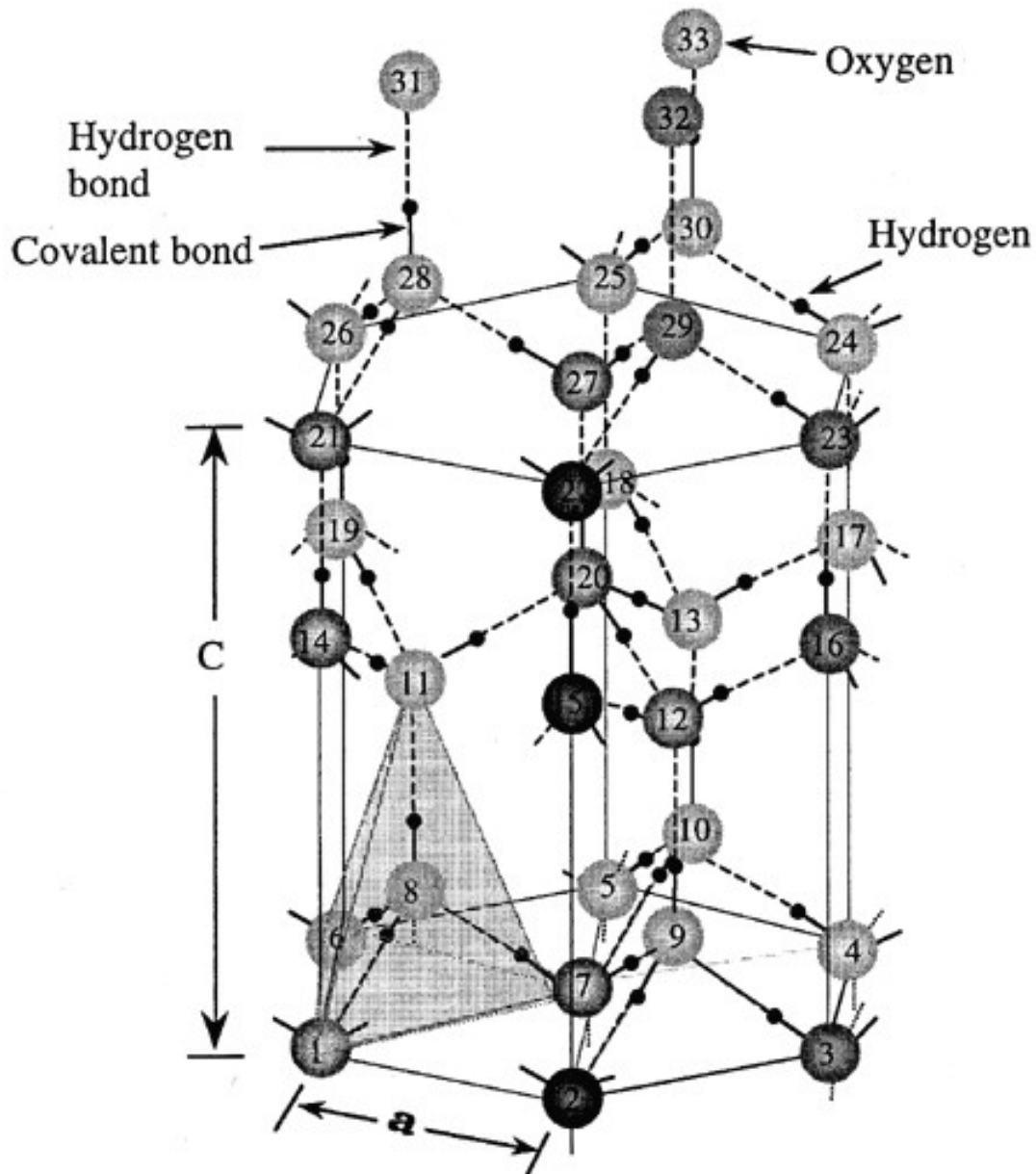
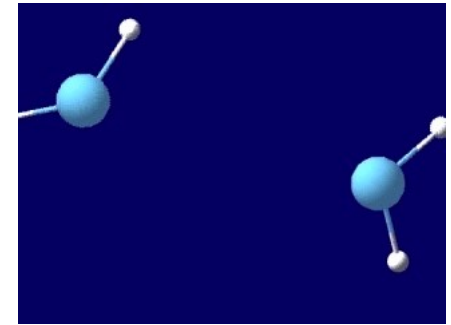
b)







Enlace puente hidrogeno



Estructura cristalina del hielo

$$a = 0.4523 \text{ nm}$$

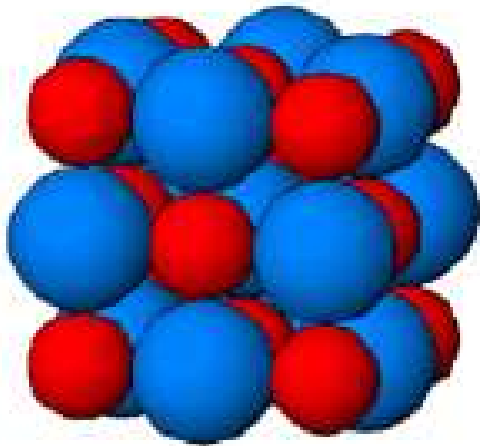
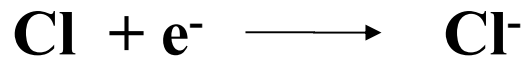
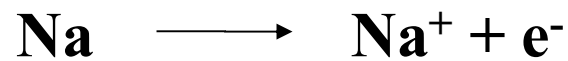
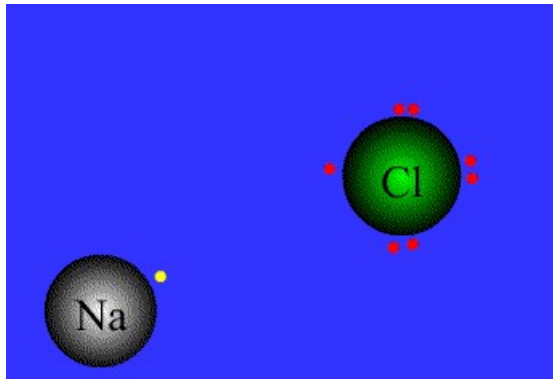
$$c = 0.7367 \text{ nm.}$$

$$c/a = 1.628 \quad (1.633)$$

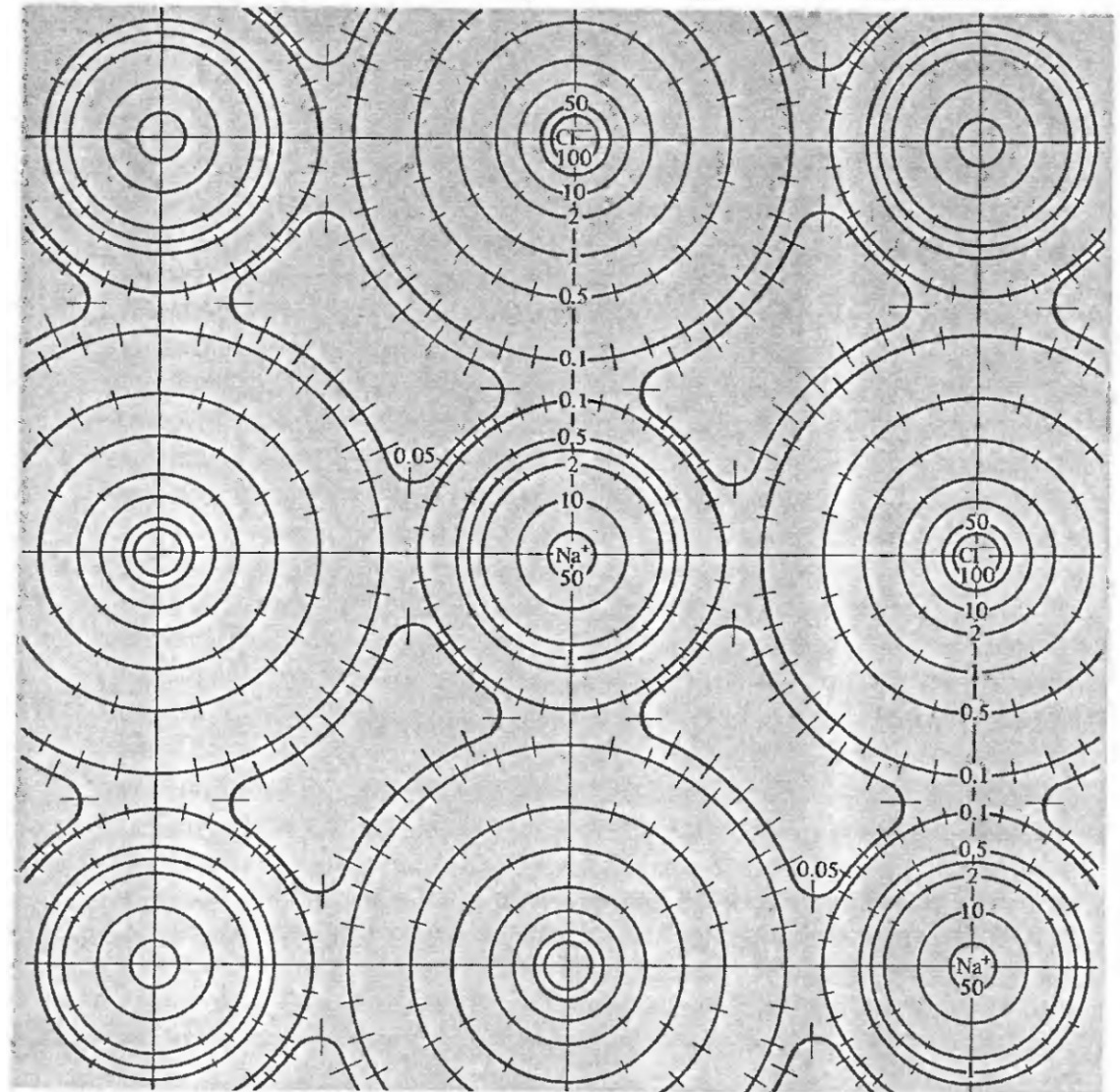
Factor de llenado: 0.34

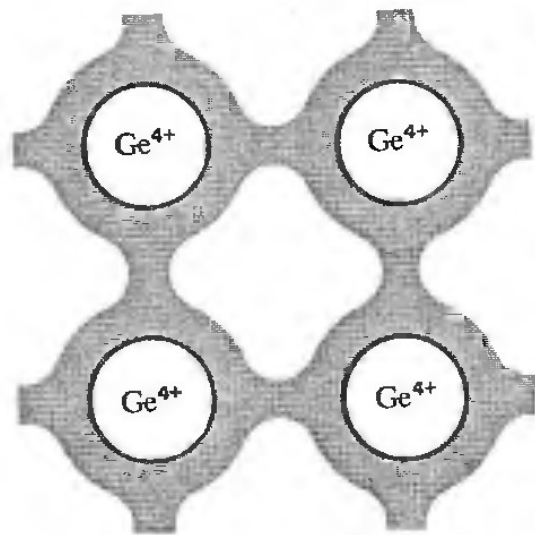
Iónica

Densidad electrónica localizada alrededor de los átomos formado iones

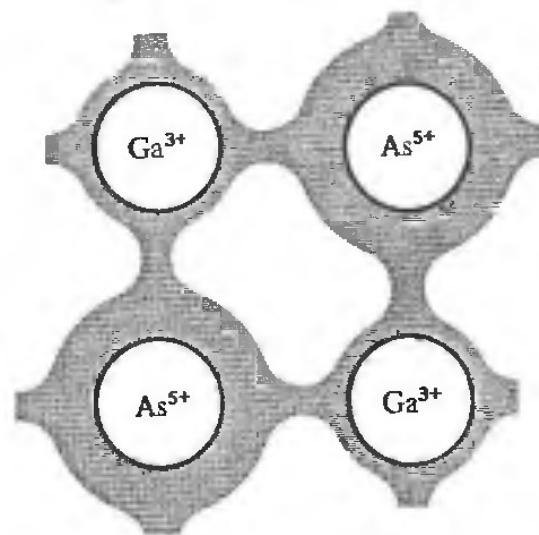


Estructura NaCl

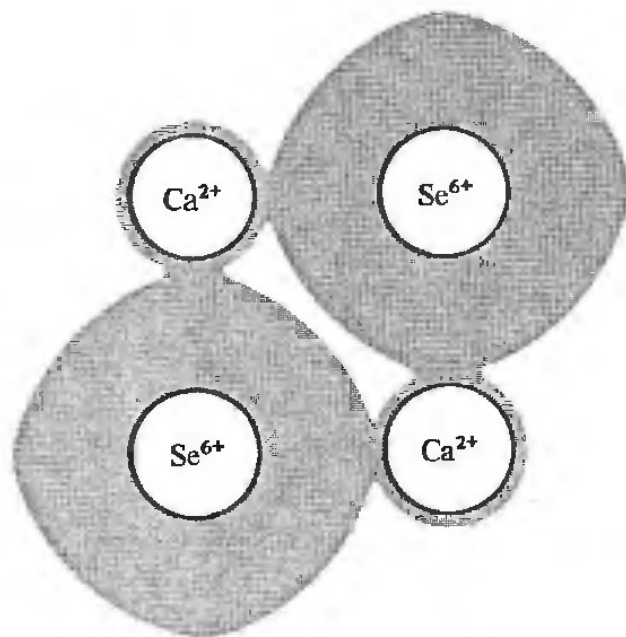




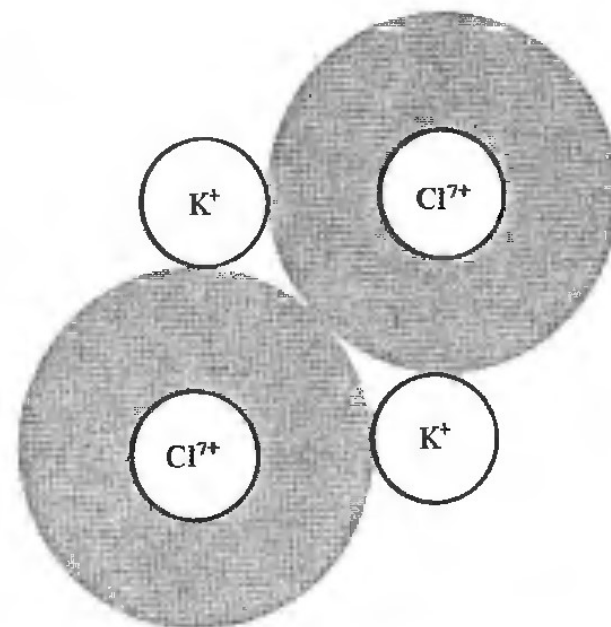
(a)



(b)



(c)

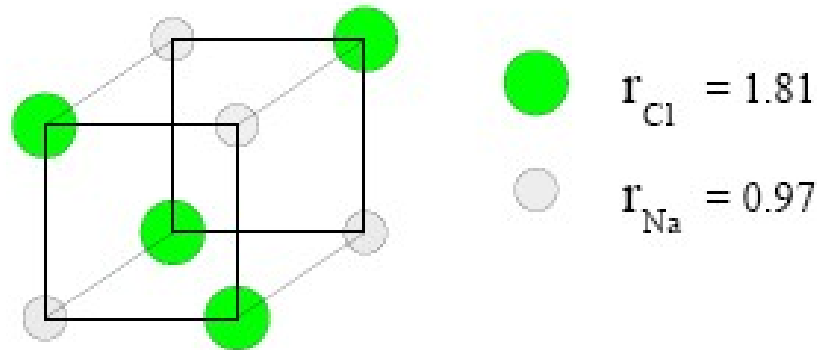
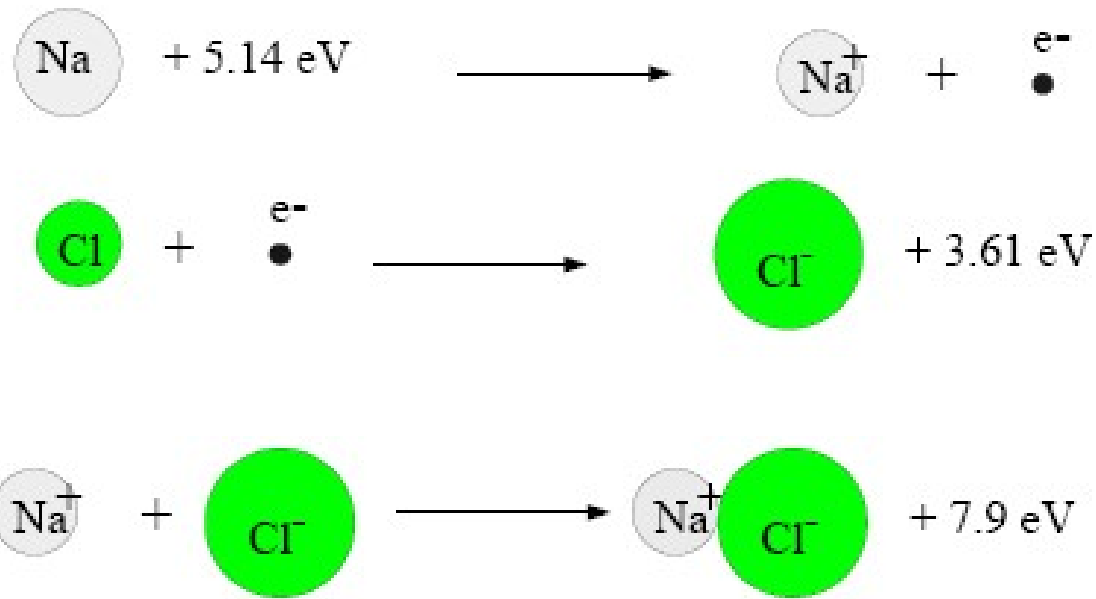


(d)

Table 8 Fractional ionic character of bonds in binary crystals

Crystal	Fractional ionic character	Crystal	Fractional ionic character
Si	0.00		
SiC	0.18	GaAs	0.31
Ge	0.00	GaSb	0.26
ZnO	0.62	AgCl	0.86
ZnS	0.62	AgBr	0.85
ZnSe	0.63	AgI	0.77
ZnTe	0.61		
		MgO	0.84
CdO	0.79	MgS	0.79
CdS	0.69	MgSe	0.79
CdSe	0.70		
CdTe	0.67	LiF	0.92
		NaCl	0.94
InP	0.42	RbF	0.96
InAs	0.36		
InSb	0.32		

After J. C. Phillips, *Bonds and bands in semiconductors*, Academic Press, 1973, Chap. 2.

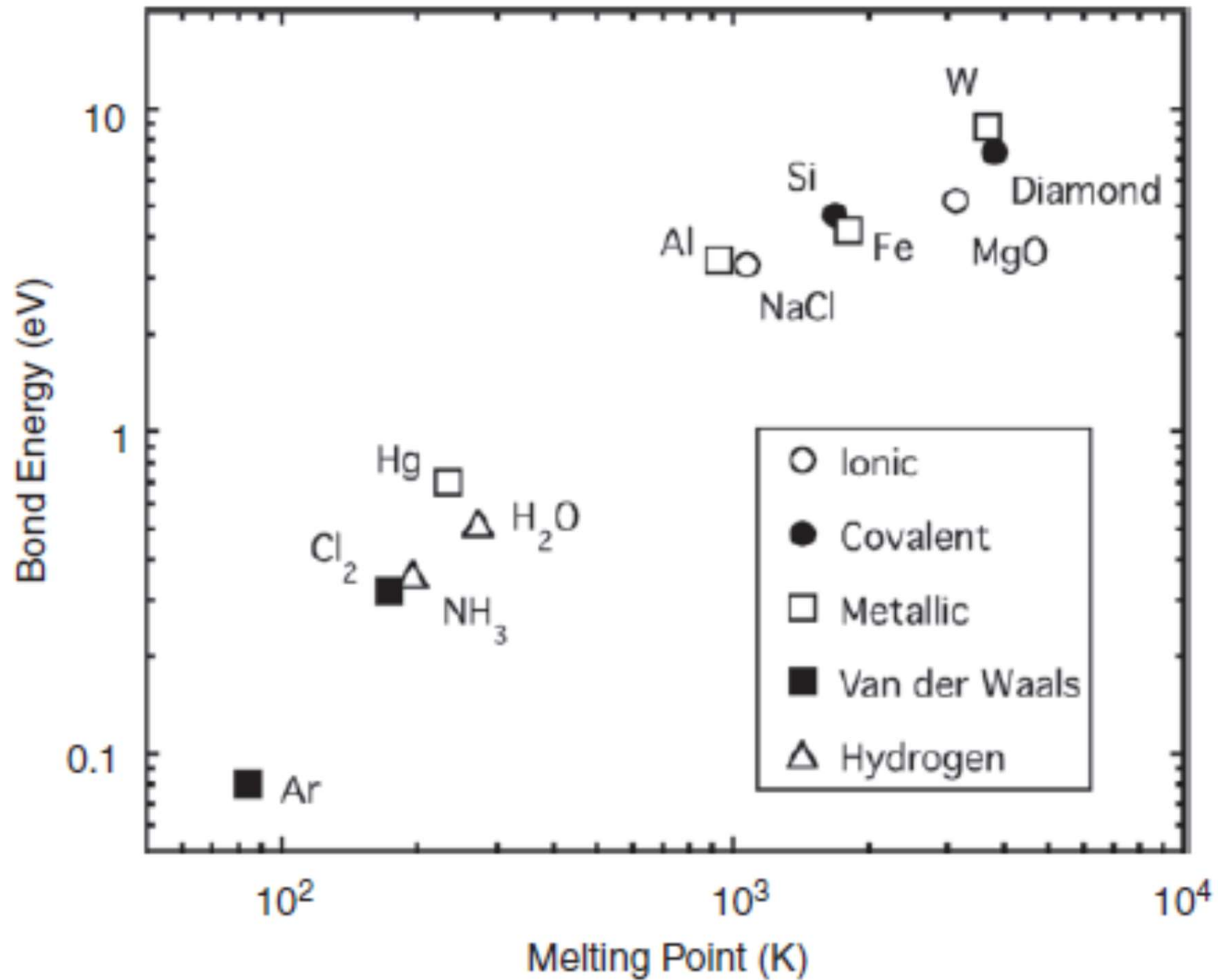


$$E_{\text{cohesión}} = E_{\text{átomos/iones libres}} - E_{\text{cristal}}$$

Table 1 Cohesive energies

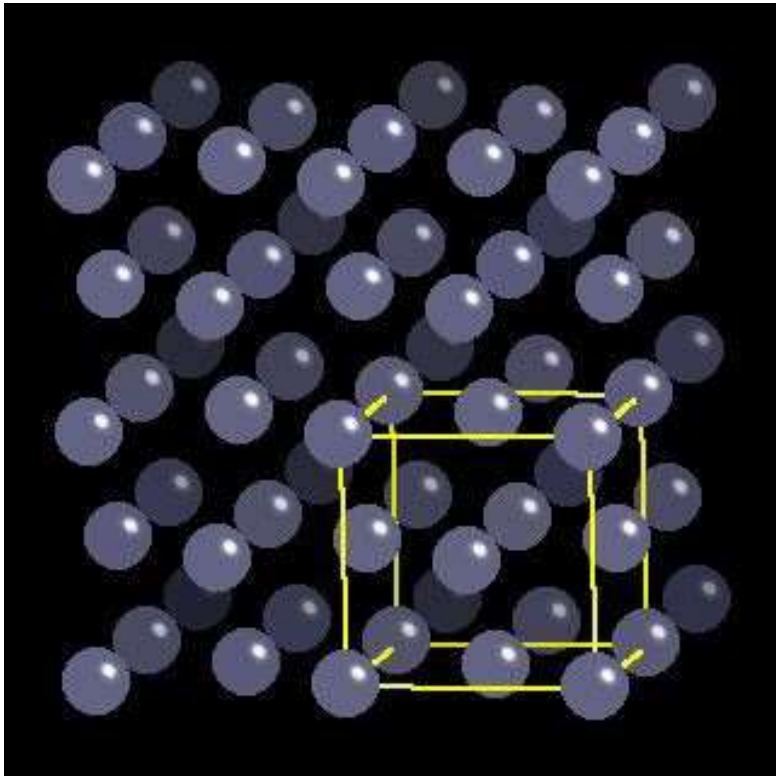
Energy required to form separated neutral atoms in their ground electronic state from the solid at 0 K at 1 atm. The data were supplied by Prof. Leo Brewer in units kcal per mole, revised to May 4, 1977, after LBL Report 3720 Rev.																																													
Li 158. 1.63 37.7	Be 320. 3.32 76.5													B 561 5.81 134	C 711. 7.37 170.	N 474. 4.92 113.4	O 251. 2.60 60.03	F 81.0 0.84 19.37	Ne 1.92 0.020 0.46																										
Na 107. 1.113 25.67	Mg 145. 1.51 34.7	←————— kJ/mol —————→												Al 327. 3.39 78.1	Si 446. 4.63 106.7	P 331. 3.43 79.16	S 275. 2.85 65.75	Cl 135. 1.40 32.2	Ar 7.74 0.080 1.85																										
←————— eV/atom —————→																																													
←————— kcal/mol —————→																																													
K 90.1 0.934 21.54	Ca 178. 1.84 42.5	Sc 376 3.90 89.9	Ti 468. 4.85 111.8	V 512. 5.31 122.4	Cr 395. 4.10 94.5	Mn 282. 2.92 67.4	Fe 413. 4.28 98.7	Co 424. 4.39 101.3	Ni 428. 4.44 102.4	Cu 336. 3.49 80.4	Zn 130 1.35 31.04	Ga 271. 2.81 64.8	Ge 372 3.85 88.8	As 285.3 2.96 68.2	Se 237 2.46 56.7	Br 118. 1.22 28.18	Kr 11.2 0.116 2.68																												
Rb 82.2 0.852 19.64	Sr 166 1.72 39.7	Y 422 4.37 100.8	Zr 603. 6.25 144.2	Nb 730. 7.57 174.5	Mo 658 6.82 157.2	Tc 661. 6.85 158.	Ru 650. 6.74 155.4	Rh 554. 5.75 132.5	Pd 376. 3.89 89.8	Ag 284. 2.95 68.0	Cd 112 1.16 26.73	In 243. 2.52 58.1	Sn 303. 3.14 72.4	Sb 265. 2.75 63.4	Te 211 2.19 50.34	I 107. 1.11 25.62	Xe 15.9 0.16 3.80																												
Cs 77.6 0.804 18.54	Ba 183. 1.90 43.7	La 431. 4.47 103.1	Hf 621. 6.44 148.4	Ta 782. 8.10 186.9	W 859. 8.90 205.2	Re 775. 8.03 185.2	Os 788. 8.17 188.4	Ir 670. 6.94 160.1	Pt 564. 5.84 134.7	Au 368. 3.81 87.96	Hg 65. 0.67 15.5	Tl 182. 1.88 43.4	Pb 196. 2.03 46.78	Bi 210. 2.18 50.2	Po 144. 1.50 34.5	At	Rn 19.5 0.202 4.66																												
Fr	Ra 160. 1.66 38.2	Ac 410. 4.25 98.	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td>Ce 417. 4.32 99.7</td> <td>Pr 357. 3.70 85.3</td> <td>Nd 328. 3.40 78.5</td> <td>Pm</td> <td>Sm 206 2.14 49.3</td> <td>Eu 179. 1.86 42.8</td> <td>Gd 400. 4.14 95.5</td> <td>Tb 391. 4.05 93.4</td> <td>Dy 294. 3.04 70.2</td> <td>Ho 302. 3.14 72.3</td> <td>Er 317. 3.29 75.8</td> <td>Tm 233. 2.42 55.8</td> <td>Yb 154. 1.60 37.1</td> <td>Lu 428 4.43 102.2</td> </tr> <tr> <td>Th 598. 6.20 142.9</td> <td>Pa</td> <td>U 536. 5.65 128.</td> <td>Np 456 4.73 109.</td> <td>Pu 347. 3.60 83.0</td> <td>Am 264. 2.73 63</td> <td>Cm 385 3.99 92.1</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lr</td> </tr> </table>															Ce 417. 4.32 99.7	Pr 357. 3.70 85.3	Nd 328. 3.40 78.5	Pm	Sm 206 2.14 49.3	Eu 179. 1.86 42.8	Gd 400. 4.14 95.5	Tb 391. 4.05 93.4	Dy 294. 3.04 70.2	Ho 302. 3.14 72.3	Er 317. 3.29 75.8	Tm 233. 2.42 55.8	Yb 154. 1.60 37.1	Lu 428 4.43 102.2	Th 598. 6.20 142.9	Pa	U 536. 5.65 128.	Np 456 4.73 109.	Pu 347. 3.60 83.0	Am 264. 2.73 63	Cm 385 3.99 92.1	Bk	Cf	Es	Fm	Md	No	Lr
Ce 417. 4.32 99.7	Pr 357. 3.70 85.3	Nd 328. 3.40 78.5	Pm	Sm 206 2.14 49.3	Eu 179. 1.86 42.8	Gd 400. 4.14 95.5	Tb 391. 4.05 93.4	Dy 294. 3.04 70.2	Ho 302. 3.14 72.3	Er 317. 3.29 75.8	Tm 233. 2.42 55.8	Yb 154. 1.60 37.1	Lu 428 4.43 102.2																																
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$$1 \frac{\text{eV}}{\text{atom}} = 96.4853 \frac{\text{kJ}}{\text{mol}}$$



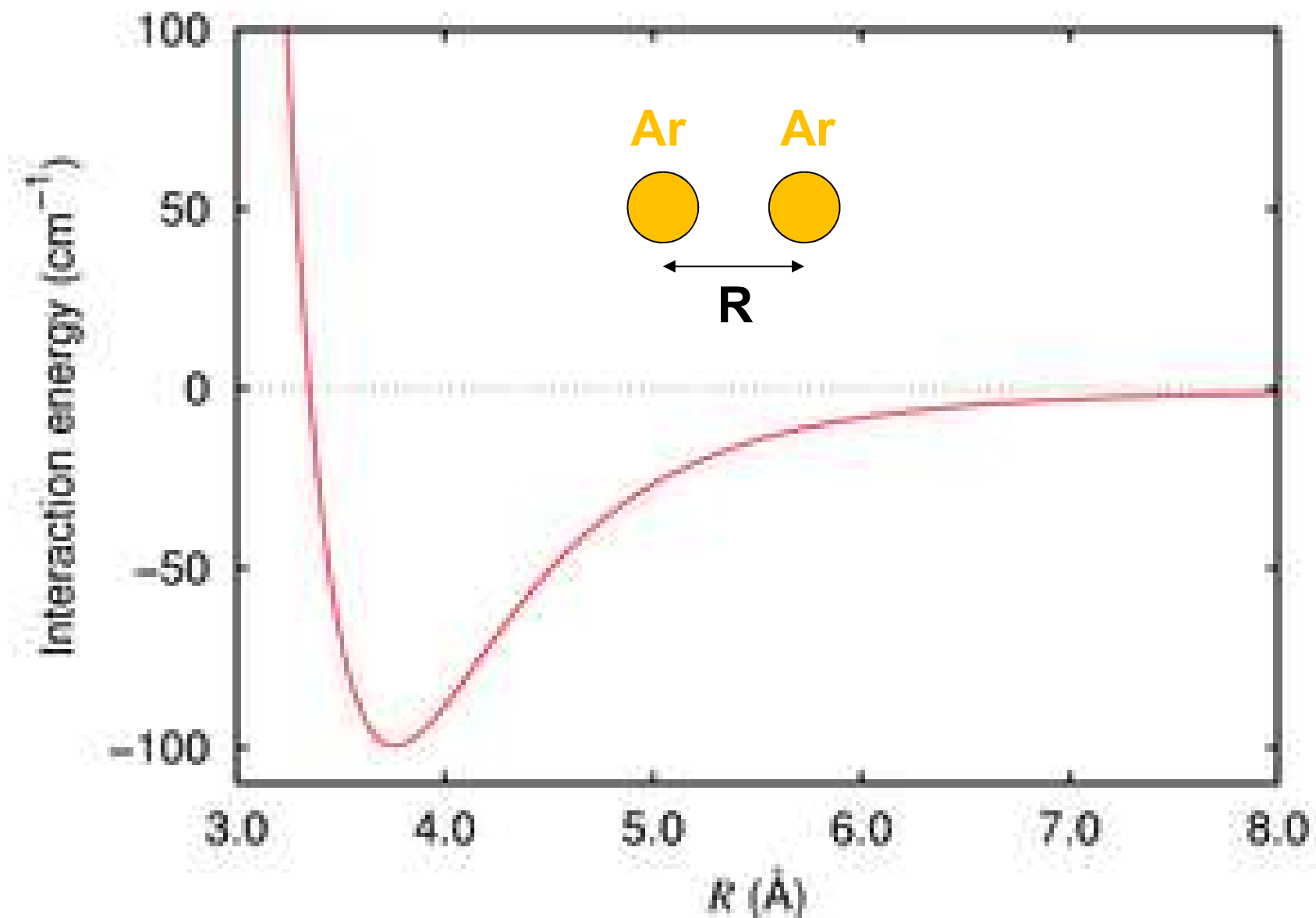
Type of Bonding	Description	Typical of which compounds	Typical Properties
Ionic	Electron is transferred from one atom to another, and the resulting ions attract each other.	Binary compounds made of constituents with very different electronegativity: e.g., group I-VII compounds such as NaCl.	<ul style="list-style-type: none"> • Hard, very brittle • High melting temperature • Electrical insulator • Water soluble
Covalent	Electron is shared between two atoms forming a bond. Energy lowered by delocalization of wavefunction.	Compounds made of constituents with similar electronegativities (e.g., III-V compounds such as GaAs), or solids made of one element only such as diamond (C).	<ul style="list-style-type: none"> • Very hard (brittle) • High melting temperature • Electrical insulators or semiconductors
Metallic	Electrons are delocalized throughout the solid forming a glue between positive ions.	Metals. Left and middle of periodic table.	<ul style="list-style-type: none"> • Ductile, malleable (due to non-directional nature of bond). Can be hardened by adding certain impurities. • Lower melting temperature • Good electrical and thermal conductors
Molecular (van der Waals, fluctuating dipole)	No transfer of electrons. Dipole moments on constituents align to cause attraction. Bonding strength increases with size of molecule or polarity of constituent.	Noble gas solids, solids made of non-polar (or slightly polar) molecules binding to each other (wax).	<ul style="list-style-type: none"> • Soft, weak • Low melting temperature • Electrical insulators
Hydrogen	Involves hydrogen ion bound to one atom but still attracted to another. Special case because H is so small.	Important in organic and biological materials. Holds together ice.	<ul style="list-style-type: none"> • Weak bond (stronger than vdW though) • Important for maintaining shape of DNA and proteins

Concentrémonos en los gases nobles



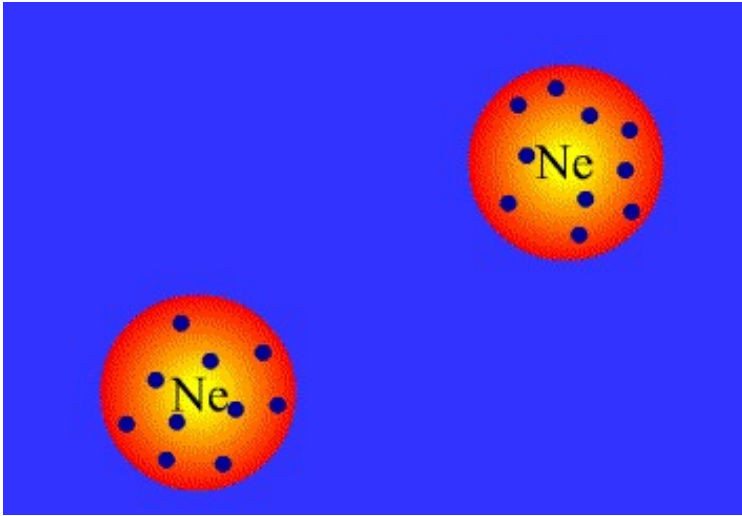
Forman cristales
con estructura fcc

Fuerza responsable de la
cohesión de un gas noble???



Energía de interacción del dímero de argón

Interacción de van der Waals



dipolo inducido – dipolo inducido



Johannes van der Waals

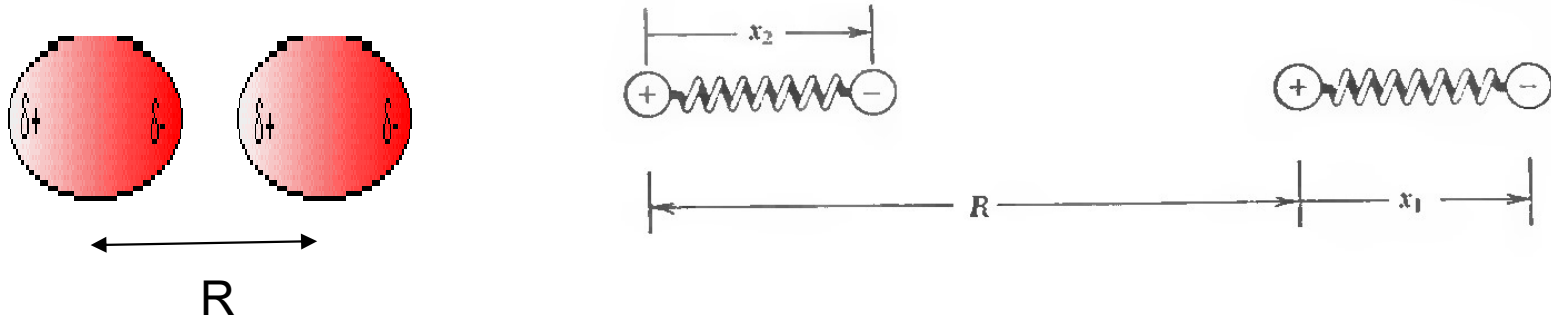
Potencial atractivo de origen cuántico

$$V(R) \sim 1/R^6$$

Potential entre dos dipolos inducidos:

$$V(R) \sim -p_2 E = -\alpha E^2 = -\frac{C}{R^6}$$

Modelo cuántico para la interacción de VdW (Probl. 1)



$$\mathcal{H}_0 = \frac{1}{2m} p_1^2 + \frac{1}{2} C x_1^2 + \frac{1}{2m} p_2^2 + \frac{1}{2} C x_2^2$$

$$\mathcal{H}_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2}$$

Aproximación $|x_1|, |x_2| \ll R \implies \mathcal{H}_1 \cong -\frac{2e^2 x_1 x_2}{R^3}$

Dos osciladores armónicos acoplados

\mathcal{H} se puede diagonalizar con una transformación a modos normales

$$x_s \equiv \frac{1}{\sqrt{2}}(x_1 + x_2) ; \quad x_a \equiv \frac{1}{\sqrt{2}}(x_1 - x_2)$$

Despejando x_1 y x_2

$$x_1 = \frac{1}{\sqrt{2}}(x_s + x_a) ; \quad x_2 = \frac{1}{\sqrt{2}}(x_s - x_a) .$$

$$p_1 \equiv \frac{1}{\sqrt{2}}(p_s + p_a) ; \quad p_2 \equiv \frac{1}{\sqrt{2}}(p_s - p_a)$$

Reemplazando en \mathcal{H}

$$\mathcal{H} = \left[\frac{1}{2m} p_s^2 + \frac{1}{2} \left(C - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[\frac{1}{2m} p_a^2 + \frac{1}{2} \left(C + \frac{2e^2}{R^3} \right) x_a^2 \right]$$

Dos osciladores armónicos desacoplados

Las frecuencias solución son:

$$\omega = \left[\left(C \pm \frac{2e^2}{R^3} \right) / m \right]^{1/2} \cong \omega_0 \left[1 \pm \frac{1}{2} \left(\frac{2e^2}{CR^3} \right) - \frac{1}{8} \left(\frac{2e^2}{CR^3} \right)^2 + \dots \right]$$

donde $\omega_0 = (C/m)^{1/2}$

La energía de punto cero del sistema es $\frac{1}{2}\hbar(\omega_s + \omega_a)$

Esta suma es menor al valor correspondiente cuando los dos átomos están infinitamente separados: $2 \cdot \frac{1}{2}\hbar\omega_0$

$$\Delta U = \frac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = -\hbar\omega_0 \cdot \frac{1}{8} \left(\frac{2e^2}{CR^3} \right)^2 = -\frac{A}{R^6} \cdot \text{Interacción atractiva !!}$$

Interacción de van der Waals (conocida también como London, $d_{\text{ind}}-d_{\text{ind}}$)

Origen cuántico : $\Delta U \rightarrow 0$ cuando $\hbar \rightarrow 0$.

Potencial de Lennard-Jones

$$\phi(r) = -\frac{A}{r^6} + \frac{B}{r^{12}},$$

Potencial atractivo de van der Waals

Potencial repulsivo empírico (Princip. de exclusión)



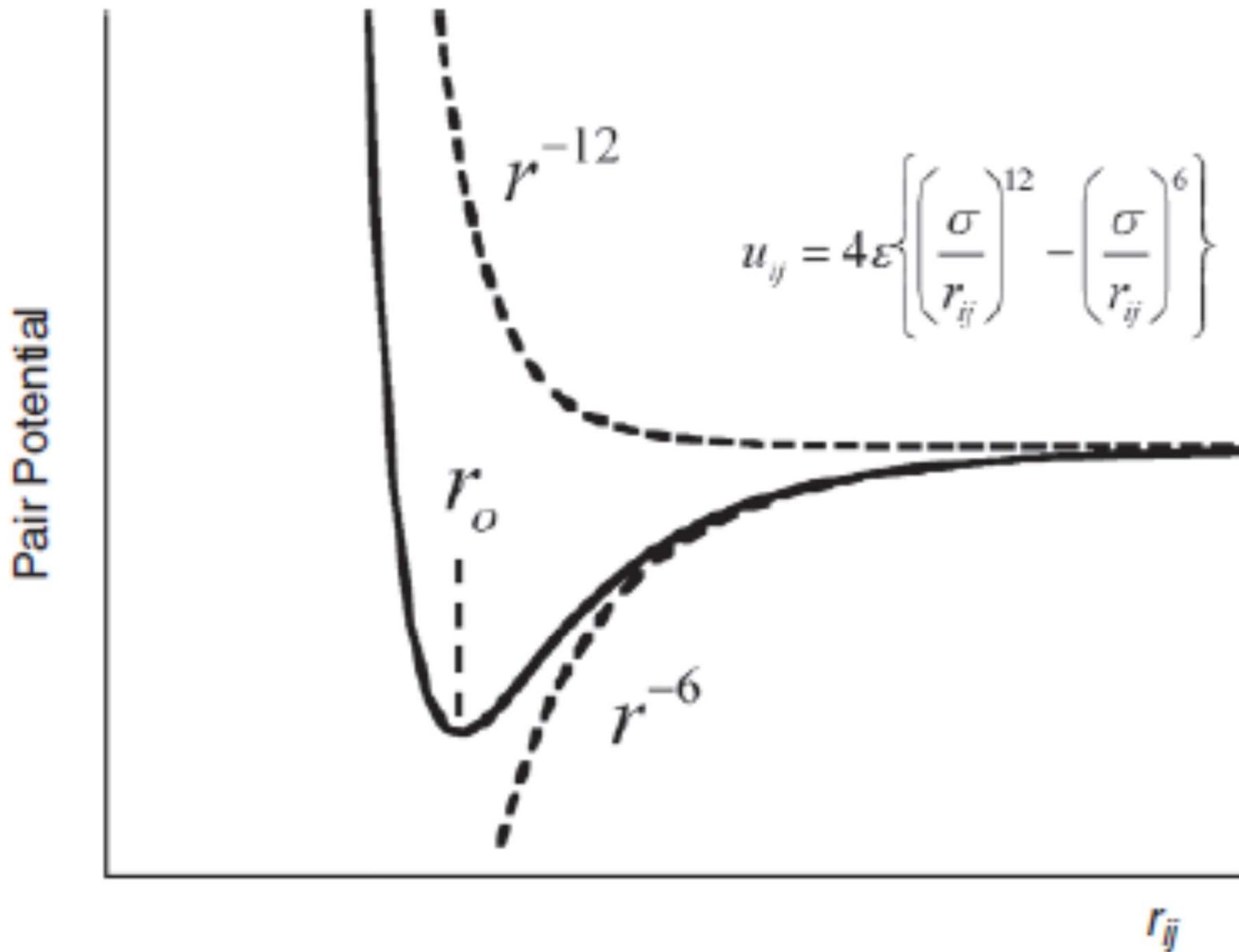
Sir John Edward Lennard-Jones

Se suele expresar de la siguiente manera:

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right],$$

$$\sigma = (B/A)^{1/6},$$

$$\epsilon = A^2/4B,$$



Problema 2: cadena de átomos equiespaciados

Table 20.1

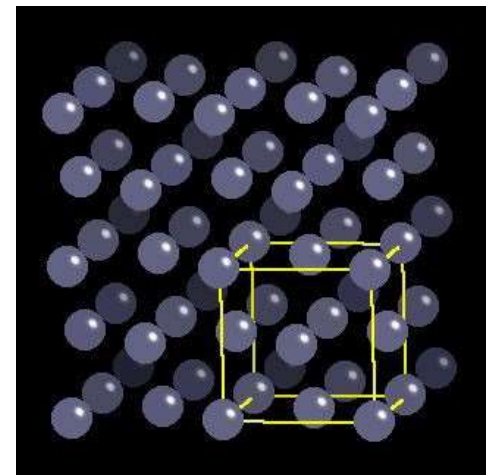
VALUES OF THE LENNARD-JONES PARAMETERS FOR THE NOBLE GASES^a

	Ne	Ar	Kr	Xe
$\epsilon(10^{-13} \text{ erg})$	0.050	0.167	0.225	0.320
$\epsilon(\text{eV})$	0.0031	0.0104	0.0140	0.0200
$\sigma(\text{\AA})$	2.74	3.40	3.65	3.98

^a As deduced from properties of the low-density gases (second virial coefficient).
Source: N. Bernardes, *Phys. Rev.* **112**, 1534 (1958).

Propiedades de los cristales ??

- Constante de red ?
- Energía de cohesión ?
- Modulo de bulk ?



La energía total se puede escribir:

$$E_0 = \sum_{i \neq j} 4\epsilon \left[\left(\frac{\sigma}{p_{ij} r_0} \right)^{12} - \left(\frac{\sigma}{p_{ij} r_0} \right)^6 \right]$$
$$= \frac{1}{2} N 4\epsilon \left[A_{12} \left(\frac{\sigma}{r_0} \right)^{12} - A_6 \left(\frac{\sigma}{r_0} \right)^6 \right],$$

r_0 Distancia primeros vecinos

$$r_{ij} = p_{ij} r_0.$$

$$A_n = \sum_j \left(\frac{1}{p_{ij}} \right)^n$$

Derivando respecto a r_0 e igualando a cero:

$$r_0 = \left(\frac{2A_{12}}{A_6} \right)^{1/6} \sigma.$$

Distancia de equilibrio

$$\epsilon_0 = -\frac{A_6^2}{2A_{12}} \epsilon.$$

Energía por átomo en el equilibrio

$$u = 2\epsilon \left[A_{12} \left(\frac{\sigma}{r} \right)^{12} - A_6 \left(\frac{\sigma}{r} \right)^6 \right], \quad A_n = \sum_{\mathbf{R} \neq 0} \frac{1}{\alpha(\mathbf{R})^n}.$$

THE LATTICE SUMS A_n FOR THE THREE CUBIC BRAVAIS LATTICES^a

n	SIMPLE CUBIC	BODY-CENTERED CUBIC	FACE-CENTERED CUBIC
≤ 3	∞	∞	∞
4	16.53	22.64	25.34
5	10.38	14.76	16.97
6	8.40	12.25	14.45
7	7.47	11.05	13.36
8	6.95	10.36	12.80
9	6.63	9.89	12.49
10	6.43	9.56	12.31
11	6.29	9.31	12.20
12	6.20	9.11	12.13
13	6.14	8.95	12.09
14	6.10	8.82	12.06
15	6.07	8.70	12.04
16	6.05	8.61	12.03
$n \geq 17$	$6 + 12(1/2)^{n/2}$	$8 + 6(3/4)^{n/2}$	$12 + 6(1/2)^{n/2}$

Para una red FCC: $A_6 = 14.4539$ $A_{12} = 12.1319$

$$r_0 = \left(\frac{2A_{12}}{A_6} \right)^{1/6} \sigma \quad \Rightarrow \quad r_0 = 1.09 \sigma$$

$$\epsilon_0 = -\frac{A_6^2}{2A_{12}} \epsilon \quad \Rightarrow \quad \epsilon_0 = -8.61 \epsilon$$

$$B = -V(\partial P / \partial V)_T \quad ?$$

$$B = -V(\partial P/\partial V)_T$$

$$P = -dU/dV,$$

$$B = v \frac{\partial}{\partial v} \left(\frac{\partial u}{\partial v} \right).$$

$$u = U/N \quad v = V/N$$

in a fcc lattice is $v = a^3/4$,

$$a = \sqrt{2}r.$$

$$v = \frac{r^3}{\sqrt{2}}, \quad \frac{\partial}{\partial v} = \frac{\sqrt{2}}{3r^2} \frac{\partial}{\partial r},$$

$$B = \frac{\sqrt{2}}{9} r \frac{\partial}{\partial r} \frac{1}{r^2} \frac{\partial}{\partial r} u.$$

$$B_0^{\text{th}} = \frac{\sqrt{2}}{9r_0} \frac{\partial^2 u}{\partial r^2} \Big|_{r=r_0} = \frac{4\epsilon}{\sigma^3} A_{12} \left(\frac{A_6}{A_{12}} \right)^{5/2} = \frac{75\epsilon}{\sigma^3}.$$

Para una red FCC: $A_6 = 14.4539$ $A_{12} = 12.1319$

$$r_0 = \left(\frac{2A_{12}}{A_6} \right)^{1/6} \sigma \quad \Rightarrow \quad r_0 = 1.09 \sigma$$

$$\epsilon_0 = -\frac{A_6^2}{2A_{12}} \epsilon \quad \Rightarrow \quad \epsilon_0 = -8.61 \epsilon$$

$$B = -V(\partial P / \partial V)_T \quad \Rightarrow \quad B = \frac{75\epsilon}{\sigma^3}$$

NEAREST-NEIGHBOR DISTANCE r_0 , COHESIVE ENERGY u_0 , AND BULK MODULUS B_0 AT ZERO PRESSURE FOR THE SOLID NOBLE GASES^a

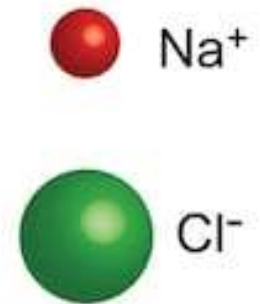
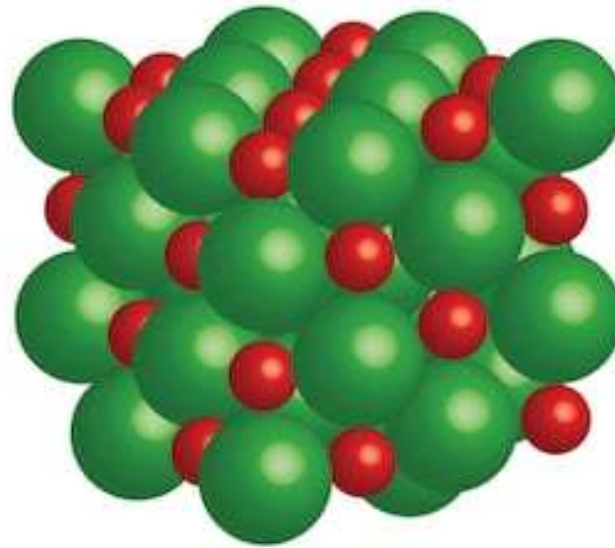
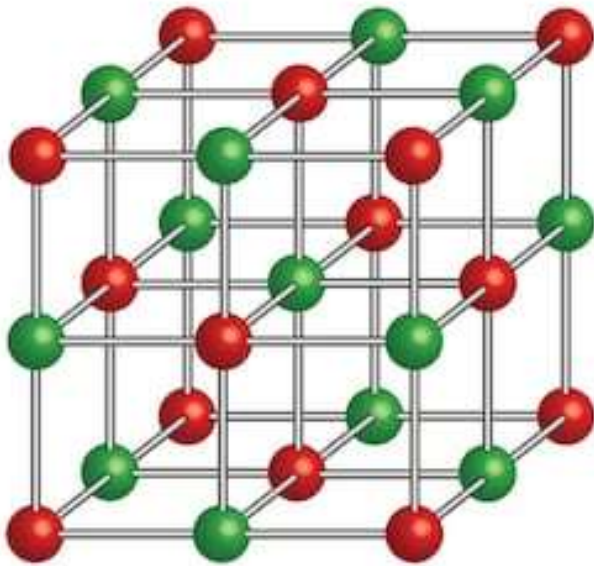
		Ne	Ar	Kr	Xe
r_0 (angstroms)	(Experiment)	3.13	3.75	3.99	4.33
$r_0 = 1.09\sigma$	(Theory)	2.99	3.71	3.98	4.34
u_0 (eV/atom)	(Experiment)	-0.02	-0.08	-0.11	-0.17
$u_0 = -8.6\epsilon$	(Theory)	-0.027	-0.089	-0.120	-0.172
B_0 (10^{10} dyne/cm ²) ^b	(Experiment)	1.1	2.7	3.5	3.6
$B_0 = 75\epsilon/\sigma^3$	(Theory)	1.81	3.18	3.46	3.81

^a The theoretical values are those calculated from the elementary classical theory.

^b One atmosphere of pressure = 1.01×10^6 dynes/cm²; 1 bar of pressure = 10^6 dynes/cm².

Source: Data quoted by M. L. Klein, G. K. Horton, and J. L. Feldman, *Phys. Rev.* **184**, 968 (1969); D. N. Batchelder, et al., *Phys. Rev.* **162**, 767 (1967); E. R. Dobbs and G. O. Jones, *Rep. Prog. Phys.* **xx**, 516 (1957).

Compuestos iónicos



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$$E = \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|} = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j \tilde{e}^2}{|R_i - R_j|}$$

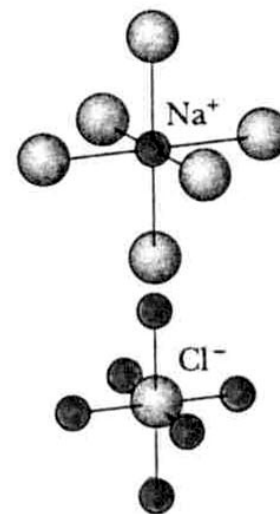
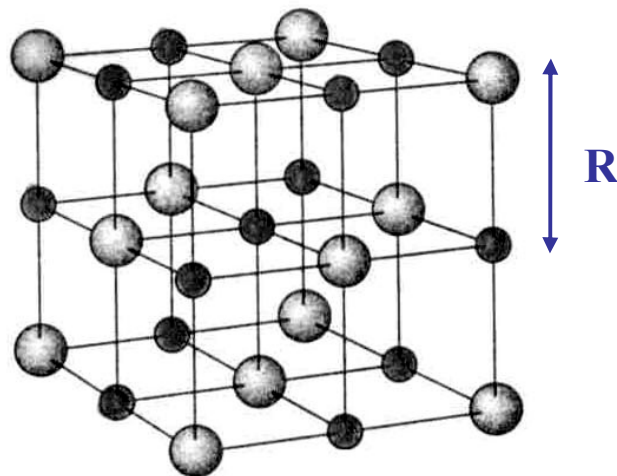
Energía de Madelung

$$U_{\text{tot}} = NU_i \longrightarrow U_i = \sum_j' U_{ij}$$

N moléculas
2N iones

$$U_{ij} = \begin{cases} \lambda \exp(-R/\rho) - \frac{q^2}{R} & \text{(nearest neighbors)} \\ \pm \frac{1}{p_{ij}} \frac{q^2}{R} & \text{(otherwise).} \end{cases}$$

Potencial de Born-Mayer



Na⁺ y Cl⁻ tienen 6 primeros vecinos

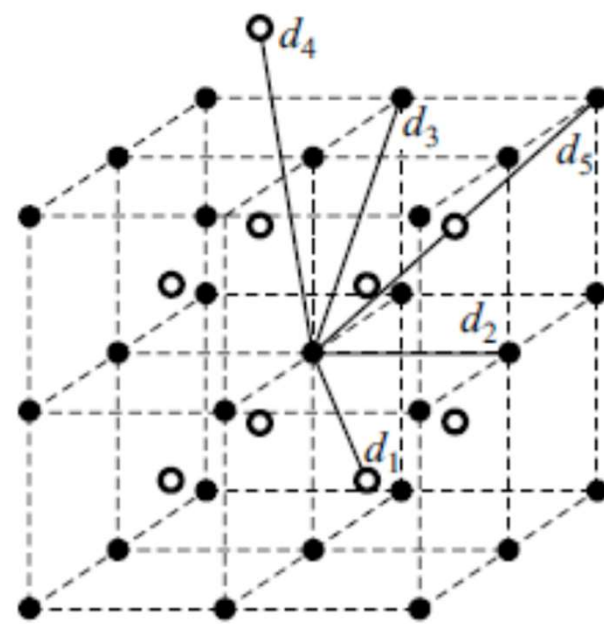
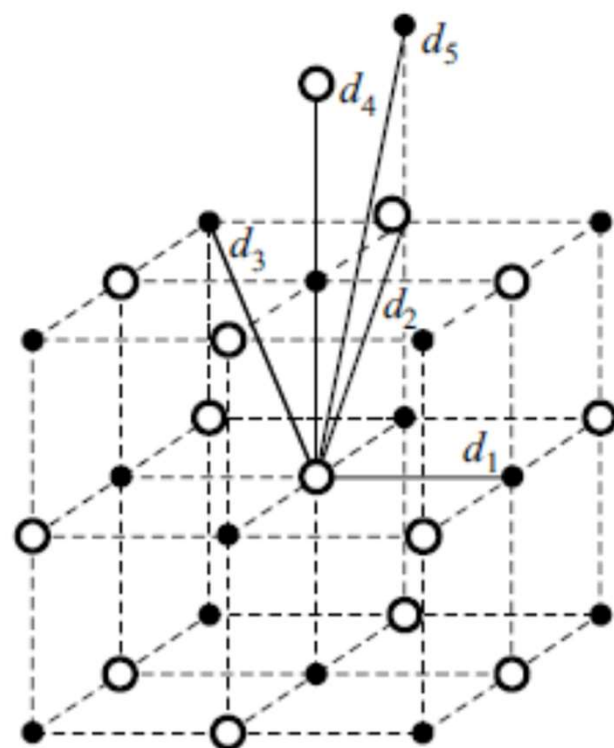
$$U_{\text{tot}} = NU_i = N \left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R} \right)$$

Donde $z.$ es el número de primeros vecinos

$$\alpha \equiv \sum_j' \frac{(\pm)}{p_{ij}}$$

Constante de Madelung

CRYSTAL STRUCTURE	MADDELUNG CONSTANT α
Cesium chloride	1.7627
Sodium chloride	1.7476
Zincblende	1.6381



$$\epsilon_{\text{Na}^+} = -\frac{\tilde{e}^2}{a} \left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} + \dots \right],$$

$$\epsilon_{\text{Cs}^+} = -\frac{\tilde{e}^2}{2a} \left[\frac{2}{\sqrt{3}} 8 - 6 - \frac{12}{\sqrt{2}} + \frac{2}{\sqrt{11}} 16 - \frac{8}{\sqrt{3}} + \dots \right].$$

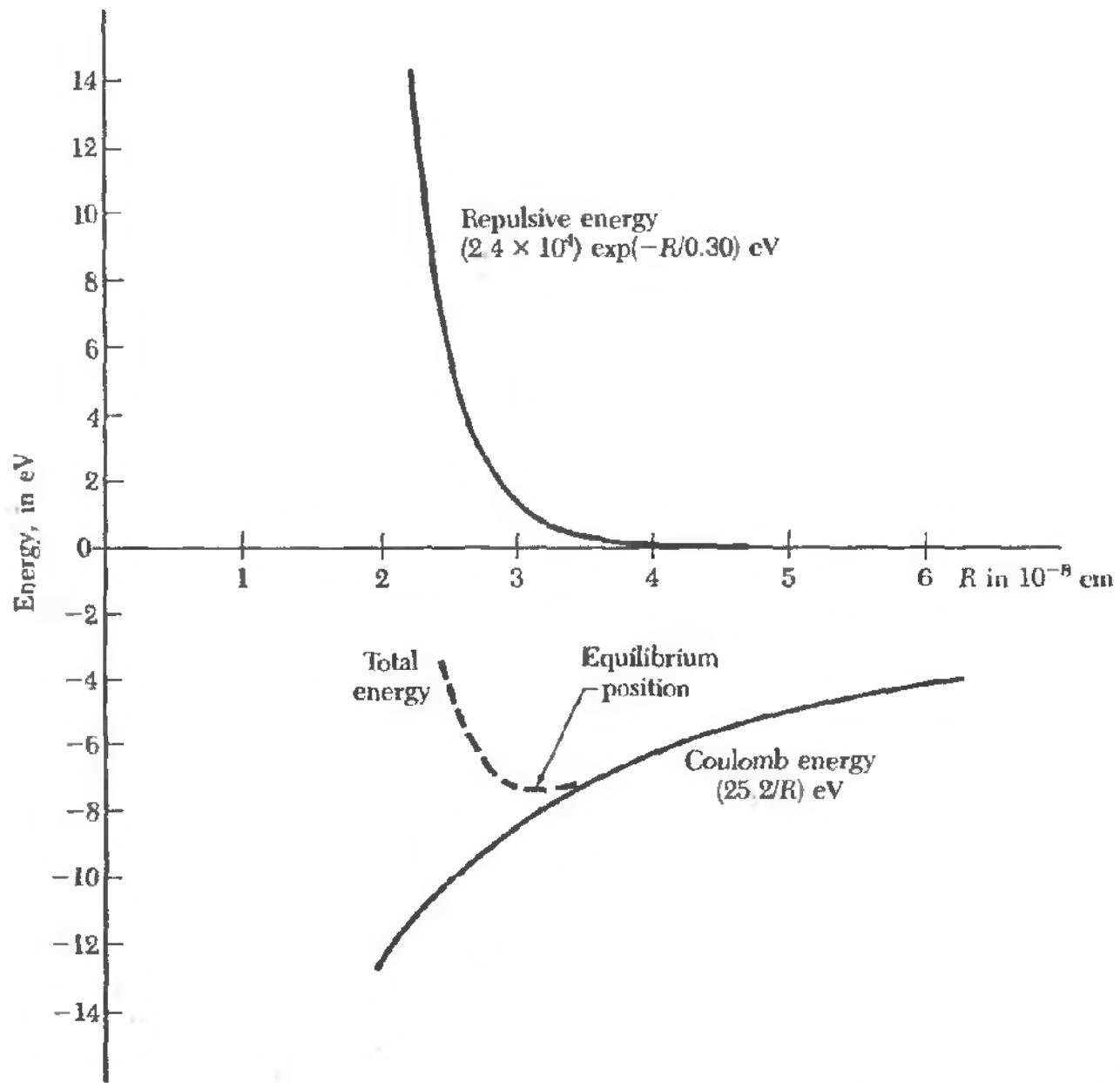


Figure 10 Energy per molecule of KCl crystal, showing Madelung and repulsive contributions.

$$U_{\text{tot}} = NU_i = N \left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R} \right)$$

$$N \frac{dU_i}{dR} = -\frac{Nz\lambda}{\rho} \exp(-R/\rho) + \frac{N\alpha q^2}{R^2} = 0$$

$$R_0^2 \exp(-R_0/\rho) = \rho\alpha q^2 / z\lambda \longrightarrow R_0$$

separación de equilibrio

$$U_{\text{tot}} = -\frac{N\alpha q^2}{R_0} \left(1 - \frac{\rho}{R_0} \right)$$

Energía total de la red

$$-N\alpha q^2 / R_0$$

Energía de Madelung

Table 7 Properties of alkali halide crystals with the NaCl structure

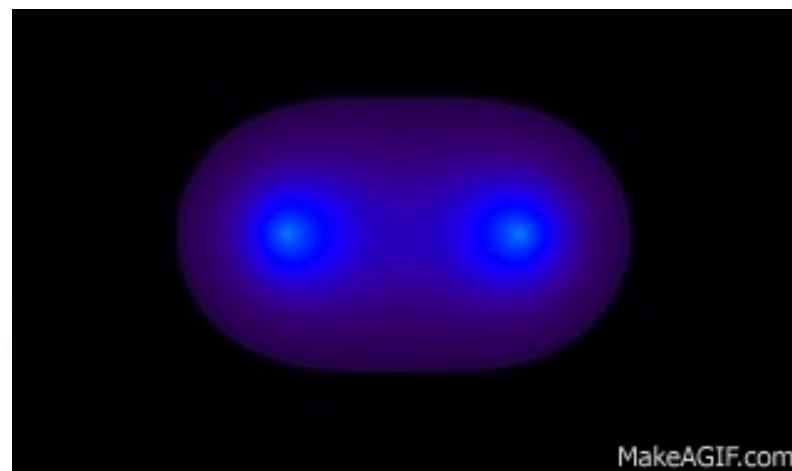
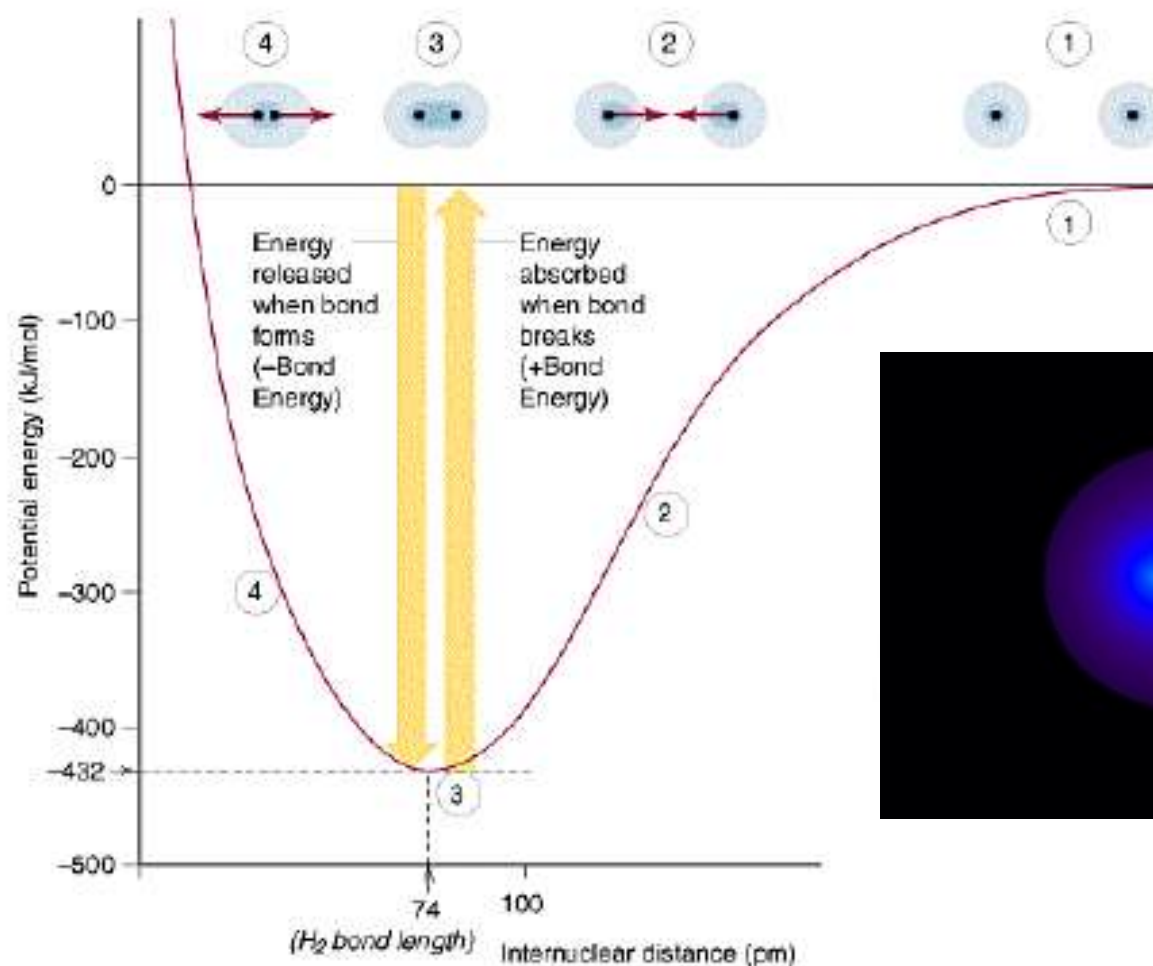
All values (except those in brackets) at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero. Values in brackets at absolute zero temperature and zero pressure, from private communication by L. Brewer.

	Nearest-neighbor separation R_0 , in Å	Bulk modulus B , in 10^{11} dyn/cm ² or 10^{10} N/m ²	Repulsive energy parameter $z\lambda$, in 10^{-8} erg	Repulsive range parameter ρ , in Å	Lattice energy compared to free ions, in kcal/mol	
					Experimental	Calculated
LiF	2.014	6.71	0.296	0.291	242.3[246.8]	242.2
LiCl	2.570	2.98	0.490	0.330	198.9[201.8]	192.9
LiBr	2.751	2.38	0.591	0.340	189.8	181.0
LiI	3.000	(1.71)	0.599	0.366	177.7	166.1
NaF	2.317	4.65	0.641	0.290	214.4[217.9]	215.2
NaCl	2.820	2.40	1.05	0.321	182.6[185.3]	178.6
NaBr	2.989	1.99	1.33	0.328	173.6[174.3]	169.2
NaI	3.237	1.51	1.58	0.345	163.2[162.3]	156.6
KF	2.674	3.05	1.31	0.298	189.8[194.5]	189.1
KCl	3.147	1.74	2.05	0.326	165.8[169.5]	161.6
KBr	3.298	1.48	2.30	0.336	158.5[159.3]	154.5
KI	3.533	1.17	2.85	0.348	149.9[151.1]	144.5
RbF	2.815	2.62	1.78	0.301	181.4	180.4
RbCl	3.291	1.56	3.19	0.323	159.3	155.4
RbBr	3.445	1.30	3.03	0.338	152.6	148.3
RbI	3.671	1.06	3.99	0.348	144.9	139.6

Data from various tables by M. P. Tosi, Solid state physics 16, 1 (1964).

Enlace covalente

El enlace covalente se debe a la compartición de electrones, que experimentan simultáneamente atracciones de aproximadamente la misma magnitud, por dos o más átomos, la cual rebaja la energía y hace, por consiguiente, que el sistema resultante sea más estable que los átomos por separado.



Introducción a la estructura electrónica de moléculas y clusters

Porqué ?

Estructura electrónica

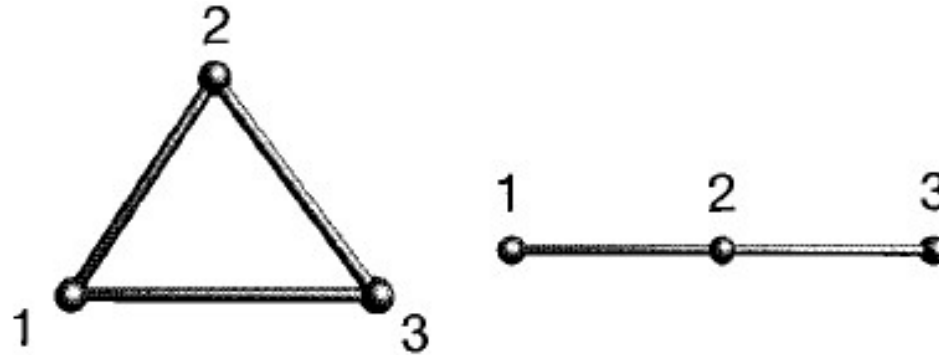


Propiedades del sistema

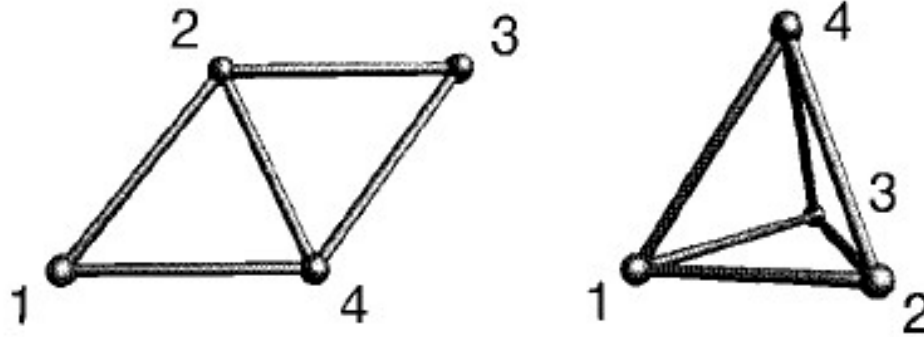
- ✧ **Estructura (molecular, cristalina)**
- ✧ **Propiedades:**
 - químicas
 - eléctricas
 - térmicas
 - magnéticas
 - ópticas

Ej.1 : estructura moléculas o clusters

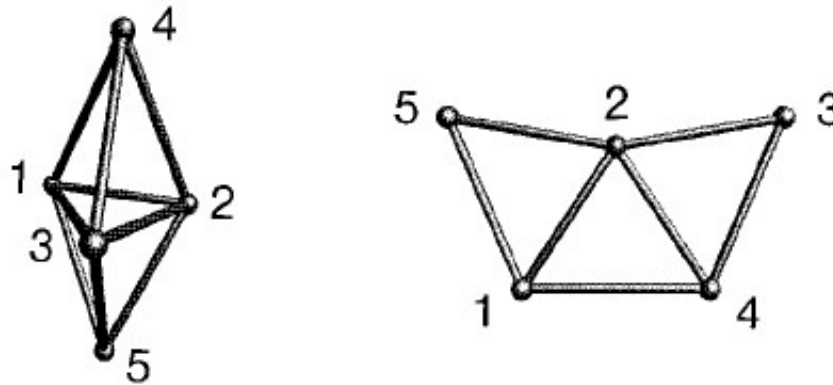
Li_3



Li_4



Li_5



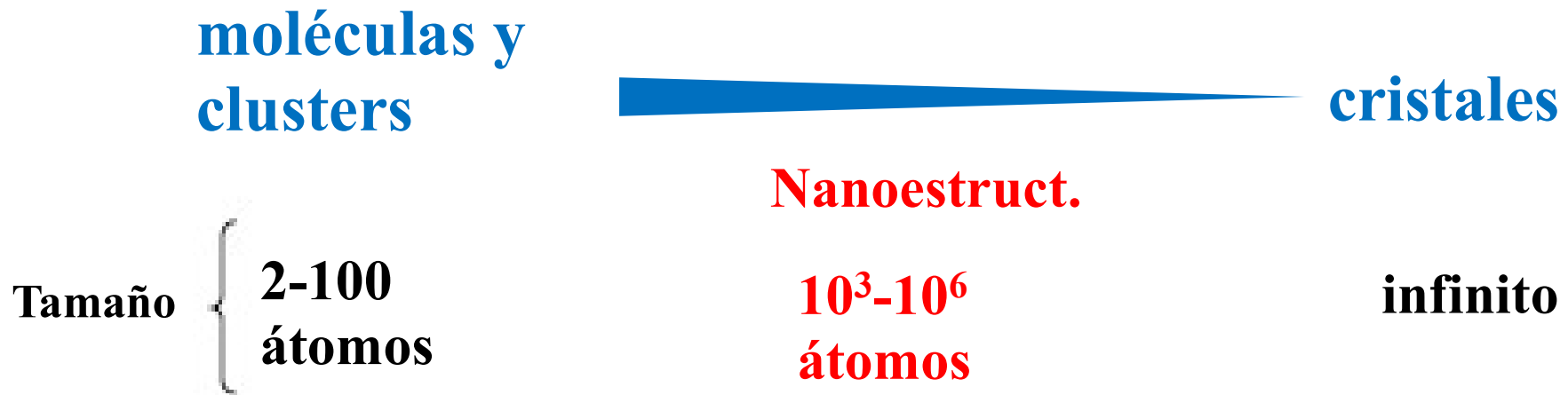
?

Ej.2 : el color de nanopartículas



Objetivo:

Brindar un panorama de la estructura electrónica de moléculas y clusters



Desde un punto de vista fundamental, se debe resolver el siguiente problema para obtener los niveles de energía de los electrones en una molécula, nanopartícula o en un cristal:

$$H\Psi = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 \Psi - Ze^2 \sum_{\mathbf{R}} \frac{1}{|\mathbf{r}_i - \mathbf{R}|} \Psi \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi = E\Psi.$$

Donde N: número de electrones

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \dots, \mathbf{r}_N s_N)$$

Na: número de átomos

R: posiciones de los núcleos atómicos

En la ecuación anterior se utilizo:

$$M_e \lll M_n \longrightarrow$$

Aproximación adiabática
Born-Oppenheimer
(R parámetro)

Molécula H_2^+ Na=2 N=1 solución exacta

$$\mathcal{H}_1 = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\tilde{e}^2}{|r_1 - R_A|} - \frac{\tilde{e}^2}{|r_1 - R_B|} + \frac{\tilde{e}^2}{|R_A - R_B|}.$$

Molécula H_2 Na=2 N=2 no existe solución exacta

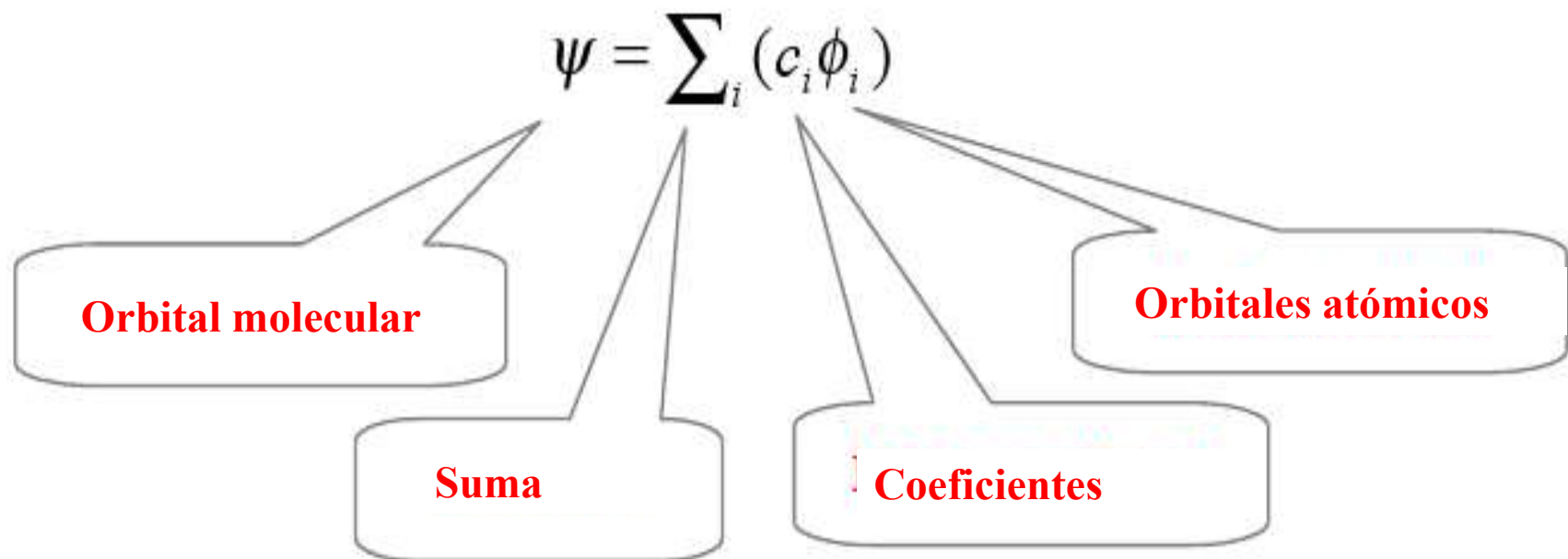
$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \sum_{i=1}^2 \frac{\tilde{e}^2}{|r_i - R_A|} - \sum_{i=1}^2 \frac{\tilde{e}^2}{|r_i - R_B|} + \frac{\tilde{e}^2}{|r_1 - r_2|} + \frac{\tilde{e}^2}{|R_A - R_B|}.$$

Resolución numérica utilizando diferentes aproximaciones.

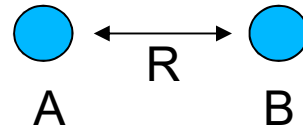
Ejemplos: Hartree-Fock, Teoría del Funcional Densidad (LDA, GGA), etc.

Utilizaremos un método simple que permite entender de manera cualitativa la estructura electrónica de moléculas y clusters (será útil también para extenderlo a cristales).

Orbitales Moleculares (MO) Combinación Lineal de Orbitales Atómicos (LCAO)



Ejemplo : H₂



Orbitales Atómicos

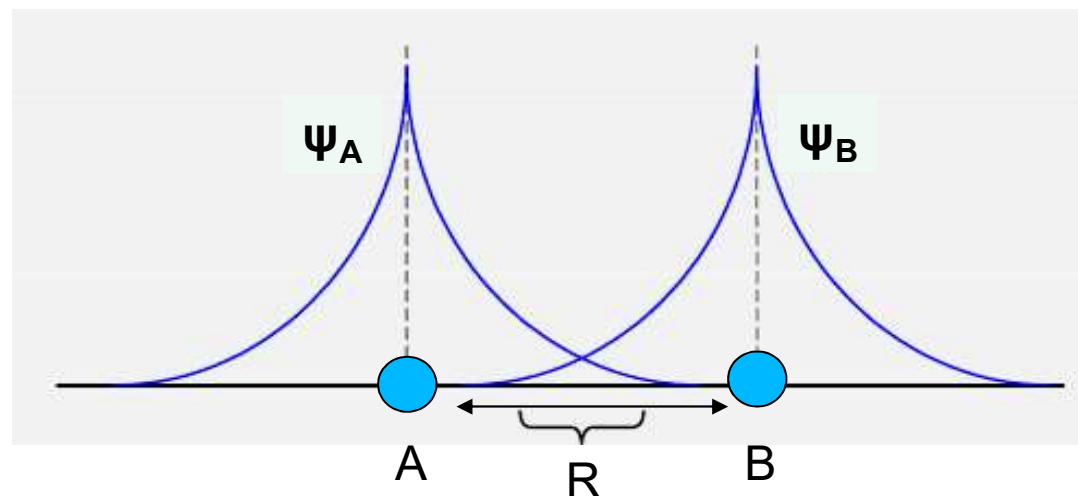


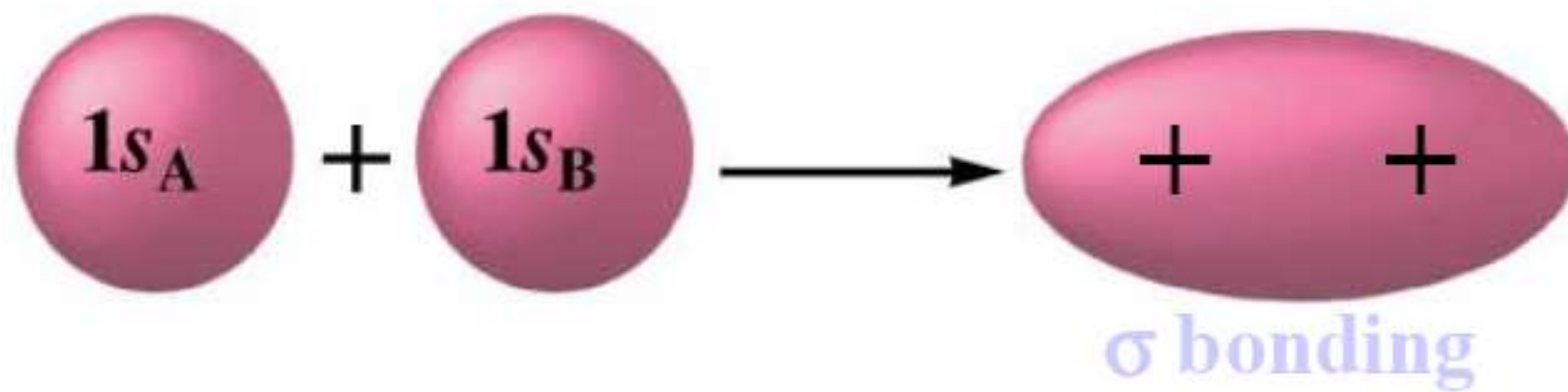
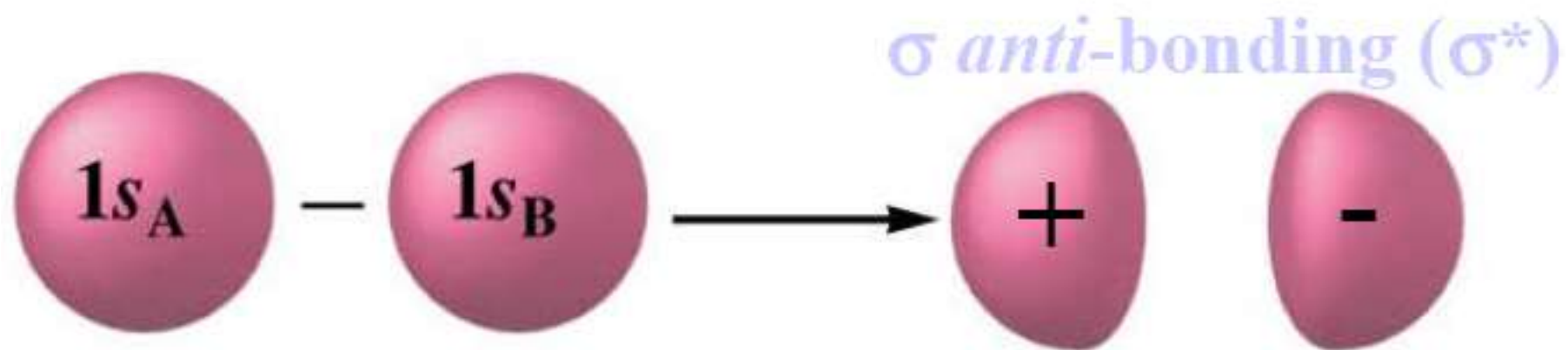
Orbitales Moleculares

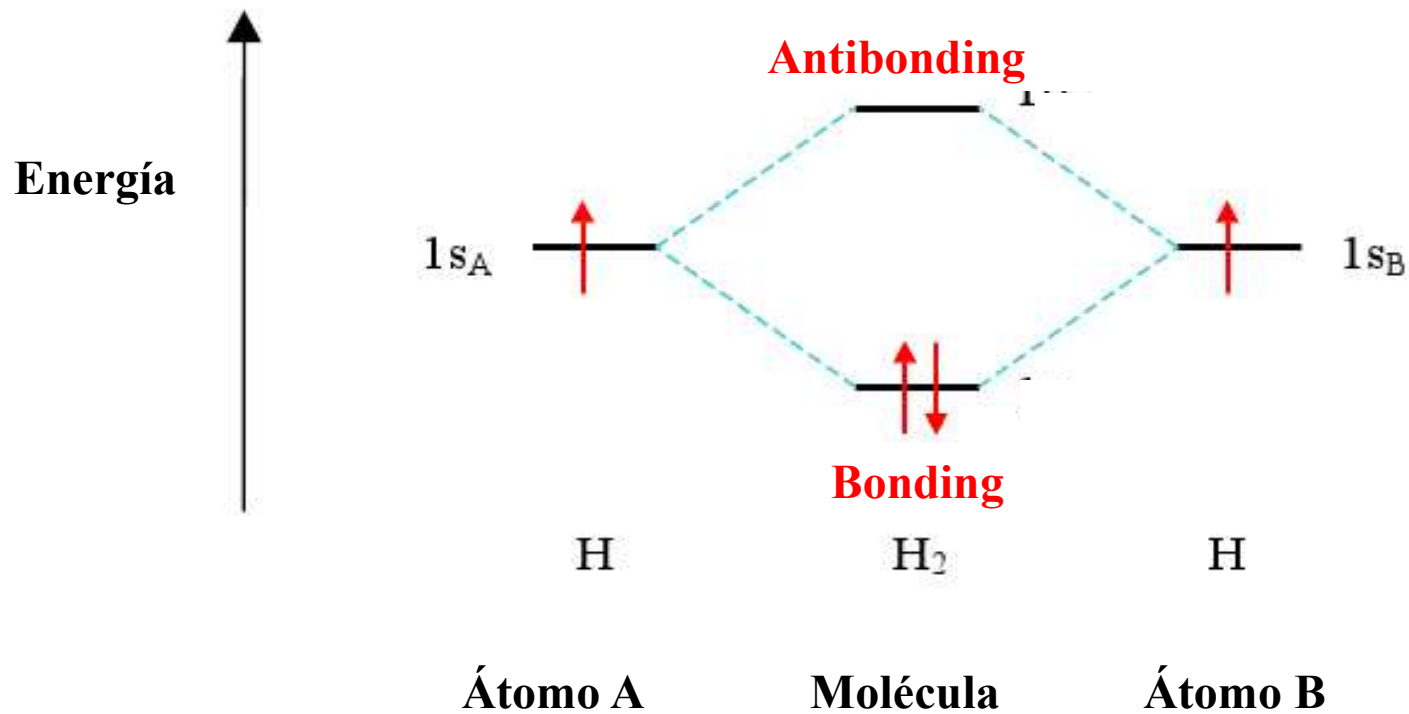
$$\psi_A(r) = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-|\mathbf{r} - \mathbf{R}_A|/a_0}$$

$$\psi = c_A \psi_A + c_B \psi_B$$

$$\psi_B(r) = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-|\mathbf{r} - \mathbf{R}_B|/a_0}$$







Resolveremos de manera detallada el caso de H₂⁺

Notación: utilizaremos subíndices numéricos para los orbitales y sus coeficientes asociados:

$$\psi = c_1\phi_1 + c_2\phi_2 \xrightarrow[\text{brakets}]{\text{Notación Dirac}} |\Psi\rangle = c_1|1\rangle + c_2|2\rangle$$

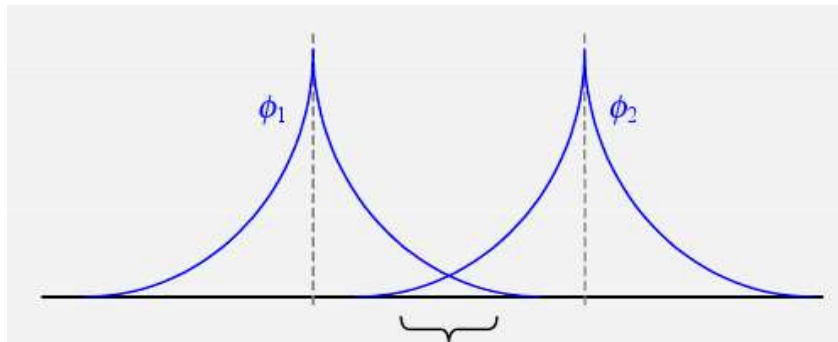
Overlap

$$S = \int \phi_1 \phi_2 \cdot d\tau$$

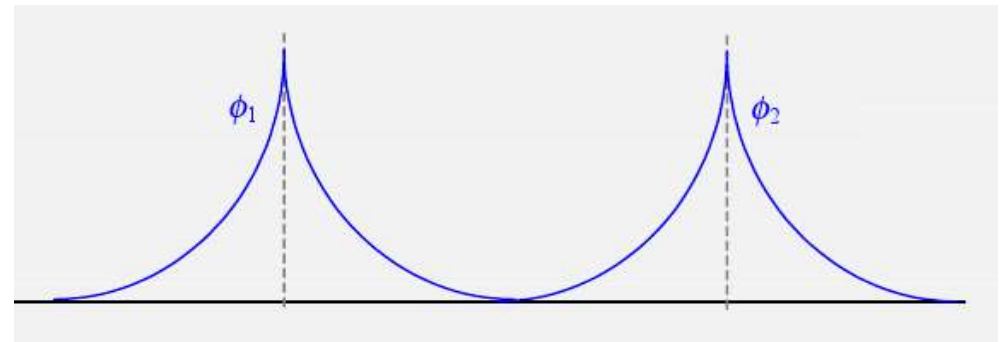
Integral over all space

1s orbital centred on nucleus 1

1s orbital centred on nucleus 2



$$S \neq 0$$



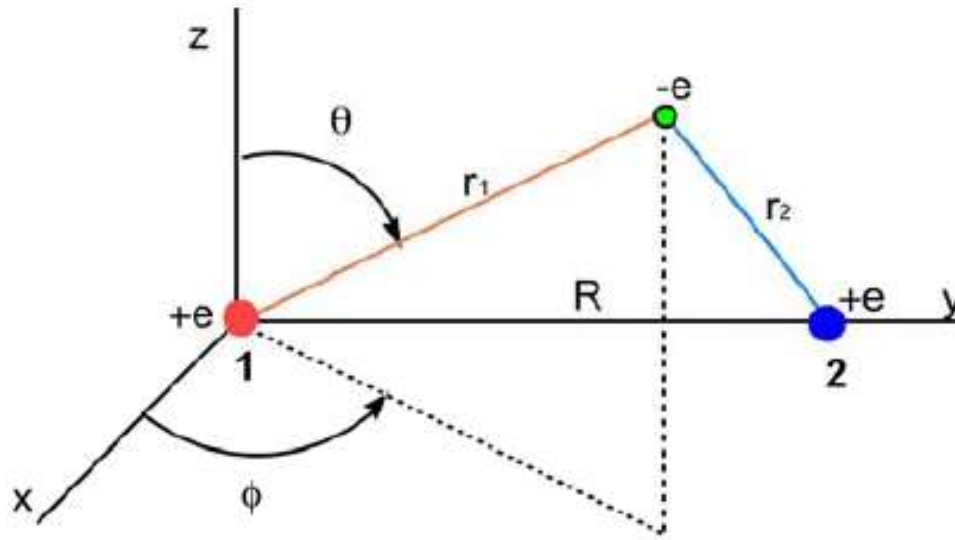
$$S = 0$$

En notación de Dirac $S = \langle 1|2 \rangle$

Tomaremos $S = 0 \rightarrow$ no produce cambios cualitativos en los resultados



$$\mathcal{H}_l = -\frac{\hbar^2}{2m_e} \nabla_l^2 - \frac{e^2}{|r_l - R_A|} - \frac{e^2}{|r_l - R_B|} + \frac{e^2}{|R_A - R_B|}$$



LCAO

$$|\Psi\rangle = c_1|1\rangle + c_2|2\rangle$$

$|1\rangle$ orbital 1s centrado en el núcleo 1

$|2\rangle$ orbital 1s centrado en el núcleo 2

donde:

$$\langle 1|2\rangle = \langle 2|1\rangle = 0 \quad \langle 1|1\rangle = \langle 2|2\rangle = 1$$

$$H|\Psi\rangle = E|\Psi\rangle \quad |\Psi\rangle = c_1|1\rangle + c_2|2\rangle$$

$$H(c_1|1\rangle + c_2|2\rangle) = E(c_1|1\rangle + c_2|2\rangle)$$

Proyecto la ecuación de Schrödinger sobre $|1\rangle$ y $|2\rangle$

$$\left. \begin{aligned} \langle 1|H(c_1|1\rangle + c_2|2\rangle) &= \langle 1|E(c_1|1\rangle + c_2|2\rangle), \\ \langle 2|H(c_1|1\rangle + c_2|2\rangle) &= \langle 2|E(c_1|1\rangle + c_2|2\rangle). \end{aligned} \right\}$$

Llamando $\langle i|H|j\rangle = H_{ij} = \int \phi_i \hat{H} \phi_j d\tau$ y $H_{11} = H_{22} = E_0$

$$\left. \begin{aligned} E_0 c_1 + H_{12} c_2 &= E c_1, \\ H_{21} c_1 + E_0 c_2 &= E c_2. \end{aligned} \right\}$$

$$\left. \begin{aligned} E_0 c_1 + H_{12} c_2 &= E c_1, \\ H_{21} c_1 + E_0 c_2 &= E c_2. \end{aligned} \right\} \longrightarrow \begin{vmatrix} E_0 - E & H_{12} \\ H_{21} & E_0 - E \end{vmatrix} = 0$$

$$E^2 - 2E_0 E + E_0^2 - H_{12} H_{21} = 0$$

$$H_{12} = H_{21} = \beta < 0$$



$$E_b = E_0 + \beta <$$

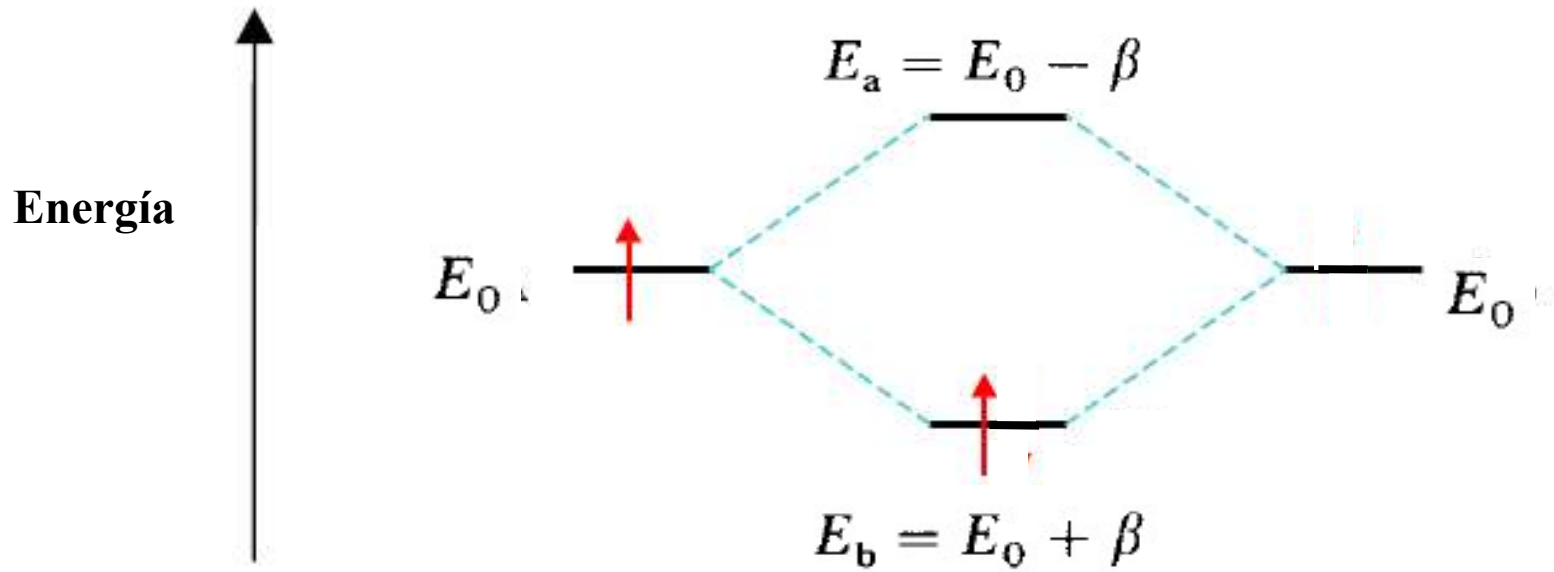
$$E_a = E_0 - \beta$$

$$|\Psi_b\rangle = \frac{1}{(2)^{1/2}} (|1\rangle + |2\rangle)$$

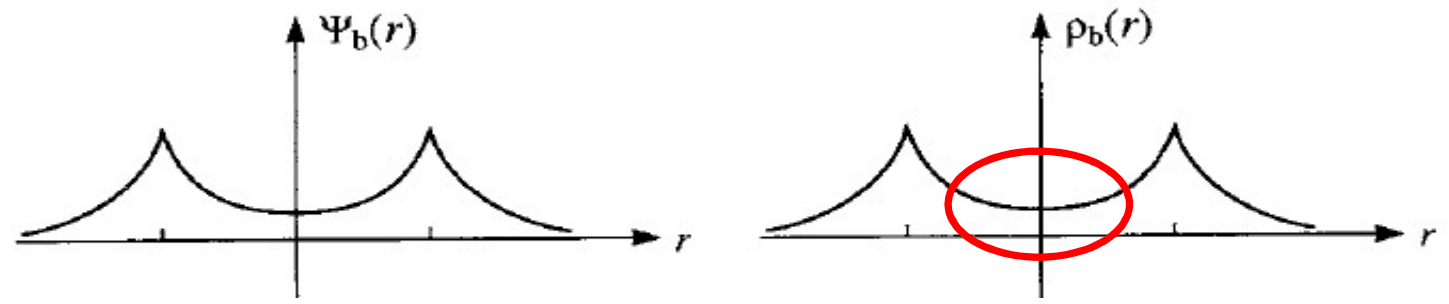
$$|\Psi_a\rangle = \frac{1}{(2)^{1/2}} (|1\rangle - |2\rangle)$$

Bonding

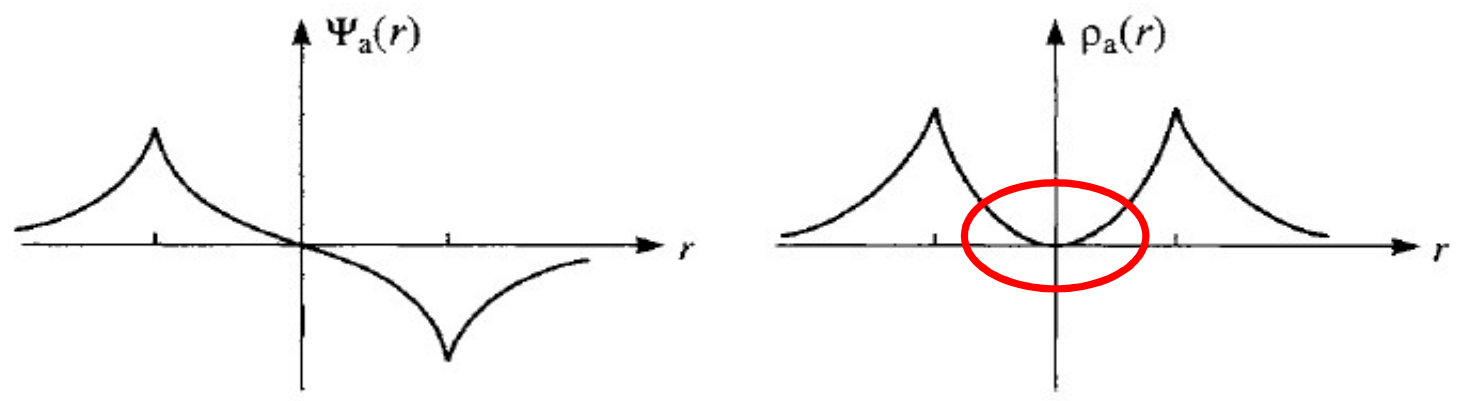
Antibonding



Bonding



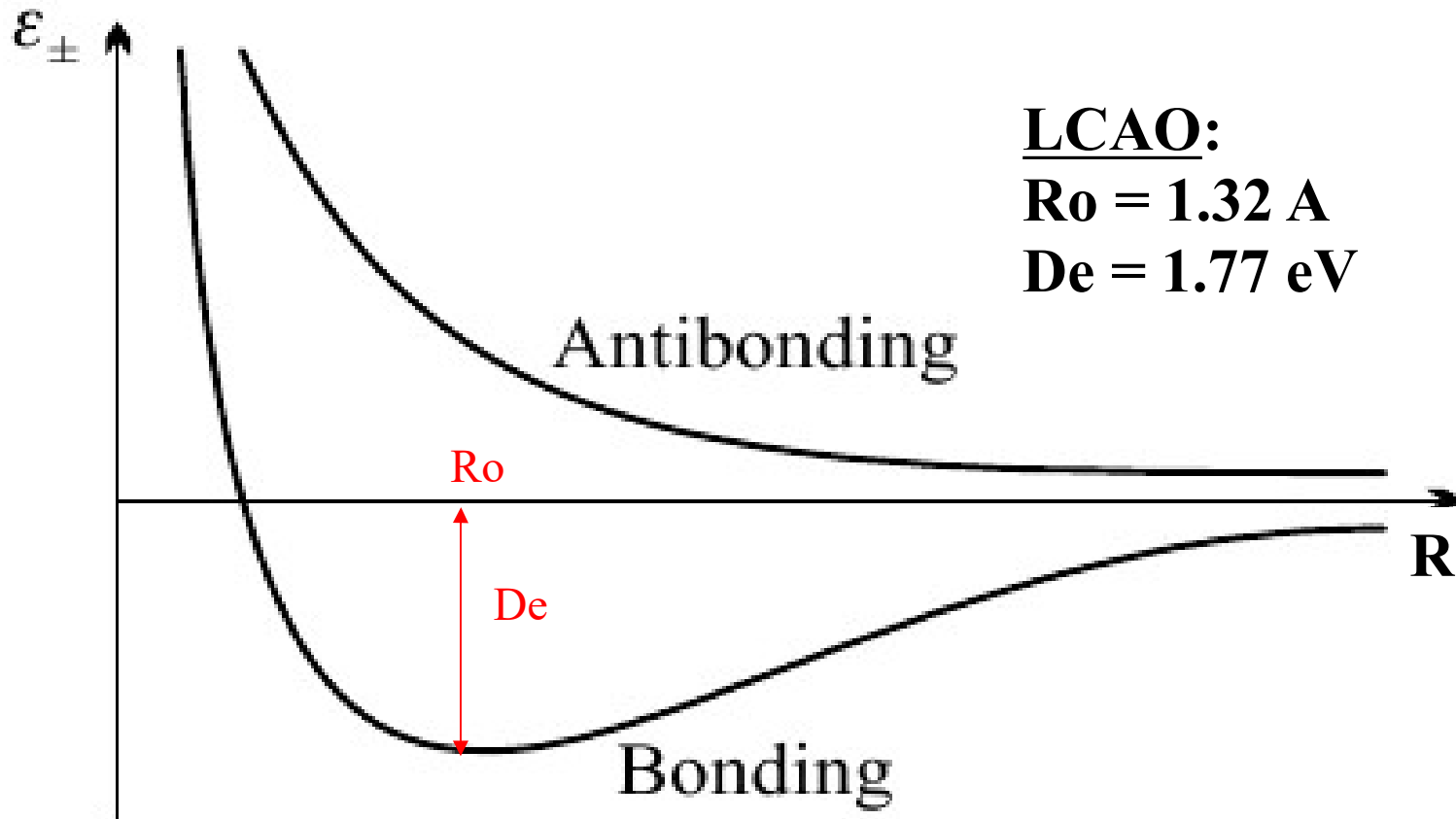
Antibonding



Notemos que

$$H_{12} = H_{21} = \beta(R)$$

$$H_{ij} = \int \phi_i \hat{H} \phi_j \cdot d\tau$$



LCAO:

$$R_0 = 1.32 \text{ \AA}$$

$$D_e = 1.77 \text{ eV}$$

Resultado exacto:

$$R_0 = 1.06 \text{ \AA}$$

$$D_e = 2.79 \text{ eV}$$

LCAO con 1s, 2s y 2p:

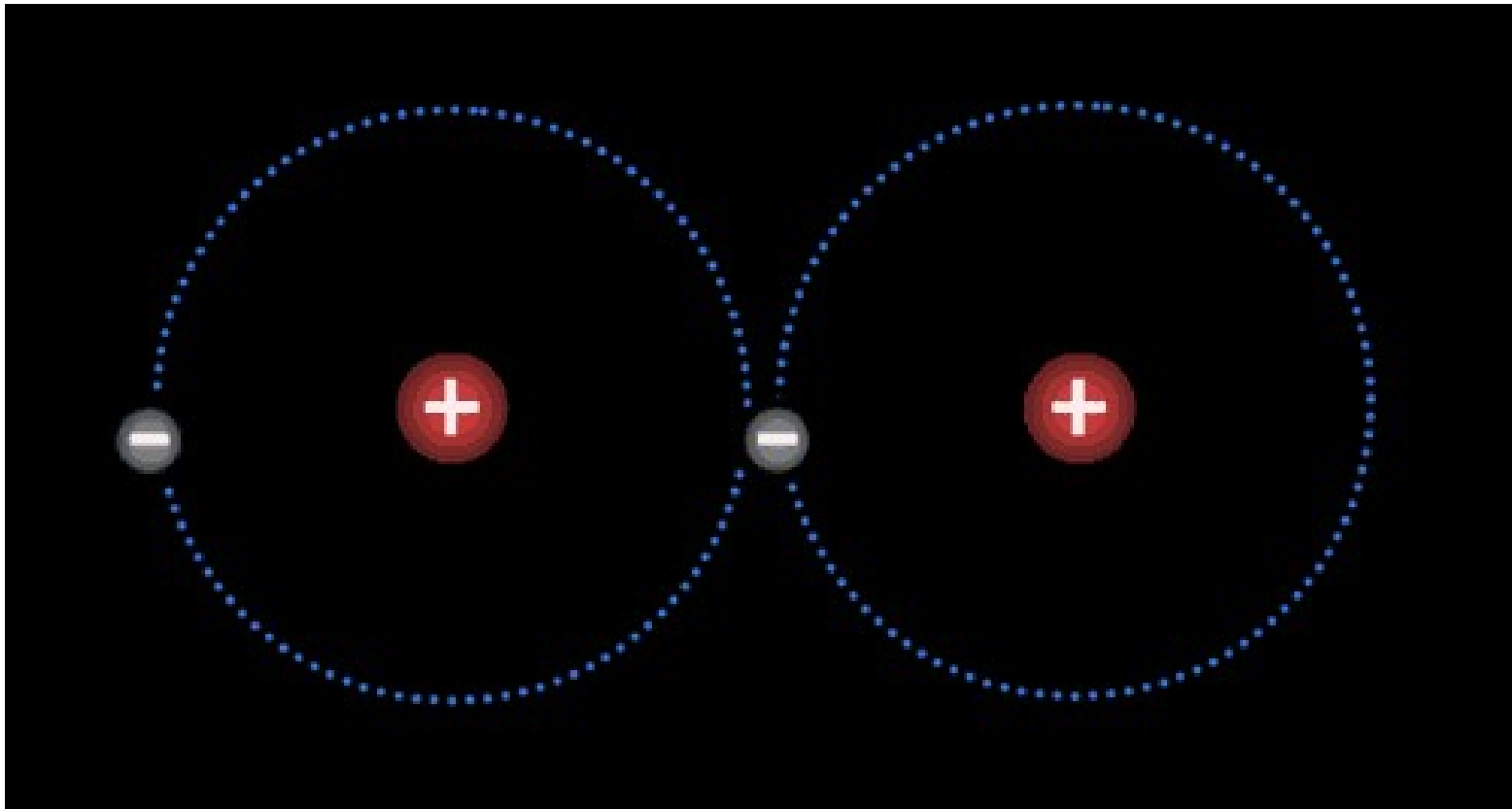
$$R_0 = 1.06 \text{ \AA}$$

$$D_e = 2.71 \text{ eV}$$

Significado físico de $H_{12} = H_{21} = \beta$

Supongamos que en $t=0$ la molécula se encuentra en el estado $|1\rangle$, es decir $c_1(0) = 1$ $c_2(0) = 0$.

Probabilidad de que a tiempo t $|\Psi\rangle = |2\rangle$



Significado físico de $H_{12} = H_{21} = \beta$

Supongamos que en $t=0$ la molécula se encuentra en el estado $|1\rangle$, es decir $c_1(0) = 1$ $c_2(0) = 0$.

Probabilidad de que a tiempo t $|\Psi\rangle = |2\rangle$,

$$i \frac{\hbar}{2\pi} \frac{d|\Psi\rangle}{dt} = H|\Psi\rangle \quad |\Psi\rangle = c_1|1\rangle + c_2|2\rangle$$

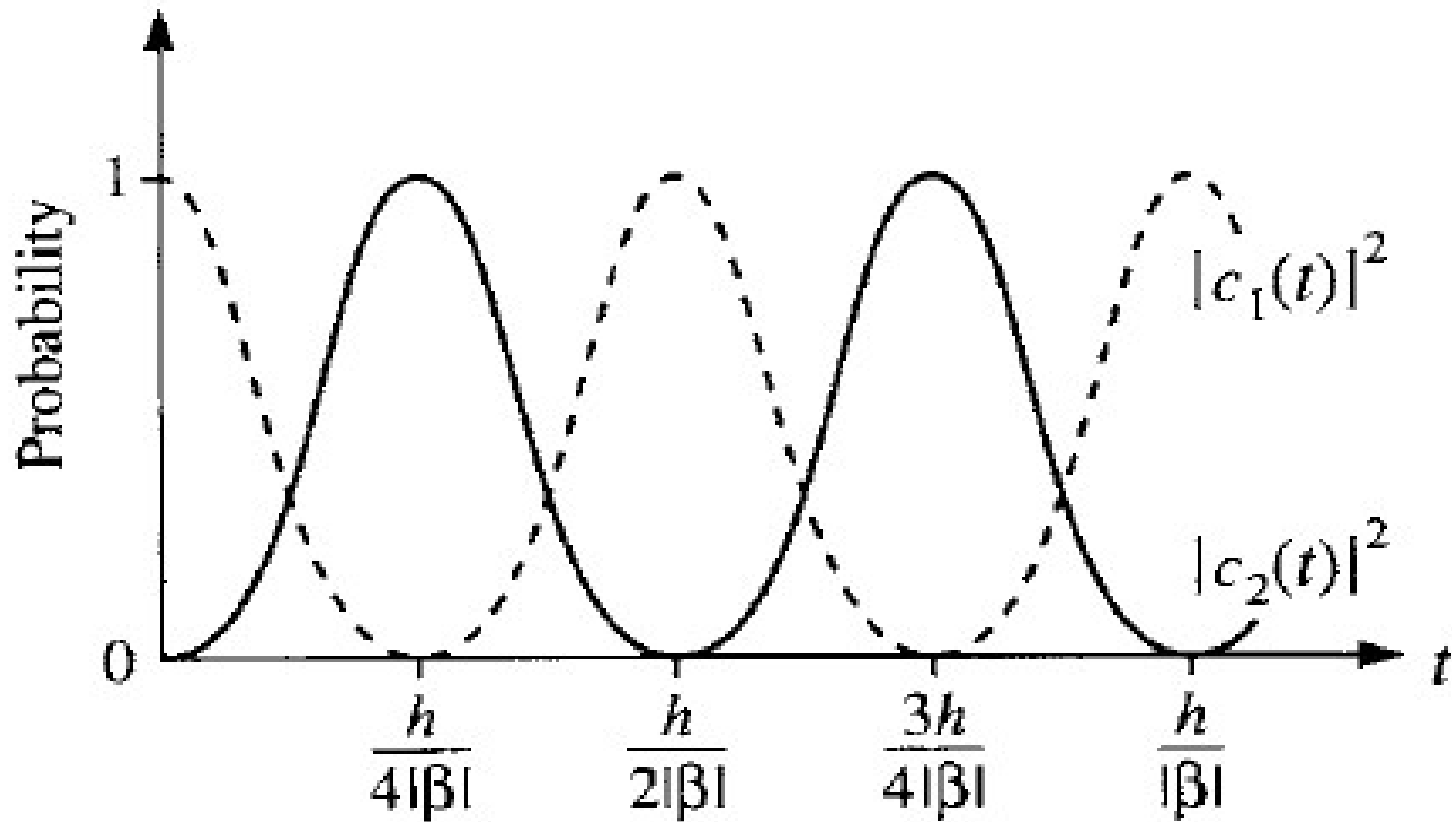
con $c_1(t)$ $c_2(t)$

Solución:

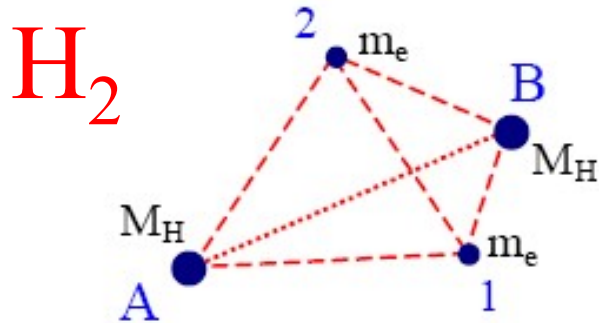
$$c_1(t) = e^{-2\pi i E_0 t / \hbar} \cos(2\pi \beta t / \hbar)$$

$$c_2(t) = e^{-2\pi i E_0 t / \hbar} \sin(2\pi \beta t / \hbar).$$

$$|c_2(t)|^2 = \sin^2 \frac{2\pi\beta t}{h}$$



$\beta \rightarrow$ **hopping**



$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \sum_{i=1}^2 \frac{\tilde{e}^2}{|r_i - R_A|} - \sum_{i=1}^2 \frac{\tilde{e}^2}{|r_i - R_B|} + \frac{\tilde{e}^2}{|r_1 - r_2|} + \frac{\tilde{e}^2}{|R_A - R_B|}$$

Aproximación de electrones independientes

Receta: 1) resolver el problema de 1 electrón

2) ocupar los niveles de energía con los Ne electrones.

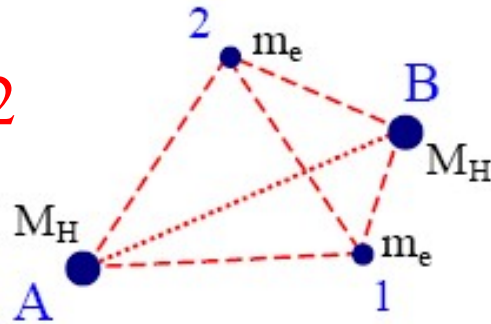
Como se llenan los orbitales moleculares (1e-MO) ?

1- Los orbitales se llenan en orden creciente de energía (principio de Aufbau)

2- Cada orbital posee una capacidad máxima de 2 electrones cuyos spines son opuestos (principio de exclusión de Pauli)

3- Al llenar dos o más orbitales de igual energía, los electrones se distribuyen, siempre que sea posible con sus spines paralelos, es decir desapareados (regla de Hund)

H_2



$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \sum_{i=1}^2 \frac{\tilde{e}^2}{|r_i - R_A|} - \sum_{i=1}^2 \frac{\tilde{e}^2}{|r_i - R_B|} + \frac{\tilde{e}^2}{|r_1 - r_2|} + \frac{\tilde{e}^2}{|R_A - R_B|}$$

$$\mathcal{H}(r_1, r_2) = \mathcal{H}_A(r_1) + \mathcal{H}_B(r_2) + \mathcal{H}_{\text{int}}(r_1, r_2),$$

$$\mathcal{H}_A(r_1) = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\tilde{e}^2}{|r_1 - R_A|},$$

$$\mathcal{H}_B(r_2) = -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{\tilde{e}^2}{|r_2 - R_B|},$$

$$\mathcal{H}_{\text{int}}(r_1, r_2) = -\frac{\tilde{e}^2}{|r_1 - R_B|} - \frac{\tilde{e}^2}{|r_2 - R_A|}$$

Aproximación de Heitler–London (Valence Bond)

$$\mathcal{H}_A(\mathbf{r}_1)\psi_A(\mathbf{r}_1) = \epsilon_A\psi_A(\mathbf{r}_1) \quad \text{Idem para B}$$

$$\psi_A(\mathbf{r}) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-|\mathbf{r}-\mathbf{R}_A|/a_0}, \quad \text{Orbital 1s}$$

La función de onda del sistema con 2 electrones :

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2).$$

Notar que:

$$\left[\mathcal{H}_A(\mathbf{r}_1) + \mathcal{H}_B(\mathbf{r}_2)\right]\psi(\mathbf{r}_1, \mathbf{r}_2) = (\epsilon_A + \epsilon_B)\psi(\mathbf{r}_1, \mathbf{r}_2).$$

Condición de antisimetría ???

$$\Psi = \psi_{\text{space}} \times \psi_{\text{spin}}$$

spin de los electrones

$$\chi(\uparrow) = |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \chi(\downarrow) = |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

$$\Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2) = \psi(\mathbf{r}_1, \mathbf{r}_2) \chi(s_1, s_2).$$



$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = N_+ [\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) + \psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)],$$

$$\chi_s(s_1, s_2) = \frac{1}{\sqrt{2}} [|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2],$$



$$\psi_A(\mathbf{r}_1, \mathbf{r}_2) = N_- [\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) - \psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)],$$

$$\chi_t(s_1, s_2) = \begin{cases} |\uparrow\rangle_1 |\uparrow\rangle_2 \\ \frac{1}{\sqrt{2}} [|\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2] \\ |\downarrow\rangle_1 |\downarrow\rangle_2. \end{cases}$$

Las constantes de normalización son:

$$N_{\pm} = \frac{1}{\sqrt{2(1 \pm |S_{AB}|^2)}}.$$

$$S_{AB} = \int \psi_A^*(r)\psi_B(r) dr$$

La energía se calcula como el valor de expectación de H

$$\varepsilon_s = \langle \psi_s | \mathcal{H} | \psi_s \rangle = \varepsilon_A + \varepsilon_B + 2N_+^2 (C + I),$$

$$\varepsilon_t = \langle \psi_t | \mathcal{H} | \psi_t \rangle = \varepsilon_A + \varepsilon_B + 2N_-^2 (C - I),$$

donde

$$C = \int \psi_A^*(r_1)\psi_B^*(r_2)\mathcal{H}_{int}\psi_A(r_1)\psi_B(r_2) dr_1 dr_2,$$

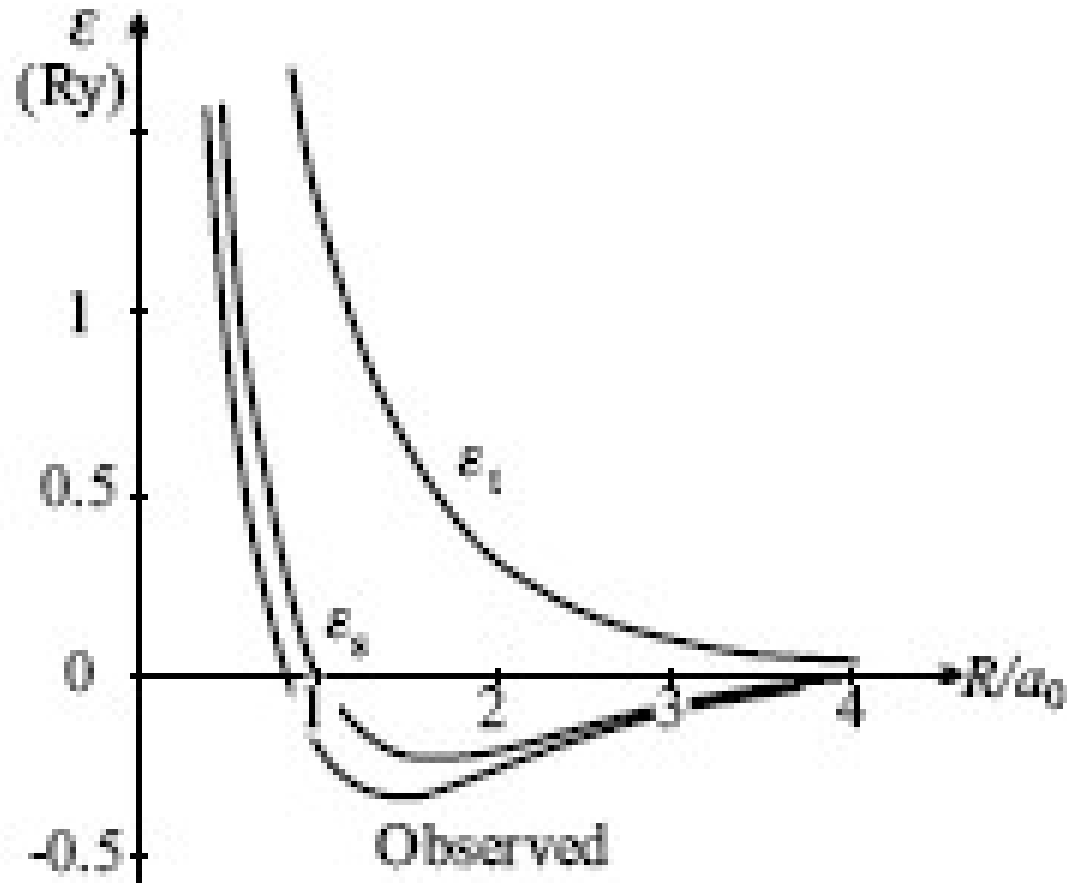
Integral de coulomb

$$I = \int \psi_A^*(r_1)\psi_B^*(r_2)\mathcal{H}_{int}\psi_B(r_1)\psi_A(r_2) dr_1 dr_2.$$

Integral de intercambio

Cuál es el estado fundamental ? Valores de ϵ_s ϵ_t

Depende del signo de I $\xrightarrow{\hspace{2cm}}$ $\epsilon_s < \epsilon_t$
 < 0 para H_2



Comentario

La aprox. de Heitler-London involucra solo configuraciones, denominadas de valence bond, donde un electrón está alrededor del núcleo A y el otro alrededor del núcleo B

$$\psi_{\text{cov}}(r_1, r_2) = \psi_A(r_1)\psi_B(r_2) + \psi_B(r_1)\psi_A(r_2).$$

Durante el movimiento de los electrones puede ocurrir que los dos electrones estén en orbitales alrededor del mismo núcleo atómico (configuraciones iónicas)

$$\psi_{\text{ion}}(r_1, r_2) = \psi_A(r_1)\psi_A(r_2) \pm \psi_B(r_1)\psi_B(r_2).$$

Aproximación de Hund-Mulliken (Orbitales Moleculares)

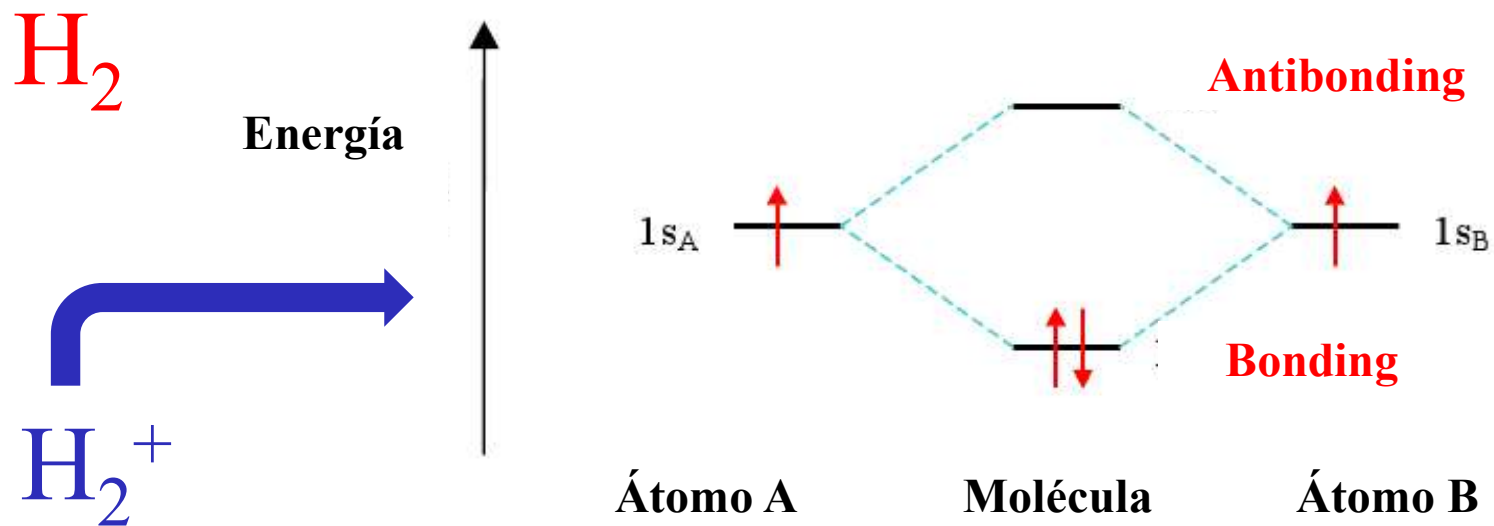
Reemplazar en el caso anterior las funciones de onda atómicas (ψ_A y ψ_B) por orbitales moleculares de un electrón **(one electron MO)**

$$\psi_{\pm}(r) = \frac{1}{\sqrt{2 \pm (S_{AB} + S_{AB}^*)}} [\psi_A(r) \pm \psi_B(r)],$$

La función de onda del estado fundamental queda:

$$\begin{aligned} \psi(r_1, r_2) = & \frac{1}{2 + S_{AB} + S_{AB}^*} [\psi_A(r_1)\psi_B(r_2) + \psi_B(r_1)\psi_A(r_2) \\ & + \psi_A(r_1)\psi_A(r_2) + \psi_B(r_1)\psi_B(r_2)]. \end{aligned}$$

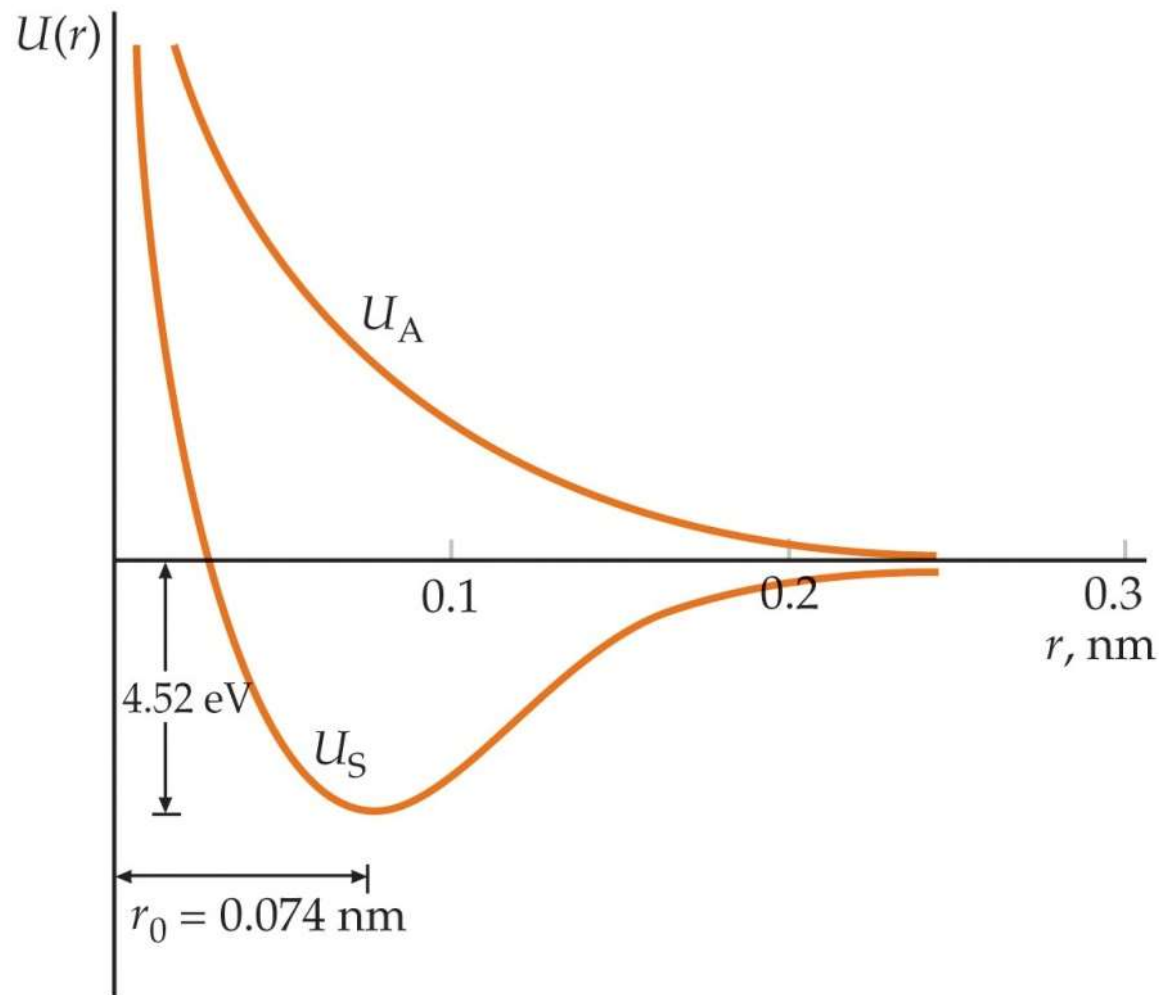
Esta función de onda incluye configuraciones covalentes (valence bond) y iónicas **con el mismo peso**.



$$\psi = \psi_+(1)\psi_+(2) \cdot \frac{1}{\sqrt{2}} [|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2]$$

Se obtiene a partir del determinante de Slater

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_+(r_1) |\uparrow\rangle_1 & \psi_+(r_1) |\downarrow\rangle_1 \\ \psi_+(r_2) |\uparrow\rangle_2 & \psi_+(r_2) |\downarrow\rangle_2 \end{vmatrix}$$



Experimental:

$R_0 = 0.74 \text{ \AA}$

$D_e = 4.72 \text{ eV}$

Heitler-London:

$R_0 = 0.80 \text{ \AA}$

$D_e = 3.20 \text{ eV}$

Hund-Mulliken :

$R_0 = 0.80 \text{ \AA}$

$D_e = 2.68 \text{ eV}$

$$\psi(r_1, r_2) = N \left[\psi_A(r_1)\psi_B(r_2) + \psi_B(r_1)\psi_A(r_2) + \lambda\psi_A(r_1)\psi_A(r_2) + \lambda\psi_B(r_1)\psi_B(r_2) \right],$$

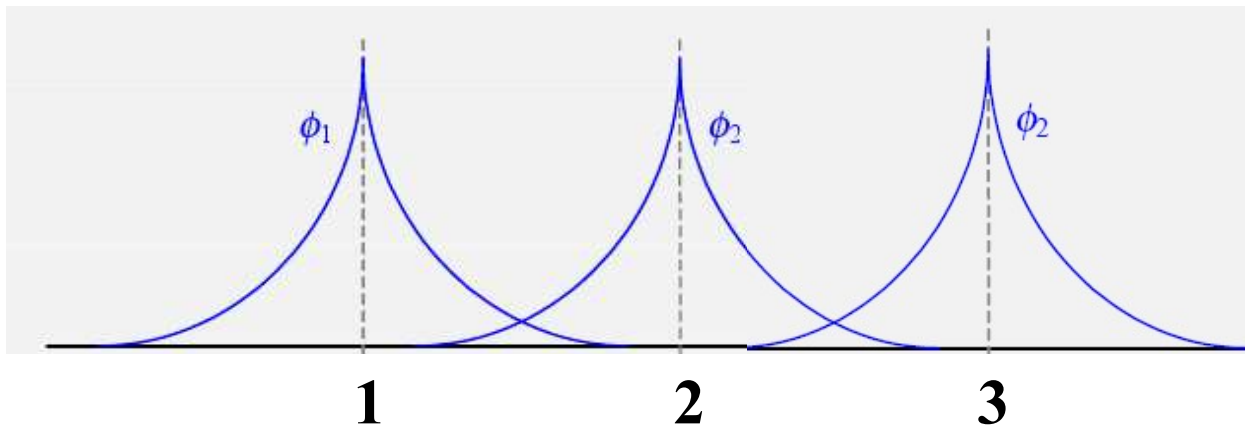
λ variacional :

$R_0 = 0.749 \text{ \AA}$

$D_e = 4.00 \text{ eV}$

Probl. 9: Molécula triatómica con 1 orbital/sitio

Configuración lineal



$$|\Psi\rangle = c_1|1\rangle + c_2|2\rangle + c_3|3\rangle$$

$$H|\Psi\rangle = E|\Psi\rangle \implies \text{Proyectar sobre los 3 estados}$$

$$H_{11} = H_{22} = H_{33} = \alpha$$

$$H_{12} = H_{23} = \beta$$

$$H_{13} = 0$$

$$c_1(\alpha - E) + c_2\beta + 0 = 0$$

$$c_1\beta + c_2(\alpha - E) + c_3\beta = 0$$

$$0 + c_2\beta + c_3(\alpha - E) = 0$$

1

2

3

1	$\alpha - E$	β	0
2	β	$\alpha - E$	β
3	0	β	$\alpha - E$

= 0



$$E = \alpha - \sqrt{2} \cdot \beta$$

$$E = \alpha$$

$$E = \alpha + \sqrt{2} \cdot \beta$$

$$\star E = \alpha$$

$$c_2 = 0$$

$$|c_1| = |c_3| = \frac{1}{\sqrt{2}}$$

$$c_1 + c_3 = 0$$

$$\star E = \alpha + \sqrt{2} \cdot \beta$$

$$c_1 = c_3$$

$$c_1 = c_3 = \frac{1}{2} \quad (= 0.500)$$

$$c_2 = \sqrt{2} \cdot c_1$$

$$c_2 = \sqrt{2} \cdot \frac{1}{2} = \frac{1}{\sqrt{2}} \quad (= 0.707)$$

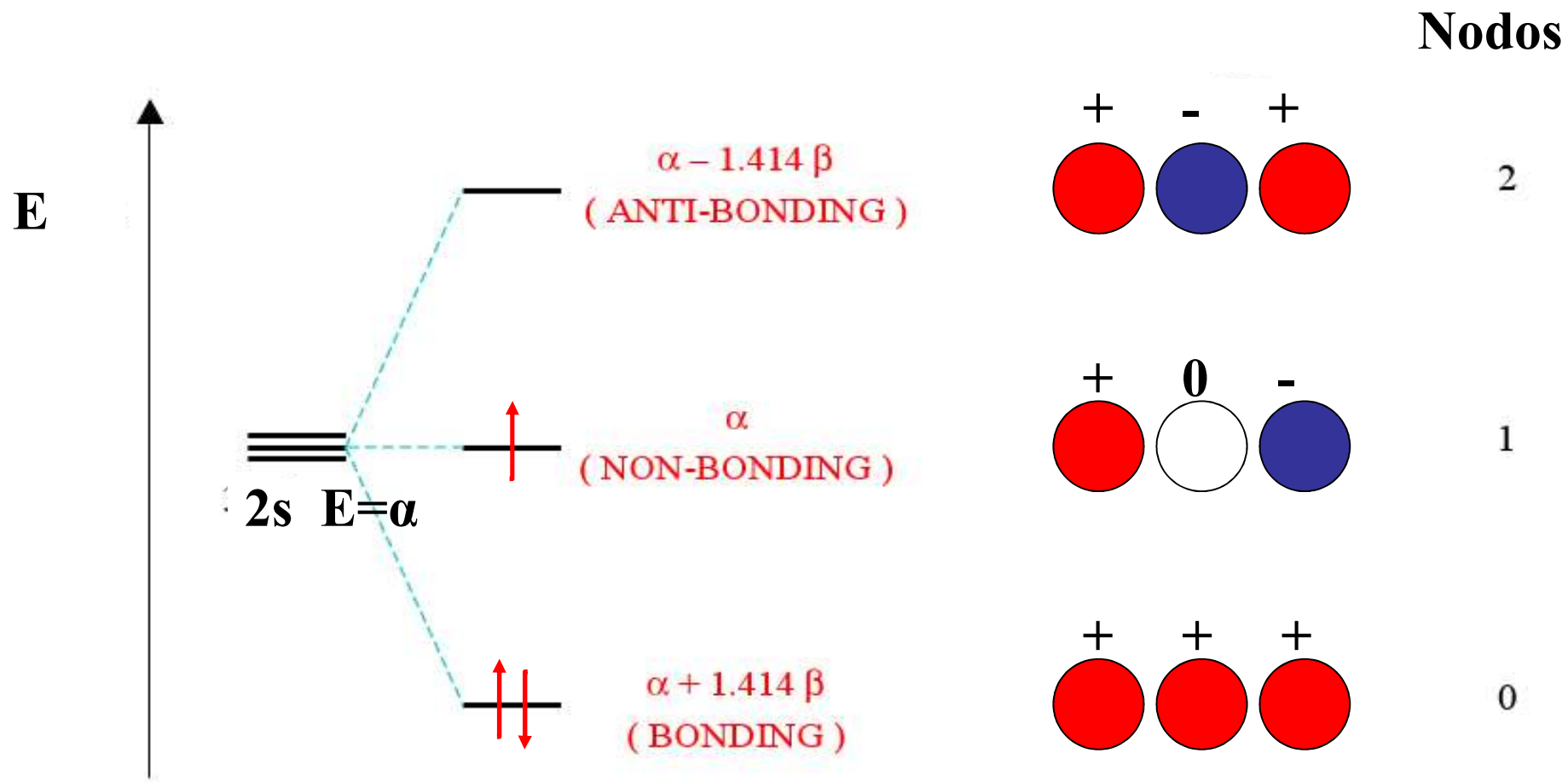
$$\star E = \alpha - \sqrt{2} \cdot \beta$$

$$c_1 = c_3$$

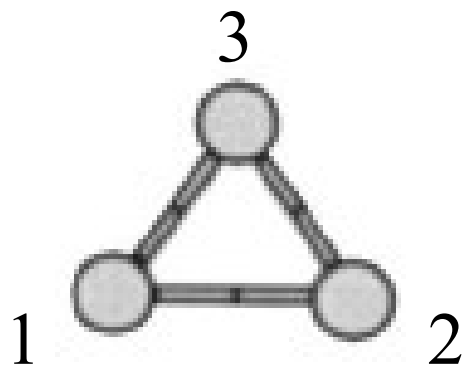
$$c_1 = c_3 = \frac{1}{2} \quad (= 0.500)$$

$$c_2 = -\sqrt{2} \cdot c_1$$

$$c_2 = \frac{-1}{\sqrt{2}} \quad (= -0.707)$$

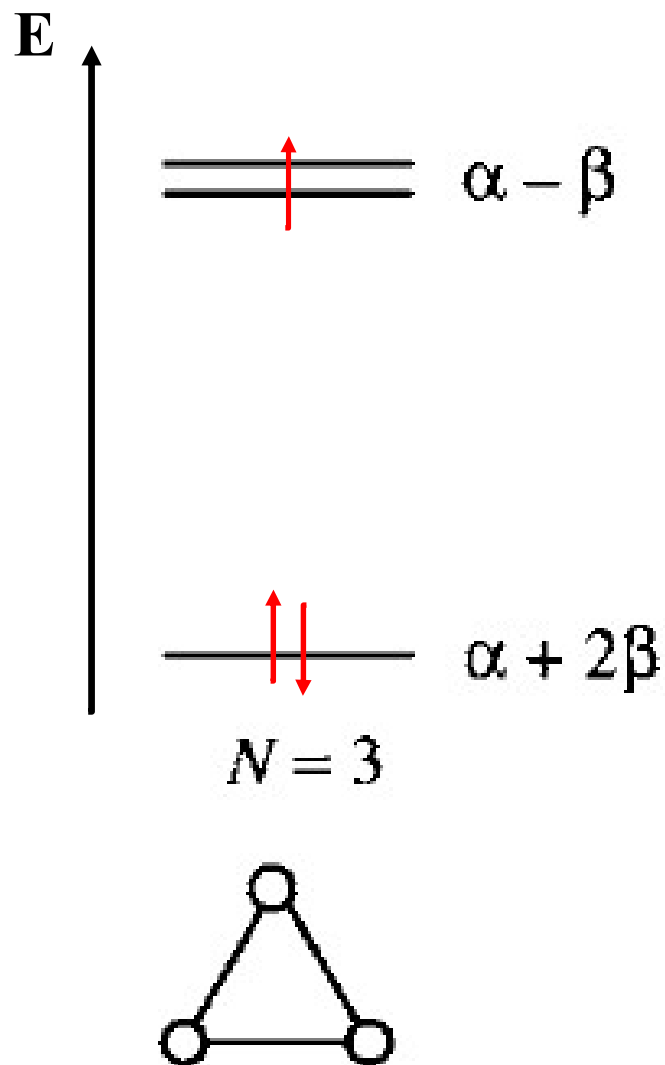


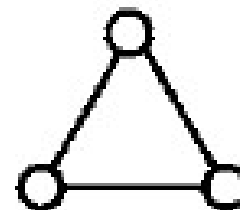
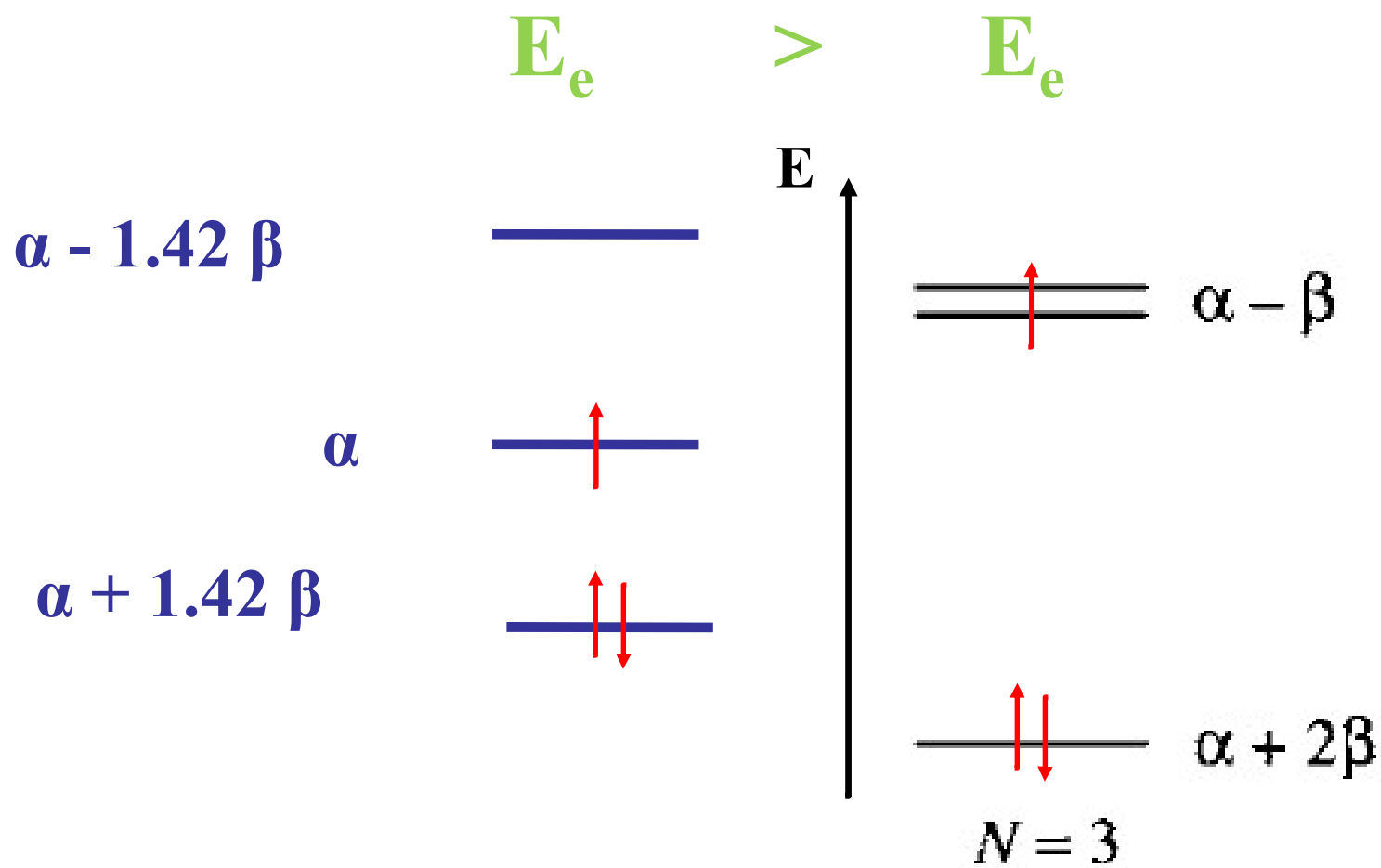
Configuración triangular



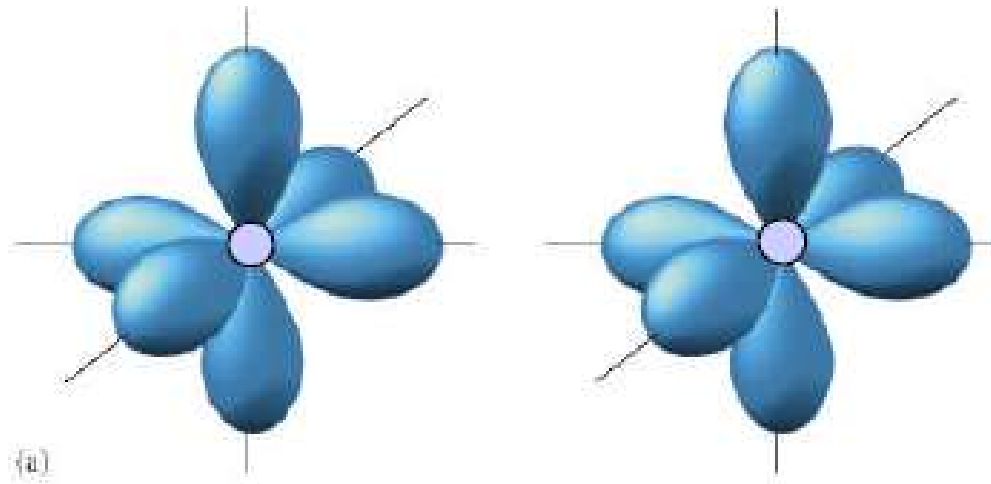
	1	2	3
1	$\alpha - E$	β	β
2	β	$\alpha - E$	β
3	β	β	$\alpha - E$

= 0



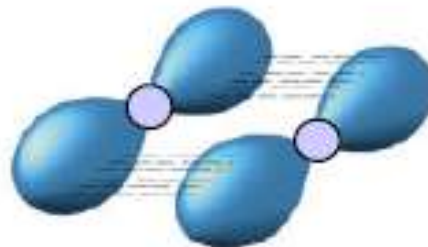
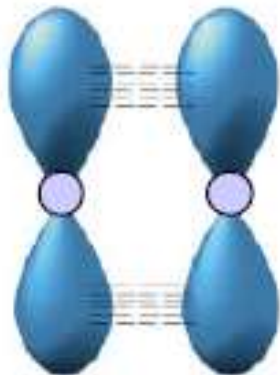


Construcción de MO a partir de orbitales p

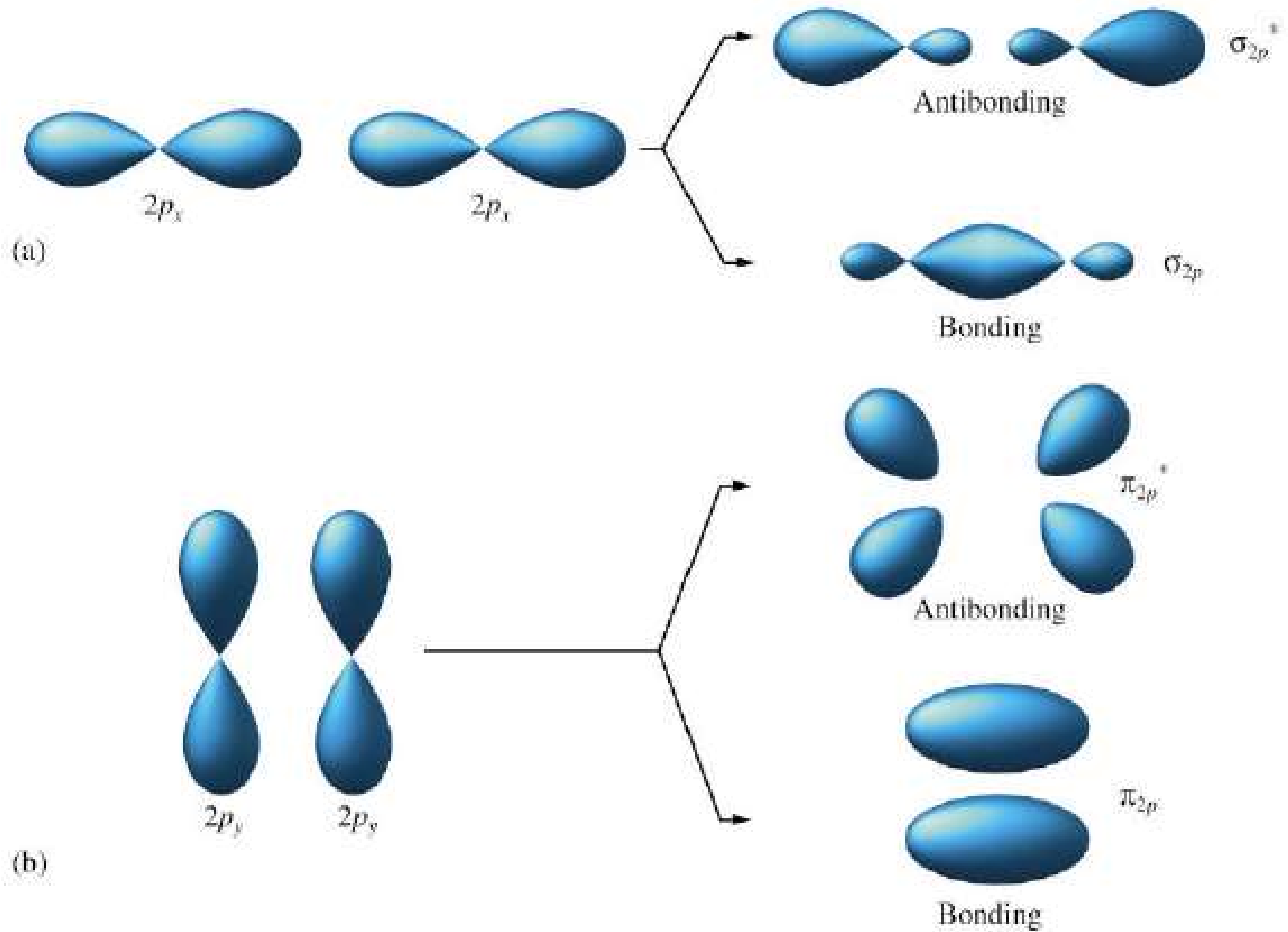


Enlace π

Enlace σ



Construcción de orbitales moleculares a partir de orbitales p

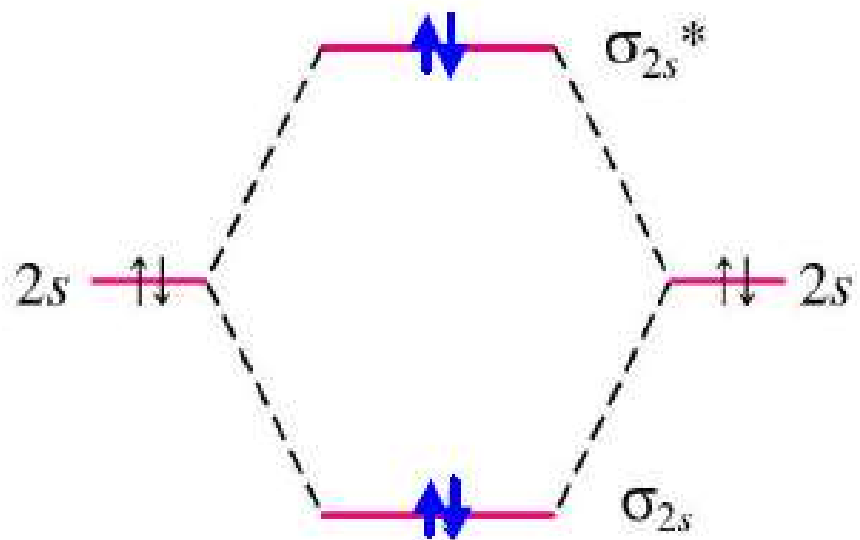
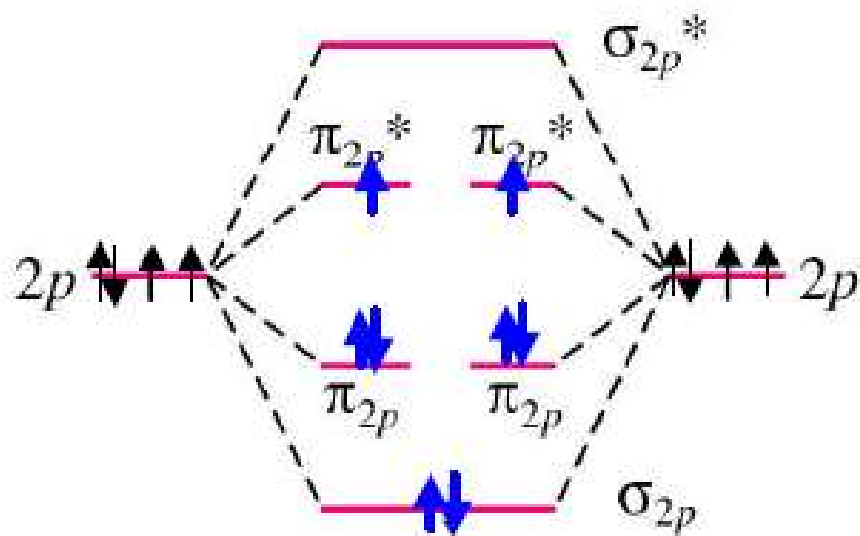


Molécula O₂

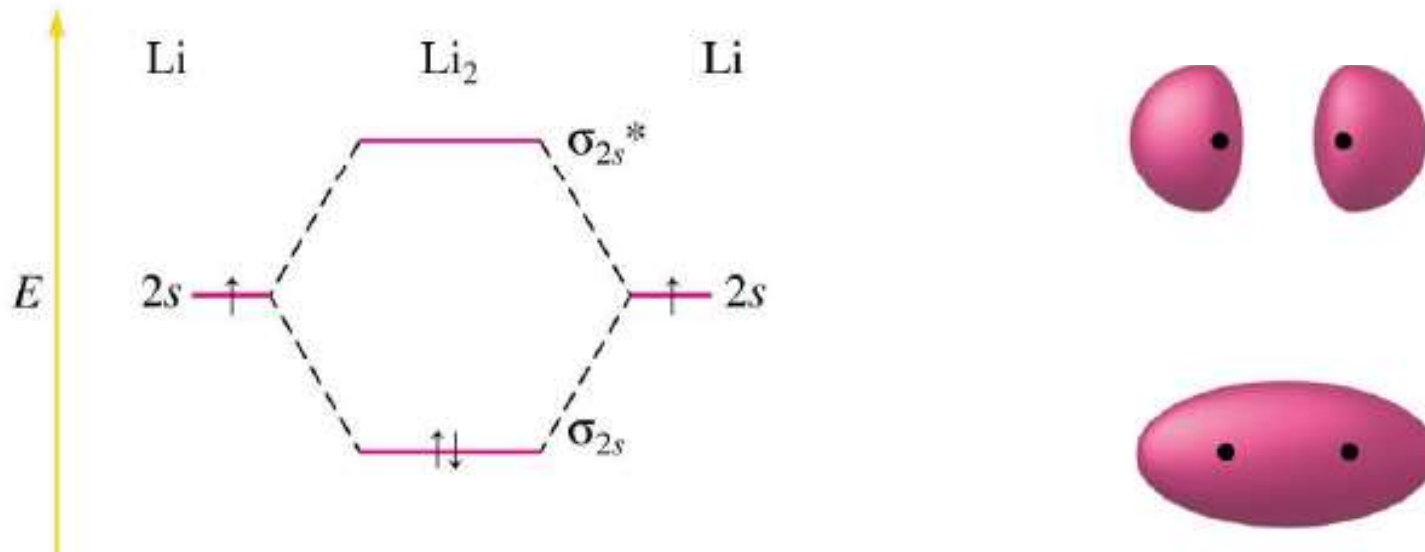
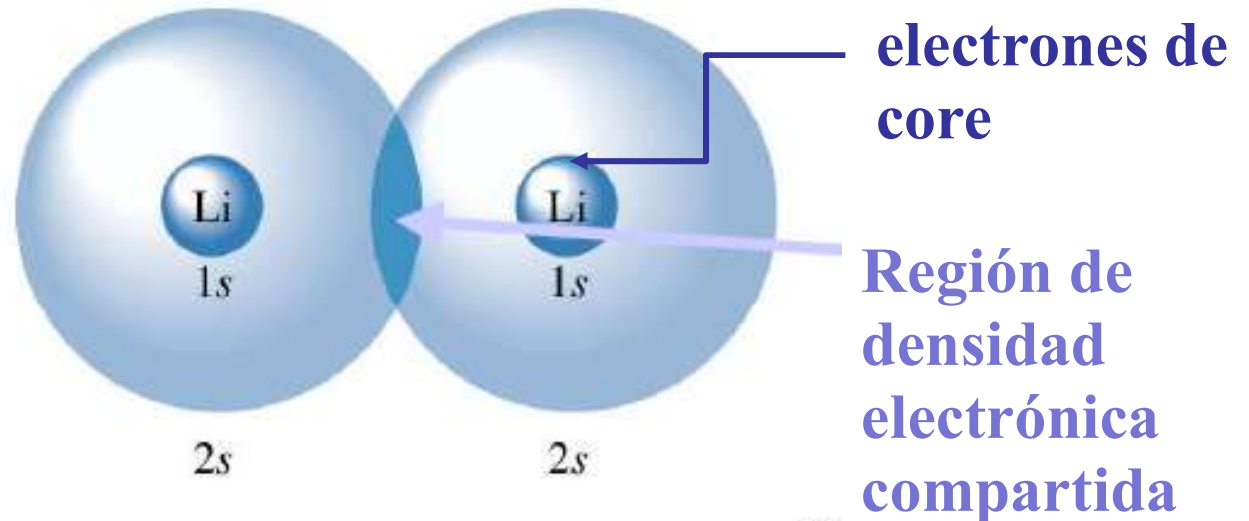
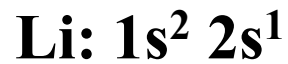
Electrones valencia $2s^2 2p^4$

para dia

	O ₂	F ₂
σ_{2p}^*	—	—
π_{2p}^*	$\uparrow \uparrow$	$\uparrow\downarrow \uparrow\downarrow$
π_{2p}	$\uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow$
σ_{2p}	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}^*	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}	$\uparrow\downarrow$	$\uparrow\downarrow$



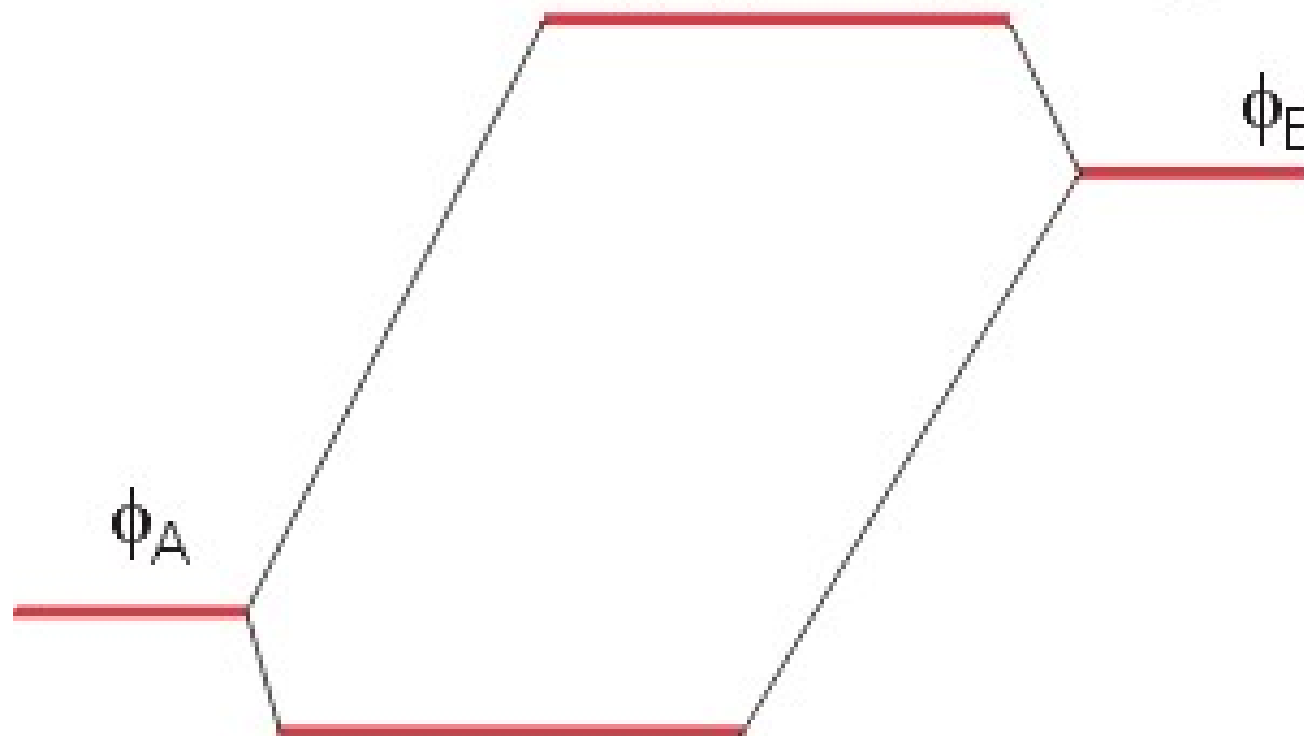
El enlace es dominado por los electrones de valencia



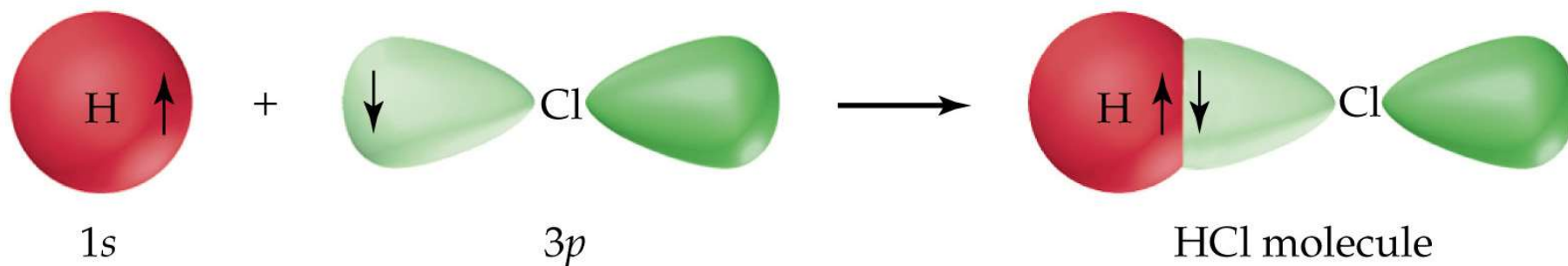
Los orbitales $1s$ son estados de core que conservan características atómicas

MOLECULAS HETERONUCLARES

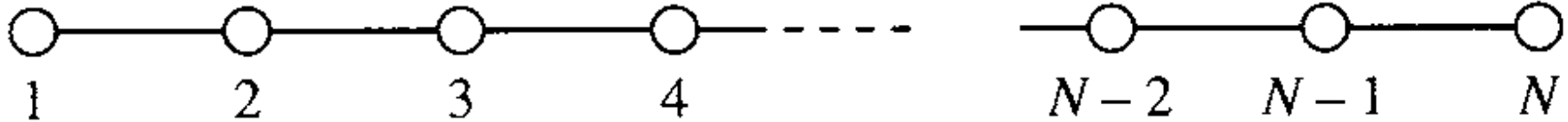
$$\psi = c'_A \phi_A - c'_B \phi_B, \quad c'_B{}^2 > c'_A{}^2$$



$$\psi = c_A \phi_A + c_B \phi_B, \quad c_A{}^2 > c_B{}^2$$



Qué pasa cuando aumenta el número de átomos ?

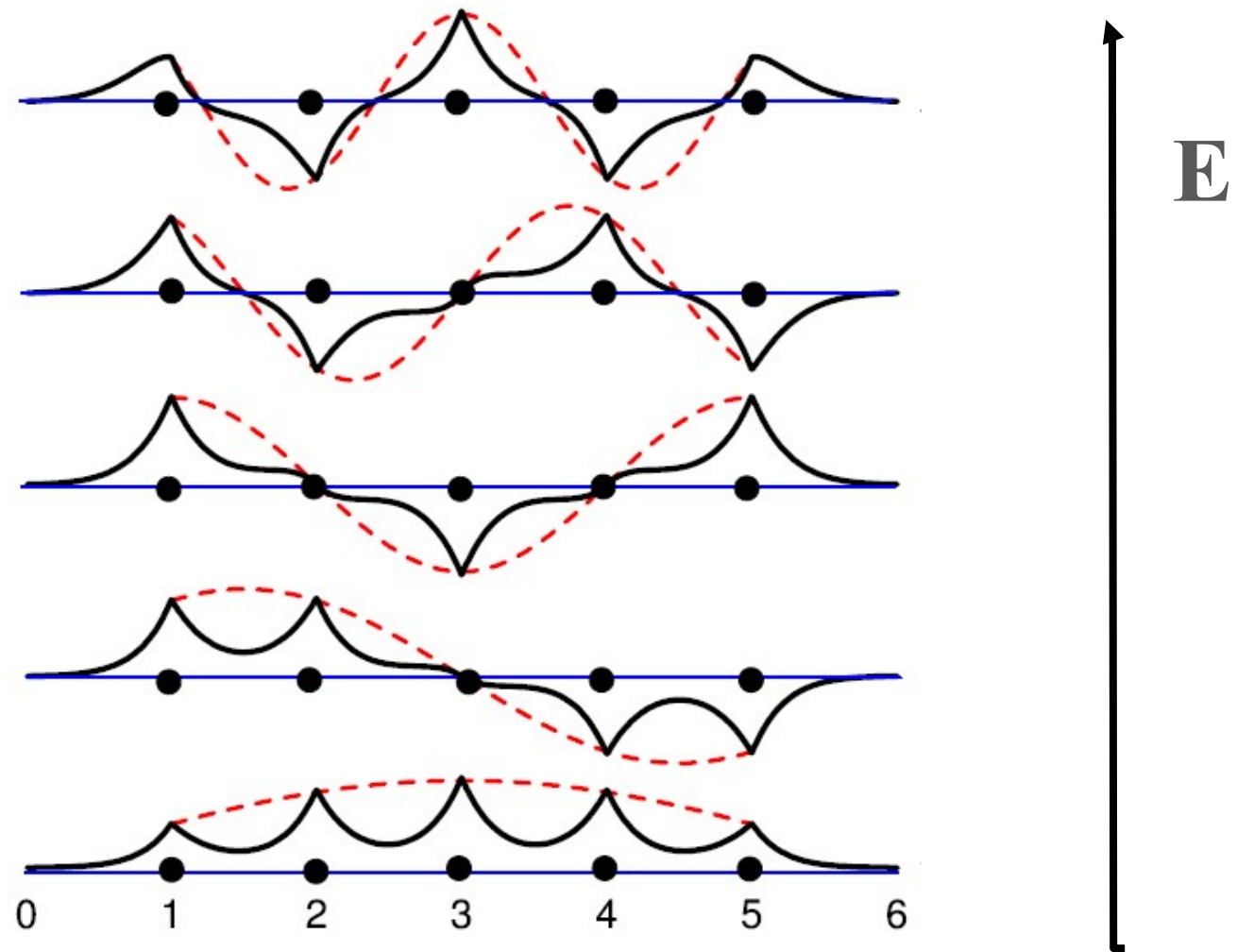


[simulación con pozos !!!!](http://phet.colorado.edu/en/simulations/category/physics)

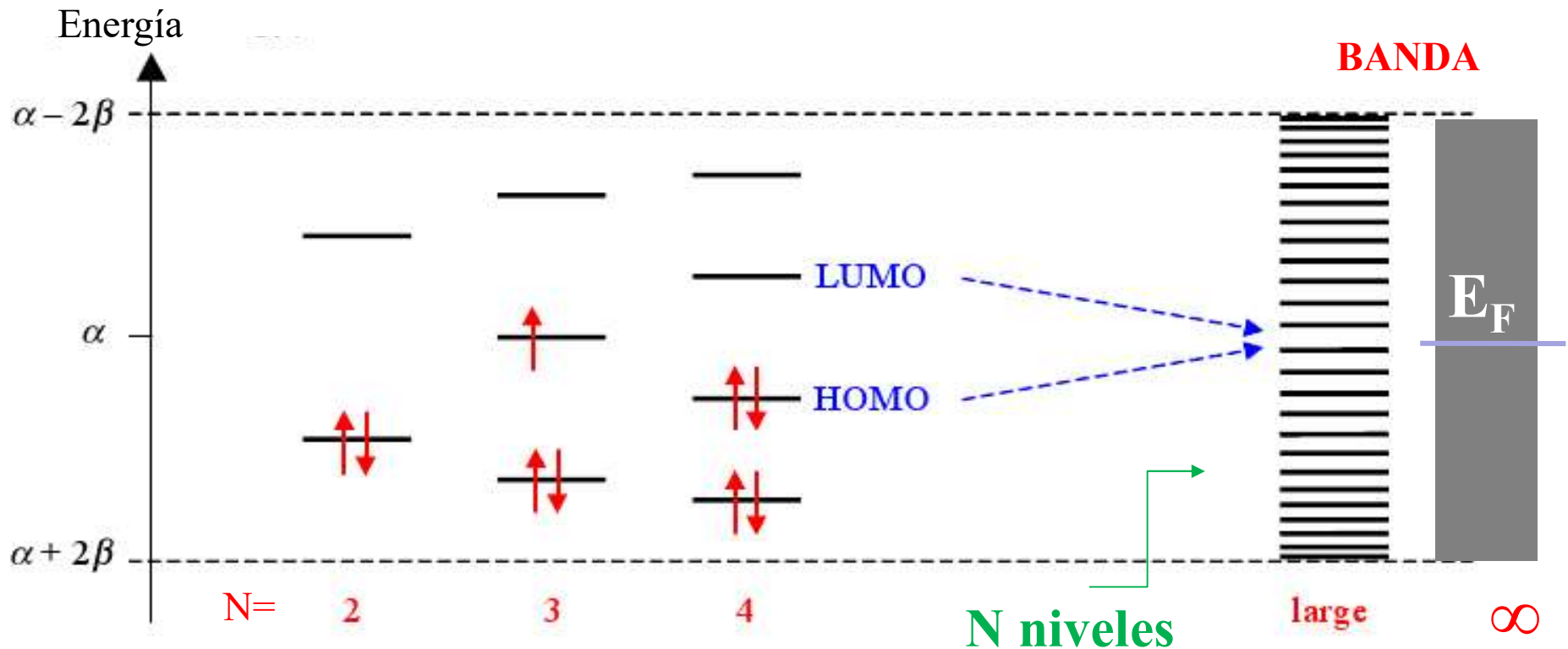
<http://phet.colorado.edu/en/simulations/category/physics>

El número de nodos aumenta con la energía

$n=5$



Cadena lineal de N sitios

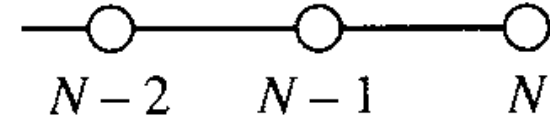
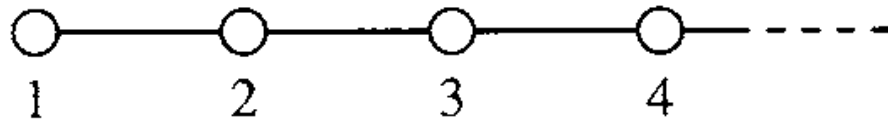


HOMO : highest occupied MO LUMO : lower unoccupied MO

Color :

$$h\nu = \Delta E = E_{\text{HOMO}} - E_{\text{LUMO}} \quad \text{disminuye cuando N aumenta}$$

UV (N pequeño) \longrightarrow **visible** (N grande)



$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & \cdots & 0 \\ \beta & \alpha - E & \beta & 0 & \cdots & 0 \\ 0 & \beta & \alpha - E & \beta & \cdots & 0 \\ 0 & 0 & \beta & \alpha - E & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & \alpha - E \end{vmatrix} = 0$$

Matriz $N \times N$

Solución \Rightarrow

$$E_k = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right)$$

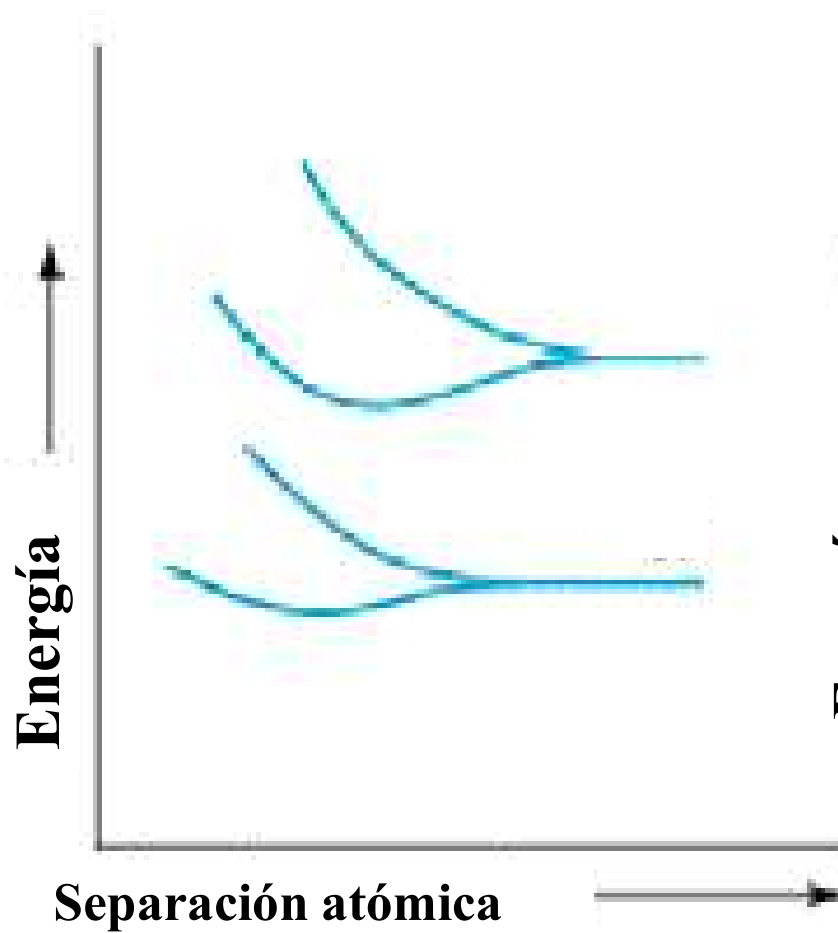
$k = 1, 2, 3, \dots, N$

Notar que cuando N se hace infinitamente grande:

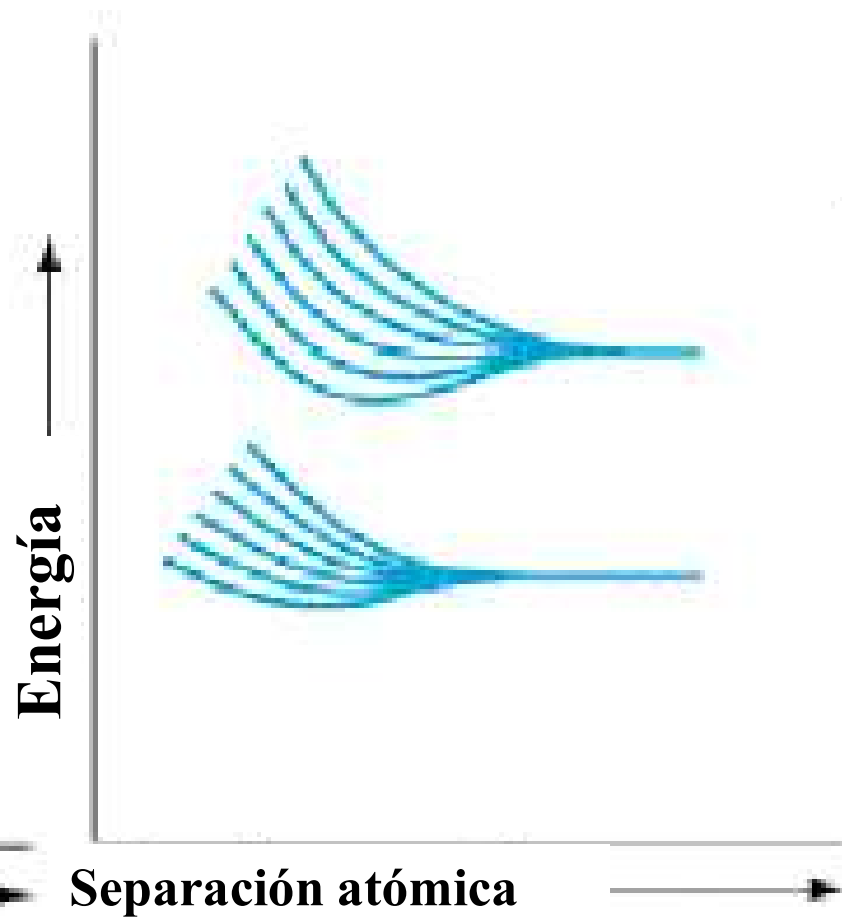
$$(E_{j+1} - E_j) \longrightarrow 0$$

$$(E_N - E_1) \longrightarrow 4\beta$$

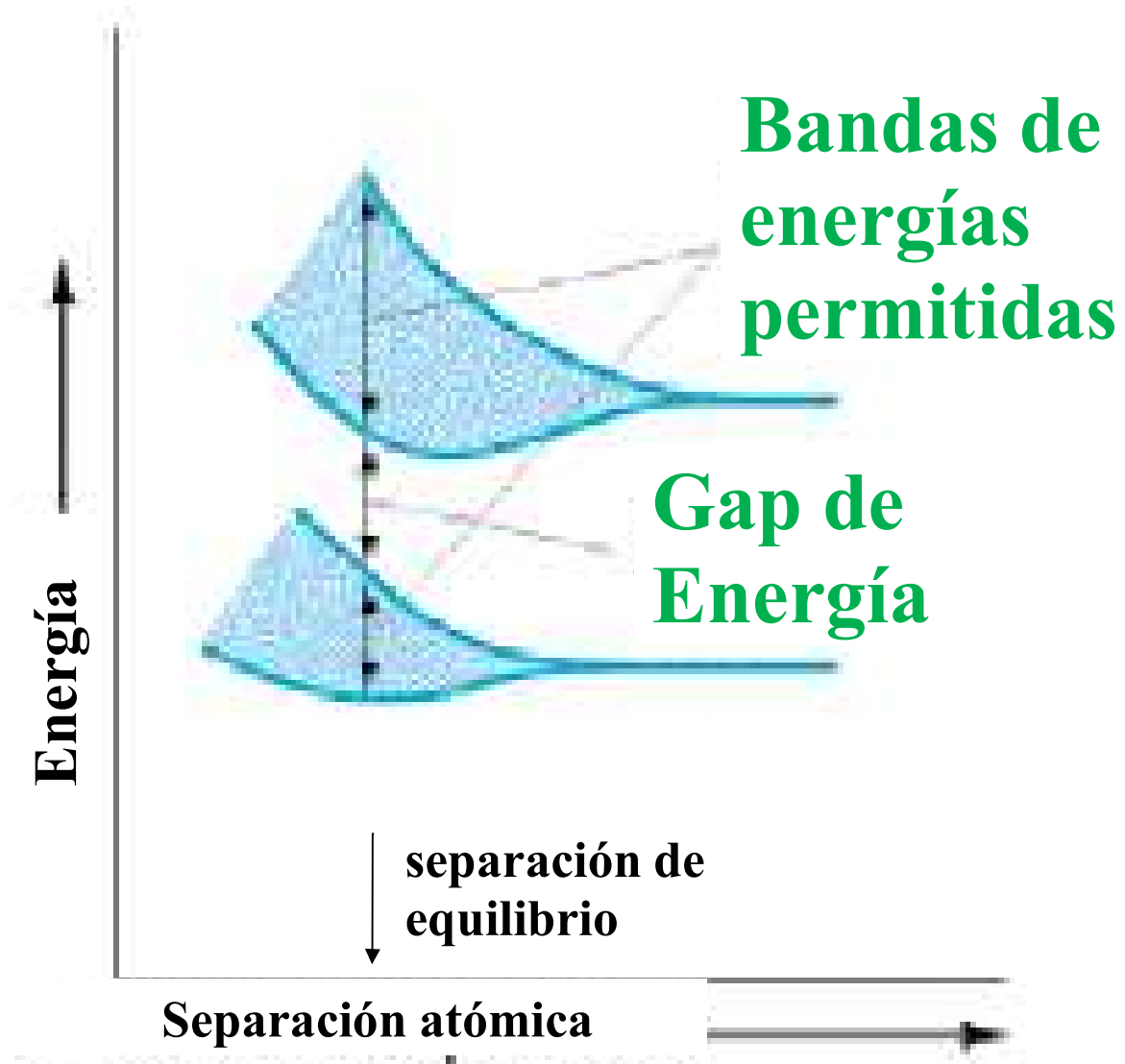
2 átomos



6 átomos

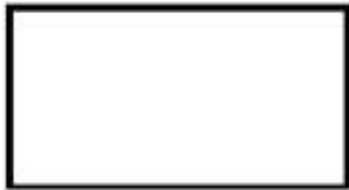


10^{23} átomos

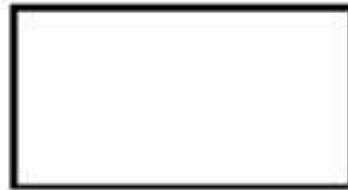


Teoría de Bandas

Aislante



Metal



Semiconductor



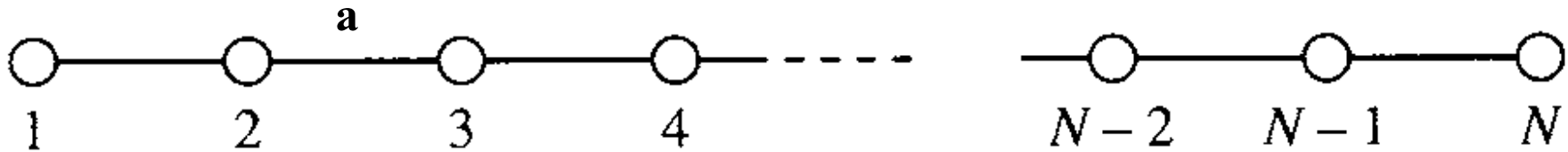
Electrones



Agujeros



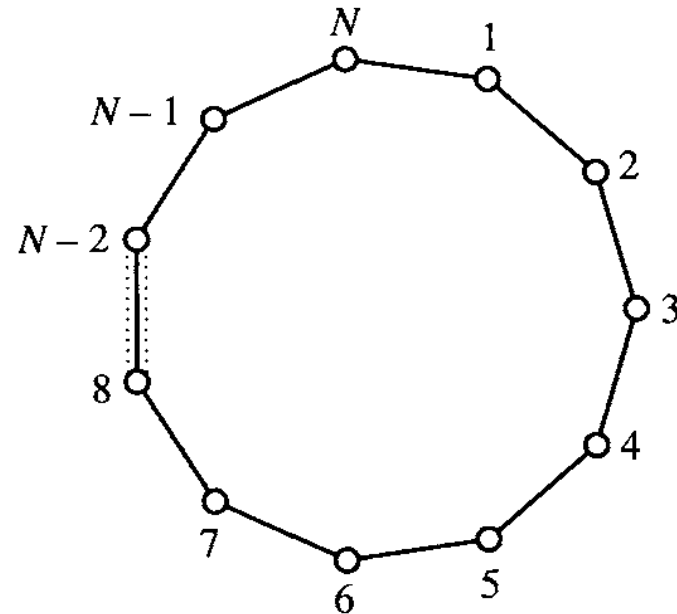
Cristal monoatómico unidimensional

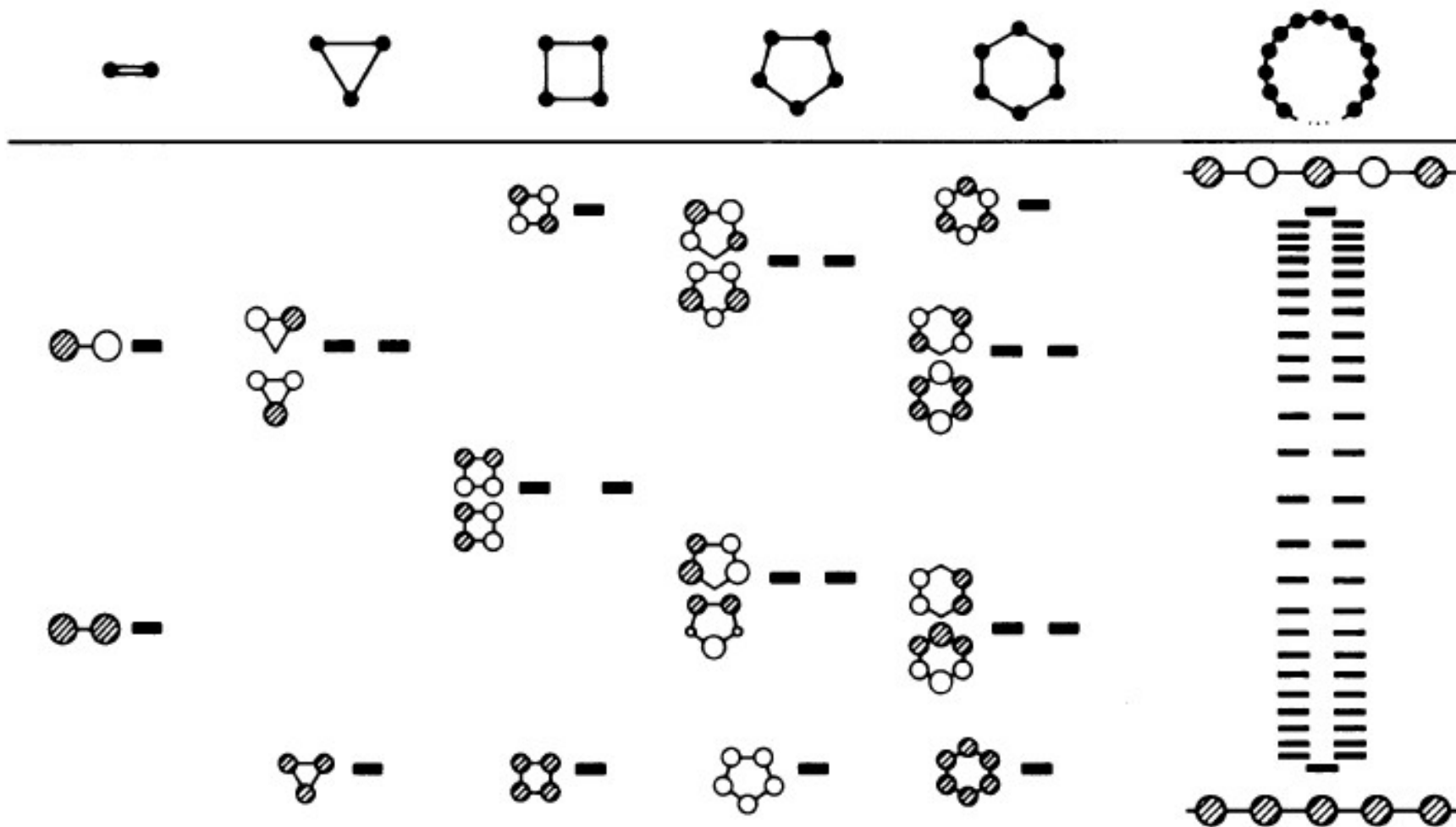


Condiciones periódicas de contorno (*Born-von Karman*)

$$\Psi(x+Na) = \Psi(x)$$

Respetar la simetría de traslación de un cristal

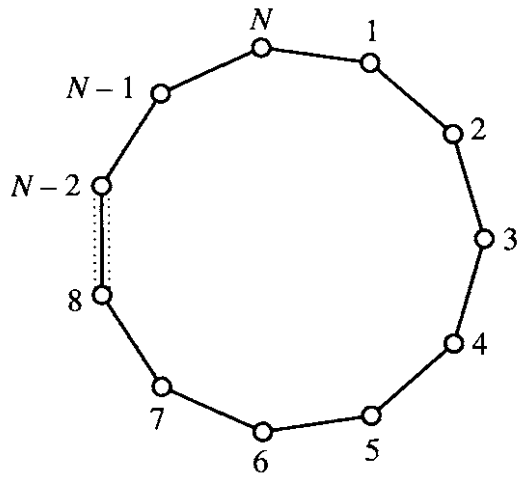




Los niveles se ubican de a pares

Excepción: el de menor y algunas veces el de mayor energía

Numero de nodos de la función de onda aumenta con la energía



$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & \dots & \beta \\ \beta & \alpha - E & \beta & 0 & \dots & 0 \\ 0 & \beta & \alpha - E & \beta & \dots & 0 \\ 0 & 0 & \beta & \alpha - E & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots \\ \beta & 0 & 0 & 0 & \dots & \alpha - E \end{vmatrix} = 0$$

$$E = \alpha + 2\beta \cos\left(\frac{2\pi m}{N}\right) \quad m = 0, 1, 2, \dots, (N - 1)$$

$$|\Psi\rangle = \sum_{j=1}^N c_j |j\rangle \longrightarrow c_j^{(m)} = \frac{1}{(N)^{1/2}} \exp\left(i \frac{2\pi jm}{N}\right)$$

$$E = \alpha + 2\beta \cos\left(\frac{2\pi m}{N}\right) \quad m = 0, 1, 2, \dots, (N - 1)$$

$$|\Psi\rangle = \sum_{j=1}^N c_j |j\rangle \quad c_j^{(m)} = \frac{1}{(N)^{1/2}} \exp\left(i \frac{2\pi jm}{N}\right)$$

Para N muy grande:

Bonding $m = 0$

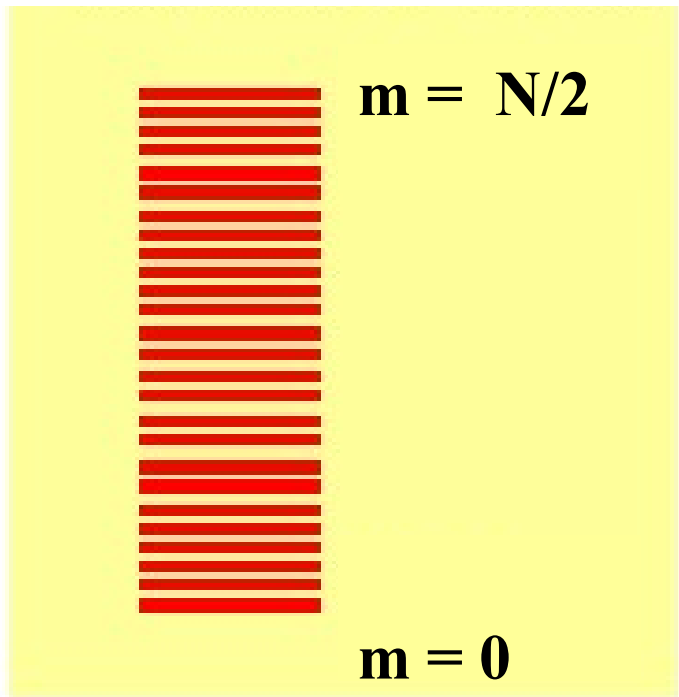
$$E_+ = \alpha + 2\beta \longrightarrow |\Psi\rangle = \frac{1}{(N)^{1/2}} \sum_{j=1}^N |j\rangle$$

Antibonding $m = N/2$

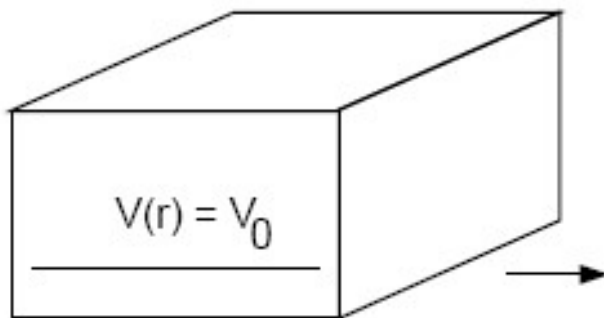
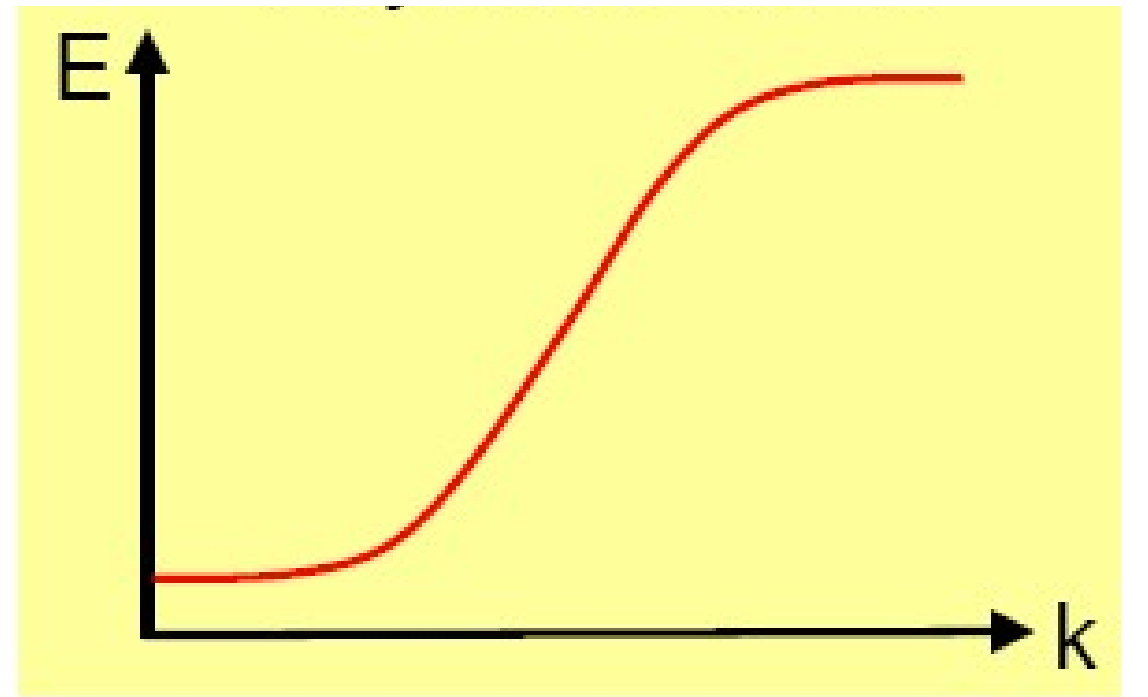
$$E_- = \alpha - 2\beta \longrightarrow |\Psi\rangle = \frac{1}{(N)^{1/2}} \sum_{j=1}^N (-1)^j |j\rangle$$

Como ve este problema un

Químico

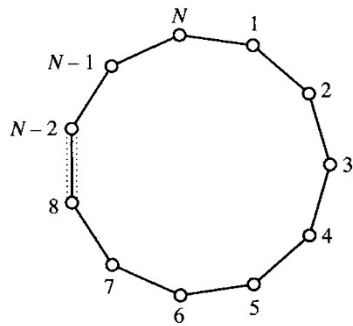


Físico



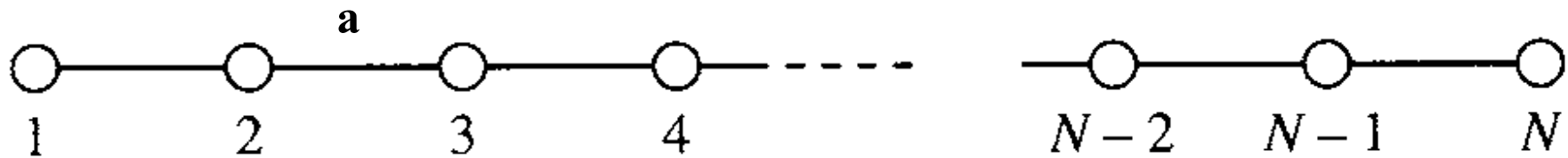
$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2 + k_z^2)$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}$$



$$E = \alpha + 2\beta \cos\left(\frac{2\pi m}{N}\right) \quad m = 0, 1, 2, \dots, (N - 1)$$

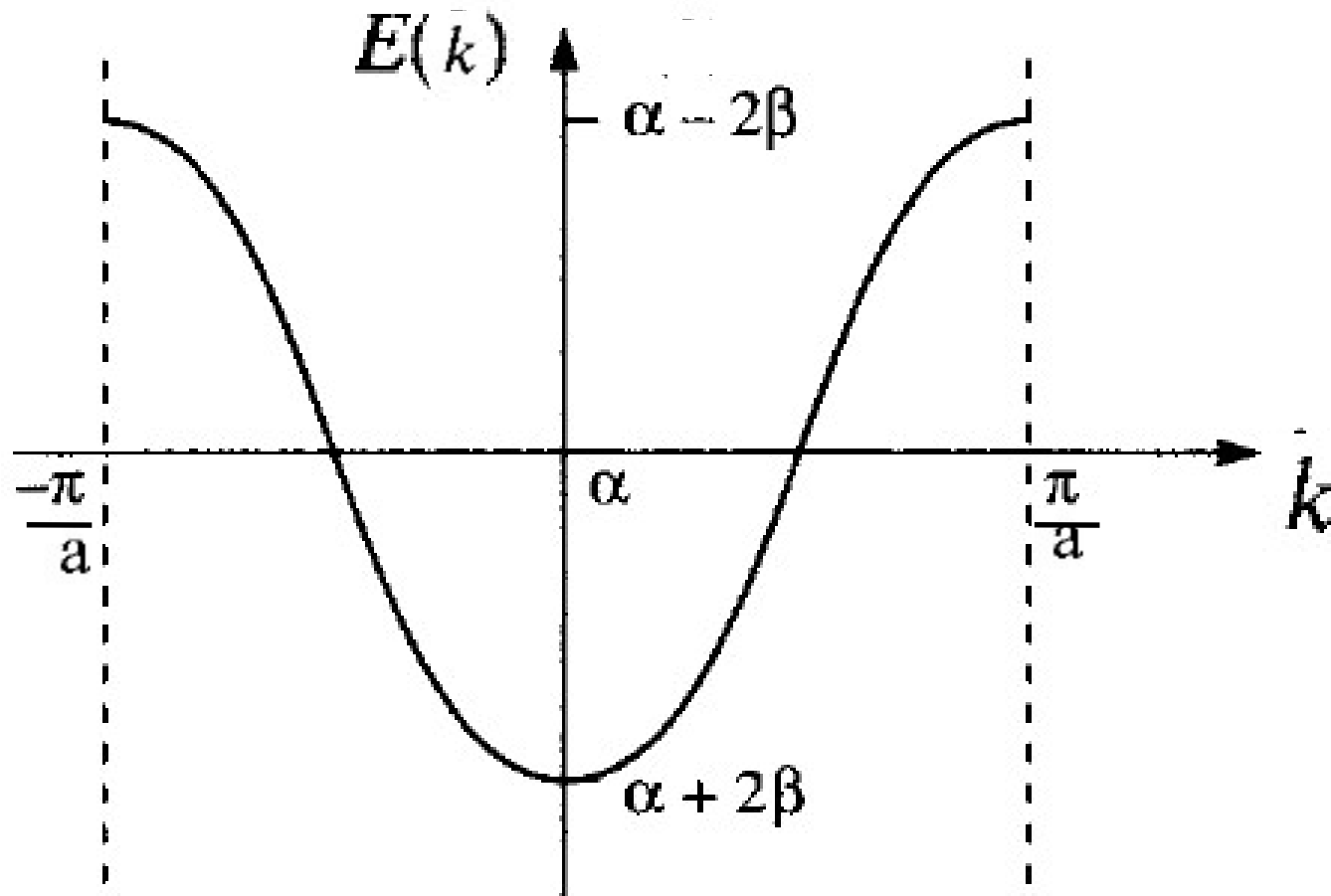
Recordemos que el problema original era:



$$\frac{2\pi m}{N} \frac{a}{a} = k a \quad \text{donde:} \quad k = \frac{2\pi m}{aN}$$

Graficaremos $E(k)$ $-\pi/a < k < \pi/a$

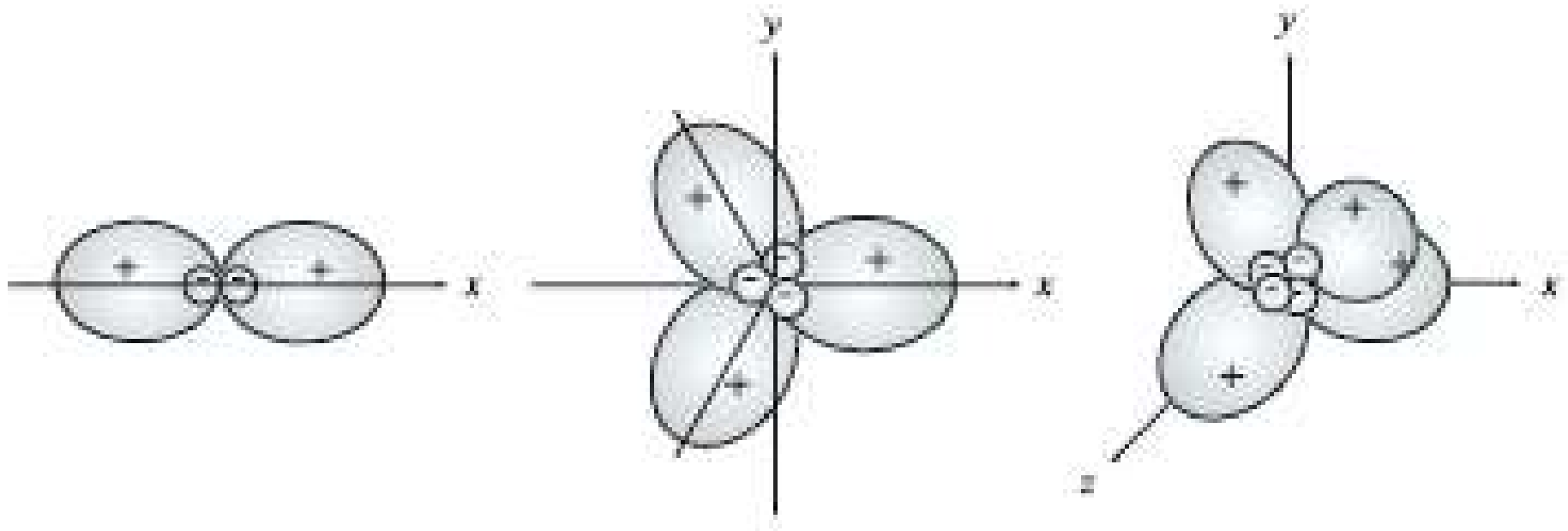
$$E = \alpha + 2\beta \cos ka \quad -\pi/a < k < \pi/a$$



Primera zona de Brillouin

Orbitales híbridos

La hibridización es una LCAO con orbitales de un mismo átomo para formar otros orbitales atómicos que recibe el nombre de orbitales híbridos.

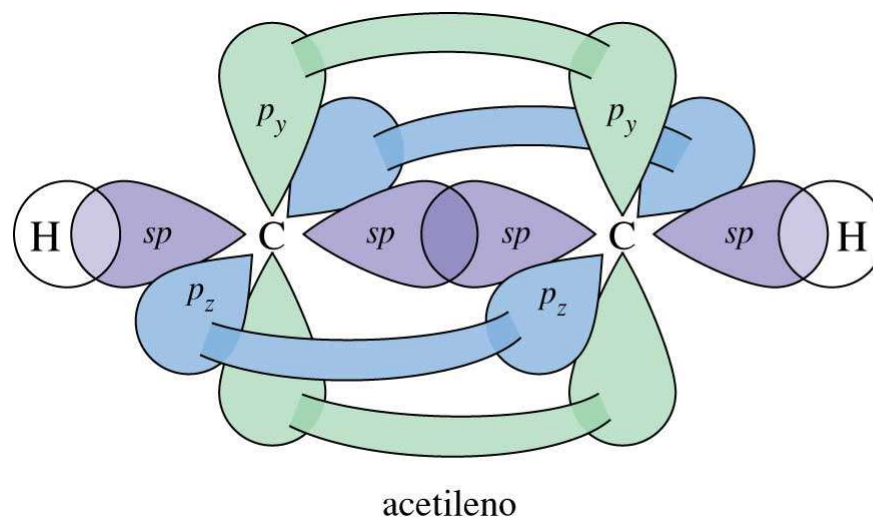
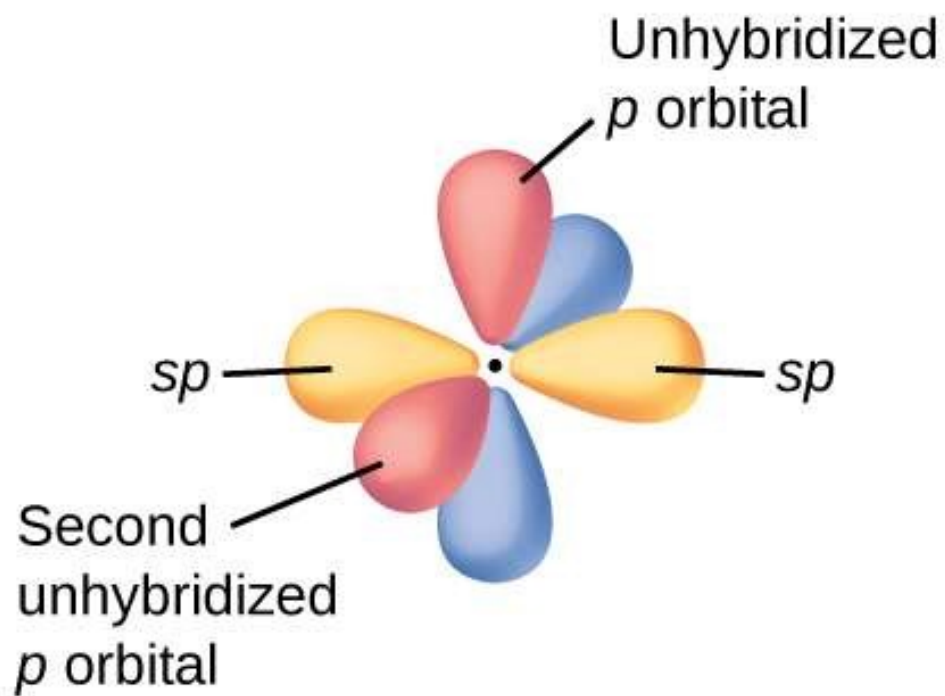
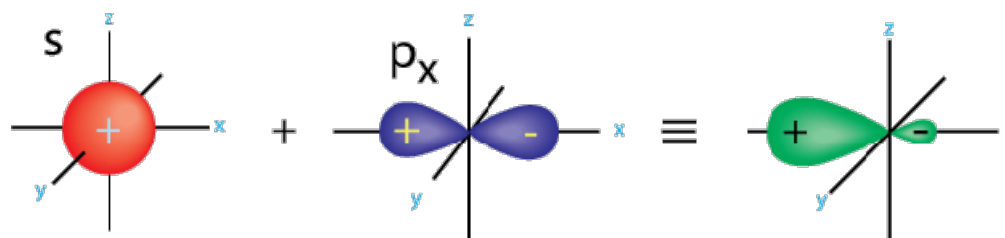
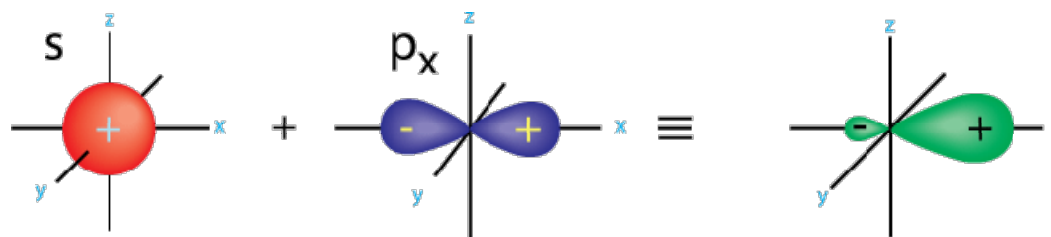


Son muy útiles para explicar la estereoquímica de las moléculas

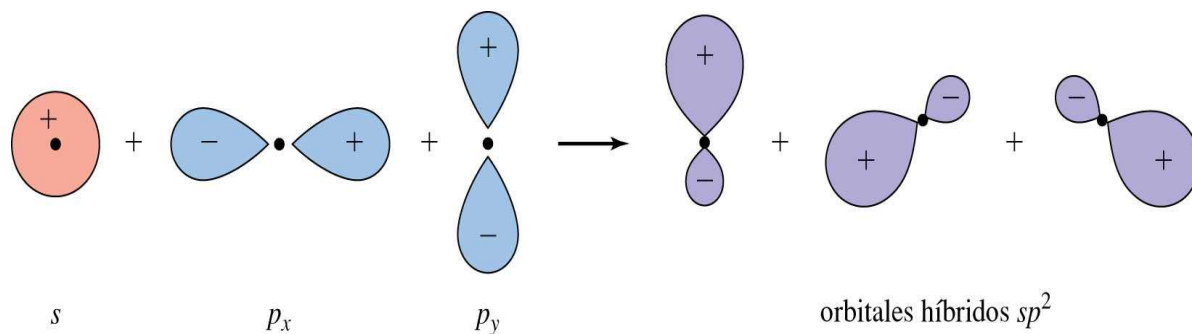
Híbridos sp

$$\Psi_1 = \frac{1}{\sqrt{2}} (s + p_x)$$

$$\Psi_2 = \frac{1}{\sqrt{2}} (s - p_x)$$



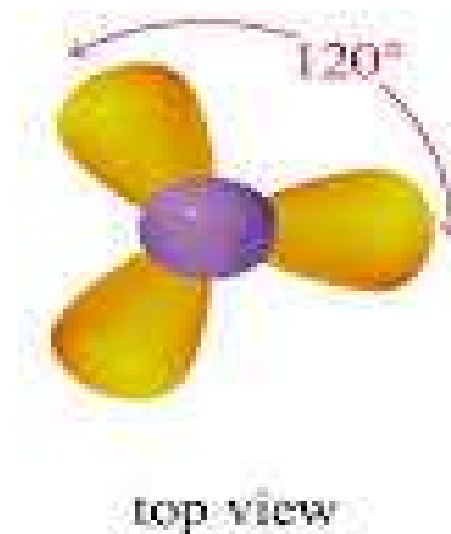
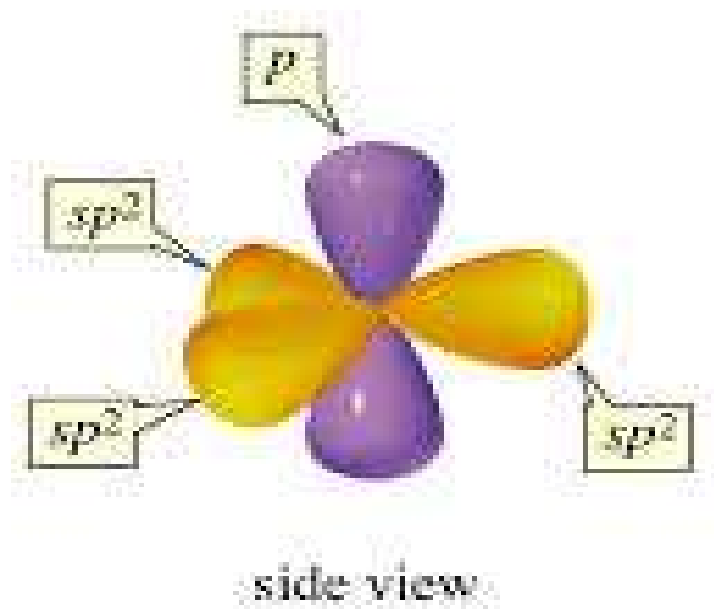
Híbridos sp^2



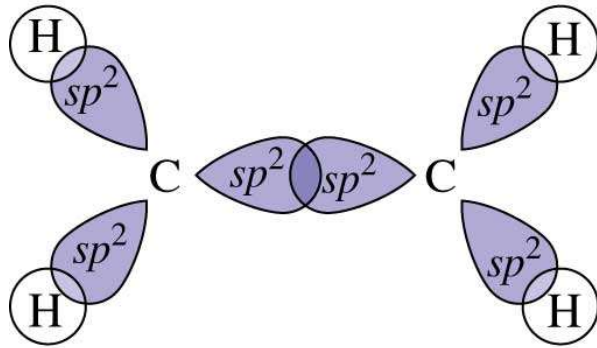
$$\Psi_1 = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_x$$

$$\Psi_2 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y$$

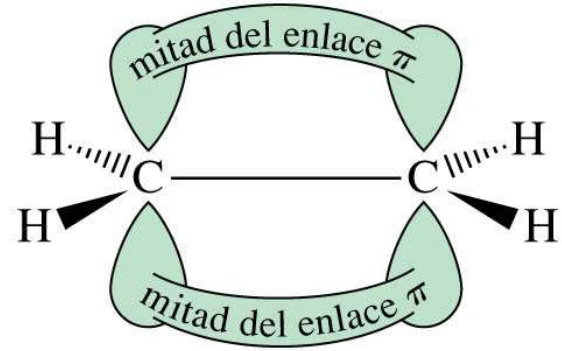
$$\Psi_3 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y$$



Etileno

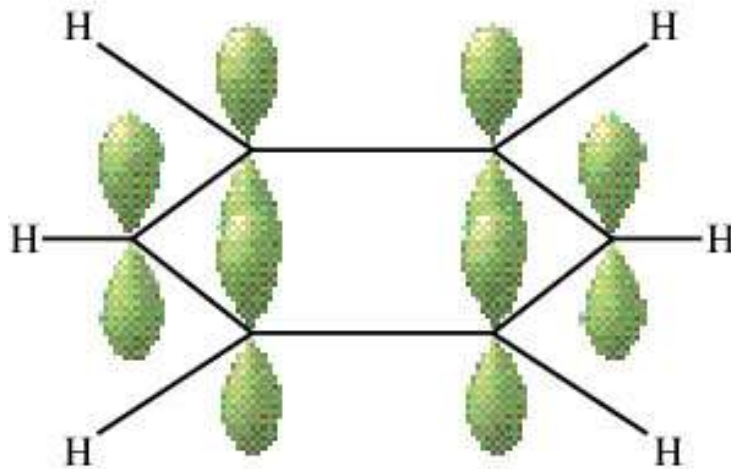


estructura de los enlaces σ
(vista desde encima del plano)

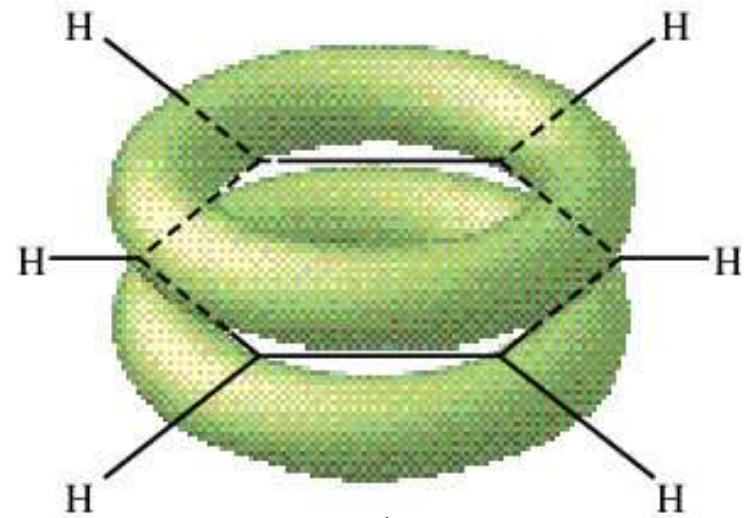


enlace π
(vista a lo largo del plano)

Benceno

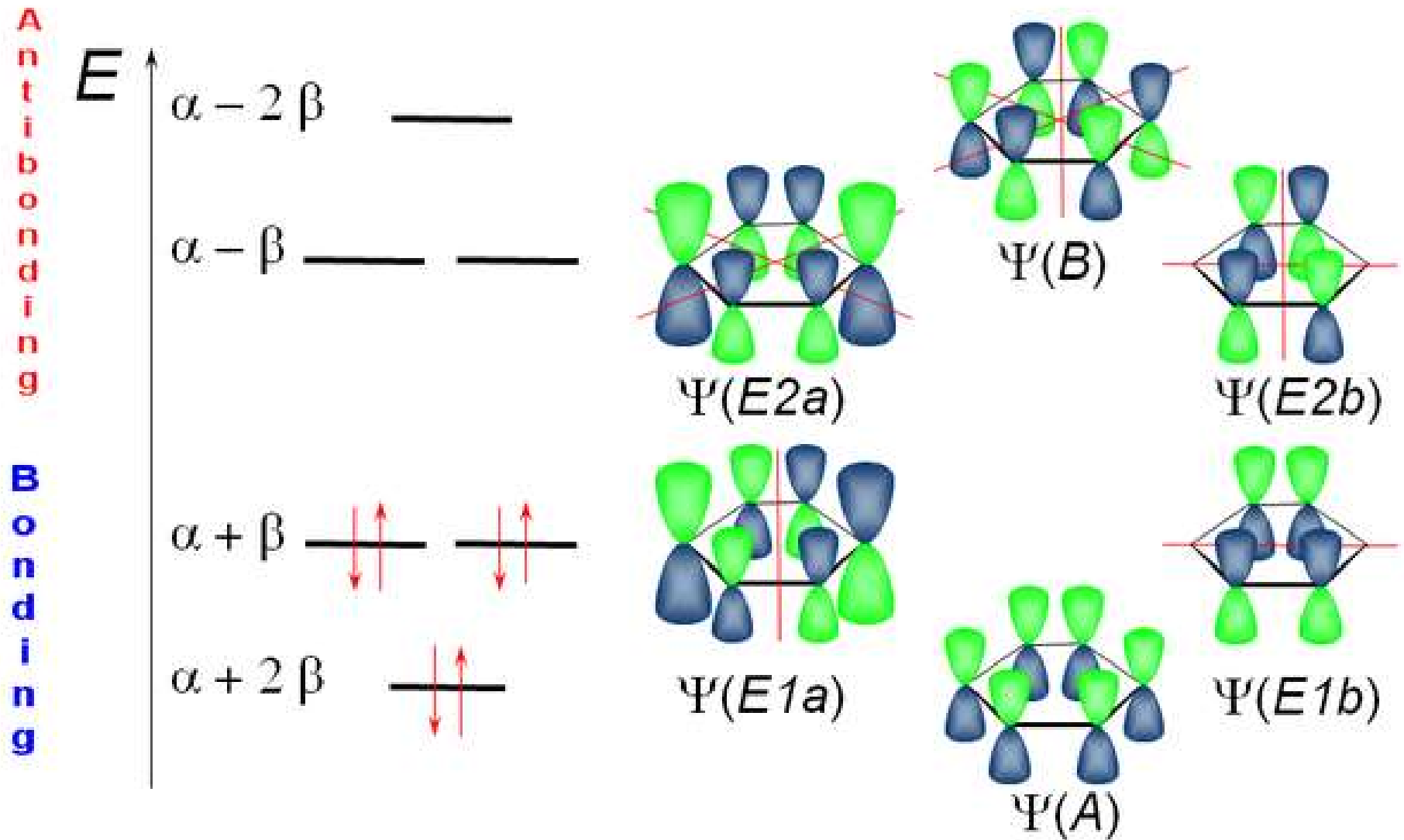


(a)



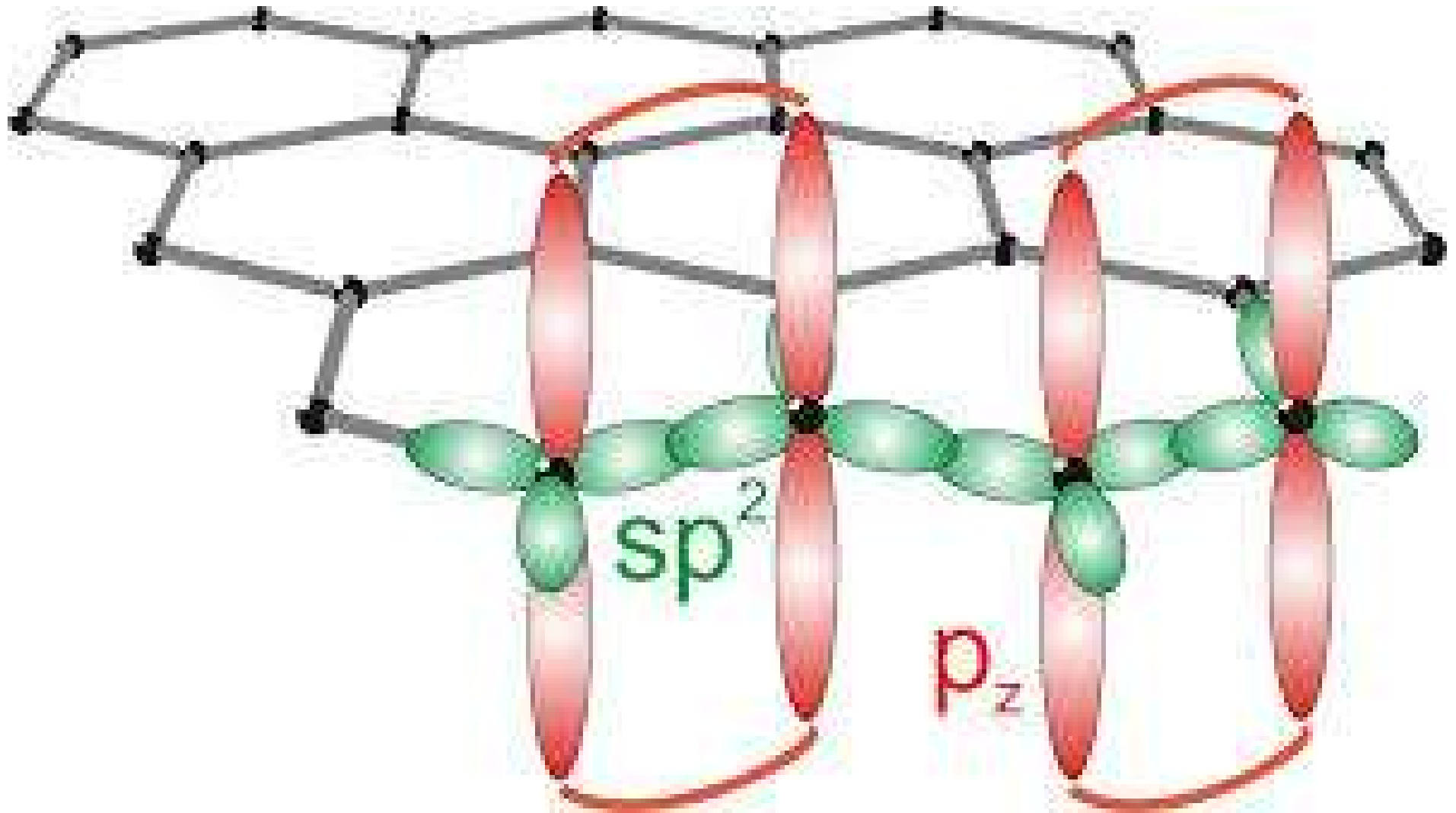
(b)

enlaces π

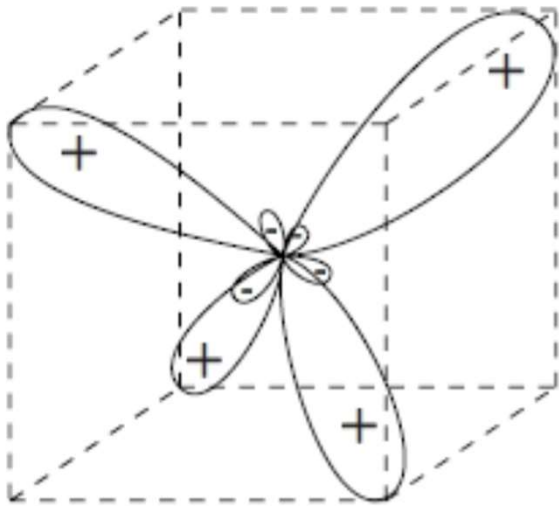


Niveles de energía de los OM π usando LCAO

Grafeno



Híbridos sp^3

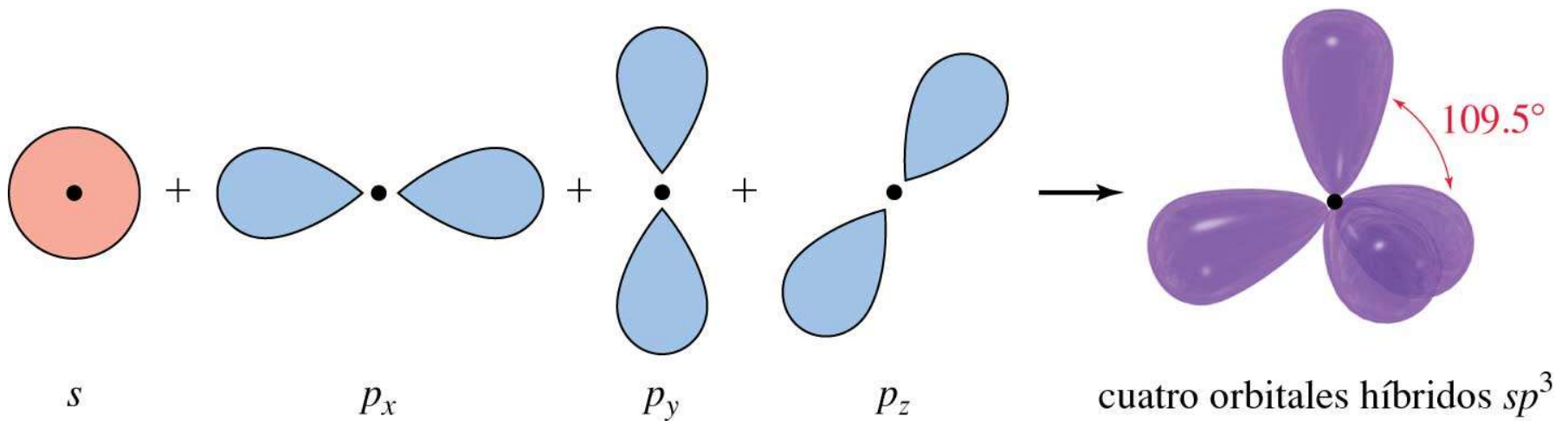


$$\Psi_1 = \frac{1}{2}(s + p_x + p_y + p_z)$$

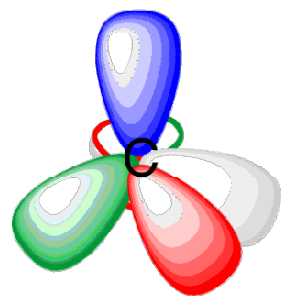
$$\Psi_2 = \frac{1}{2}(s - p_x - p_y + p_z)$$

$$\Psi_3 = \frac{1}{2}(s + p_x - p_y - p_z)$$

$$\Psi_4 = \frac{1}{2}(s - p_x + p_y - p_z)$$

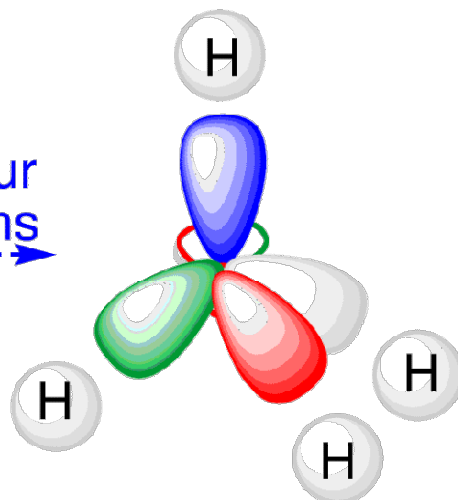


Metano

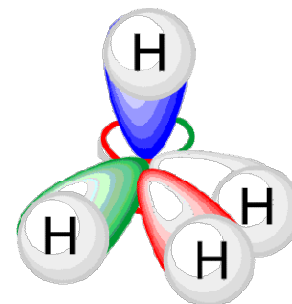


four sp^3 hybrid orbitals
form a tetrahedron

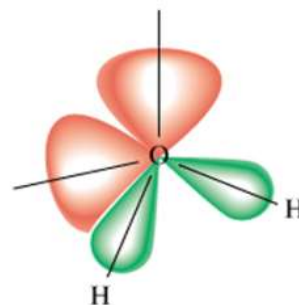
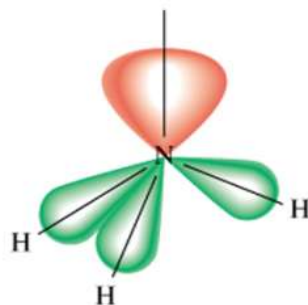
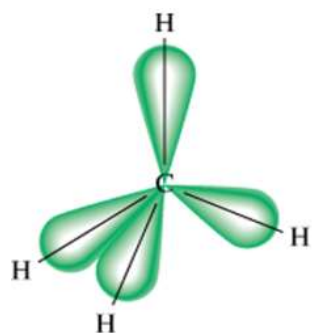
add four
H atoms
→



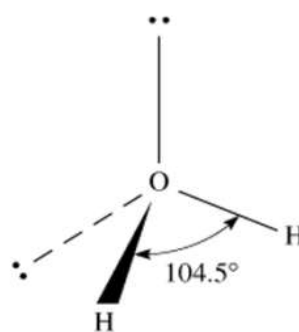
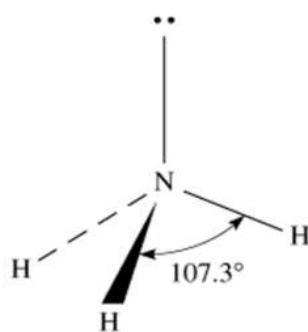
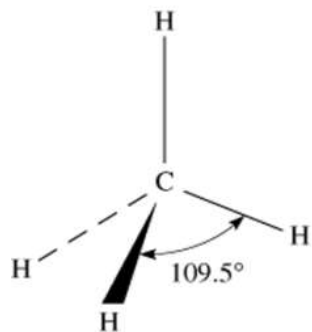
combine
 sp^3 and 1s
→



each MO orbital is
the
same and has σ
symmetry



(a)



(b)

Si – Ge- C (estructura de diamante)

