

NANOPHYSIQUE

INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch 5. Carbon Structures

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Lecture 6, 2021-2022

Carbon Structures

- Introduction
 - Histoire
 - Carbone
 - Hybridization
- Tight-binding calculations
 - Principe
 - Example: trans
 - Graphene π -liens
 - Graphene σ -liens
- Structure de carbone nanotubes
- Structure Electronique
- Synthesis
- Transport
- Multi-walled nanotubes

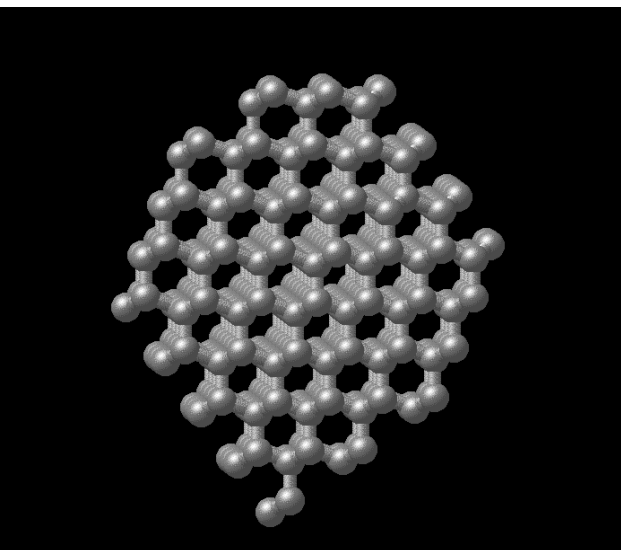
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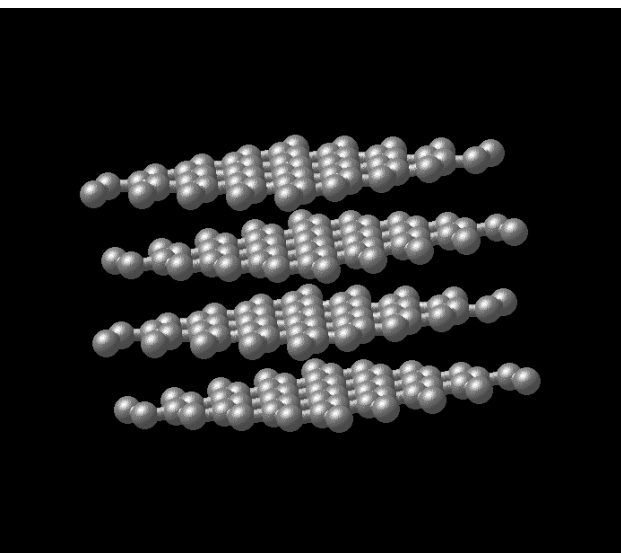
Une petite histoire

- La première fibre de carbone: Edison, 1879
- Recherche lente jusqu'à ce que les années 1950
- Aéronautique -> recherche de matériaux légers et résistants → “carbon whisker”
- Découverte de fullerenes (Kroto, Smalley 1985)
- → Recherche invitée à l'échelle du nanomètre fibres
- Spéculation théorique sur la forme et symétrie de carbone nanotubes (Smalley, Dresselhaus, ...)
- Observation de carbone nanotubes (Iijima, 1992 – utilisant TEM).

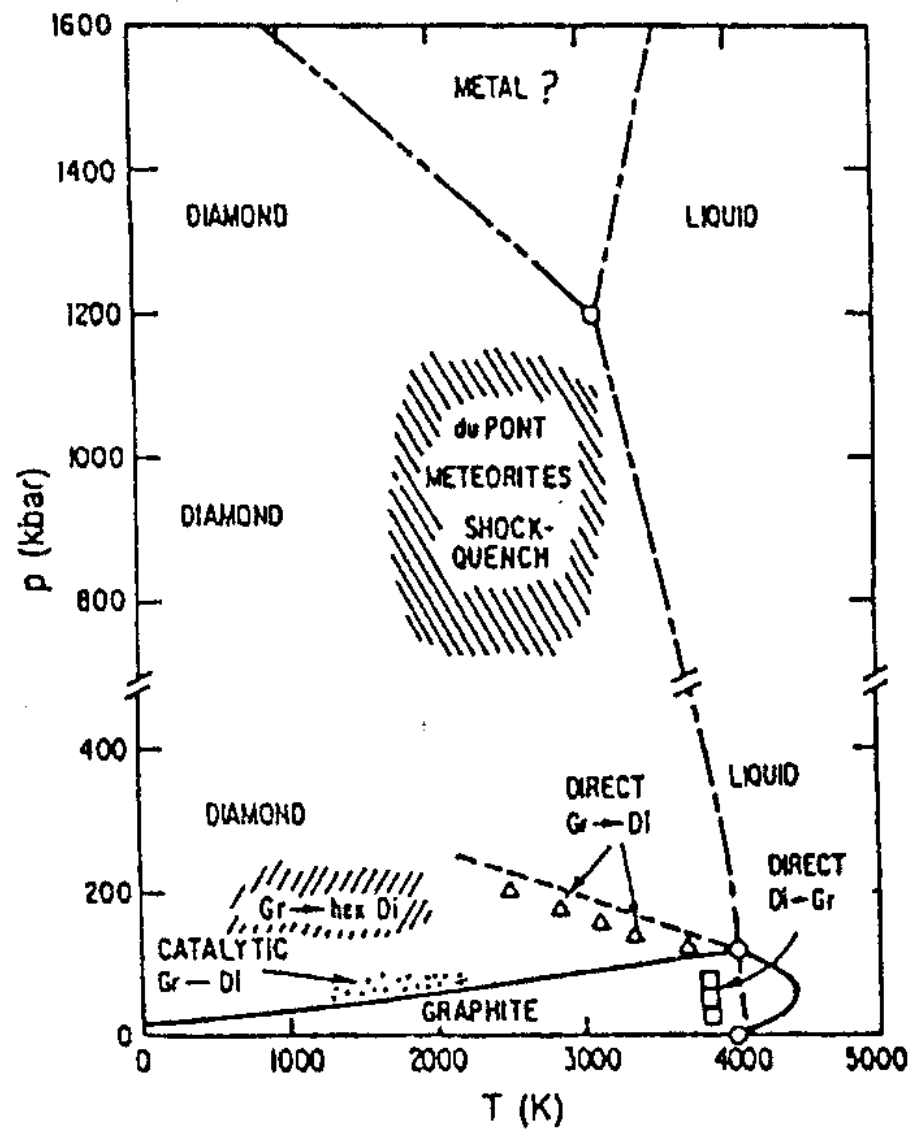
Propriétés du carbone



diamant

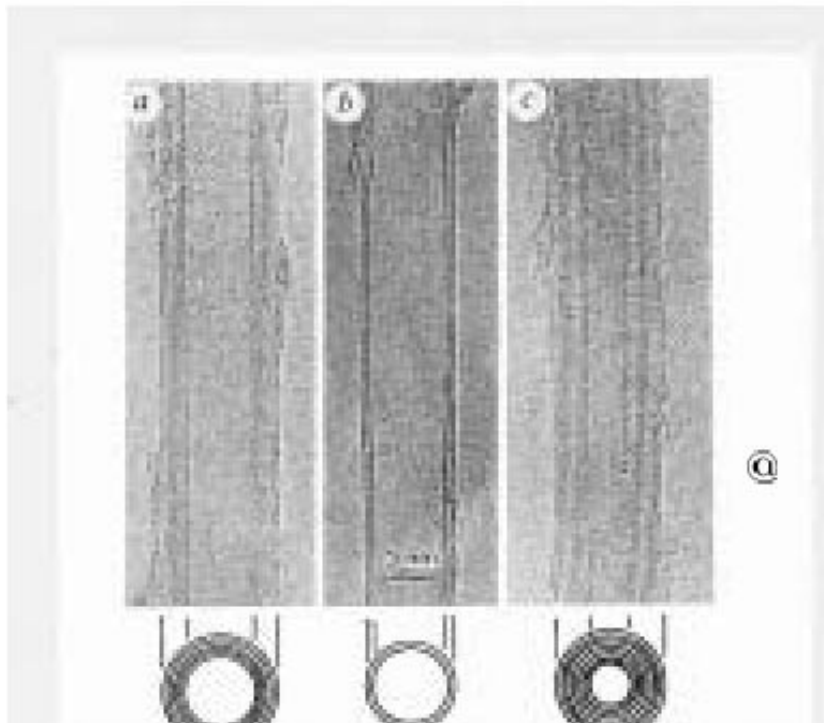


graphite

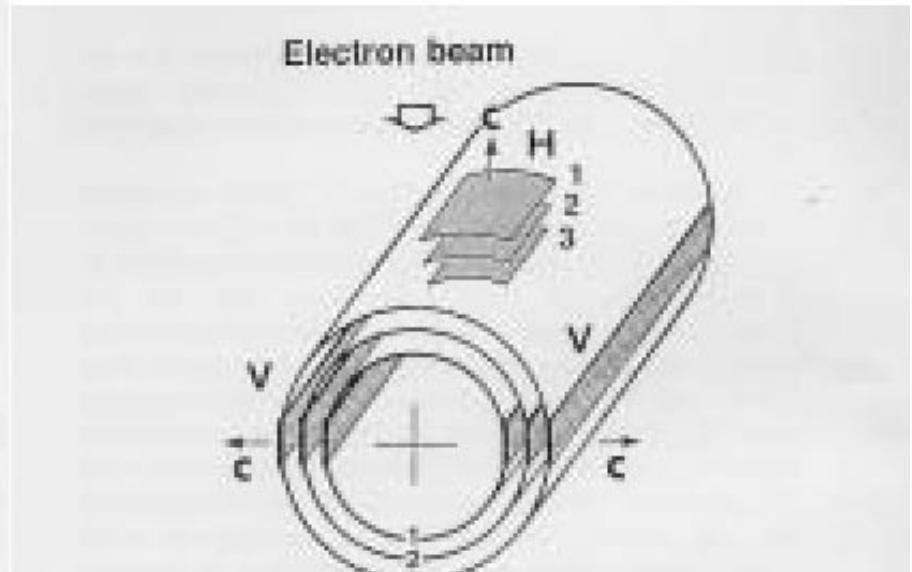


Discovery of Carbon Nanotubes

Iijima, Nature 354, 56 (1992)



Electron microscope image

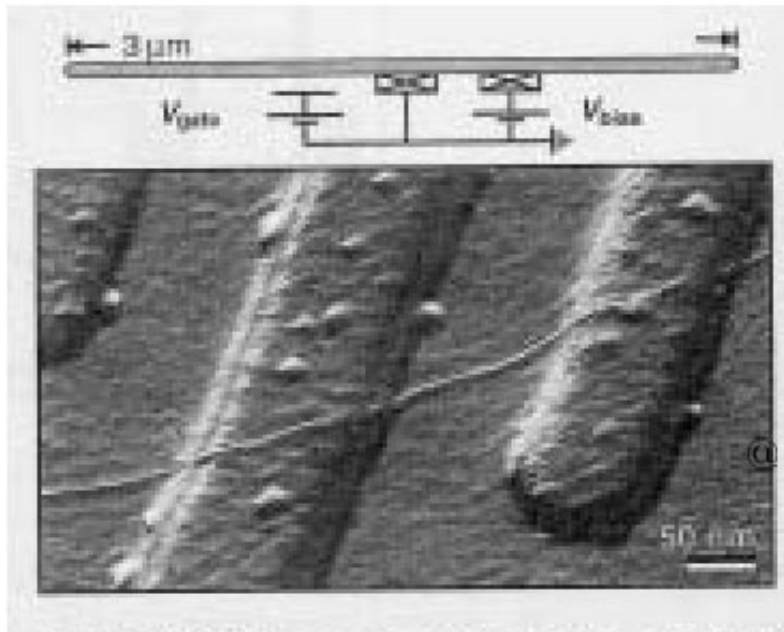


Interpretation of the images

diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

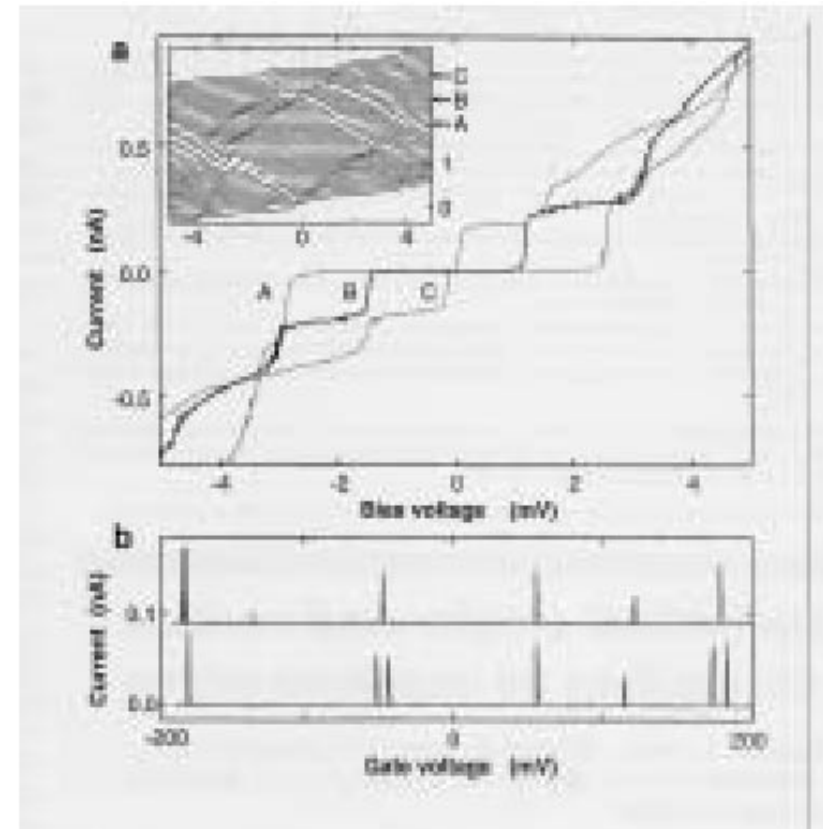
Current-voltage characteristics of CNT

S.J. Tans et al. Nature 386 474 (1997)



Electron microscope image of the system

- thin filament: Single-wall CNT
- hills: electrodes



a. Nonlinear conductance
(Coulomb staircase)

b. Controlling the number of electrons

Carbone

Carbone:

$$Z = 6$$

$$^{12}\text{C}, ^{13}\text{C} \rightarrow \text{stable}$$

$^{14}\text{C} \rightarrow$ half-life = 5,730 an
(carbon dating)

Configuration Electronique:

$1s^2 2s^2 2p^2$

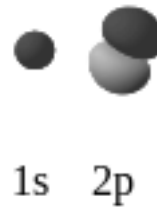
principle quantum number

occupancy

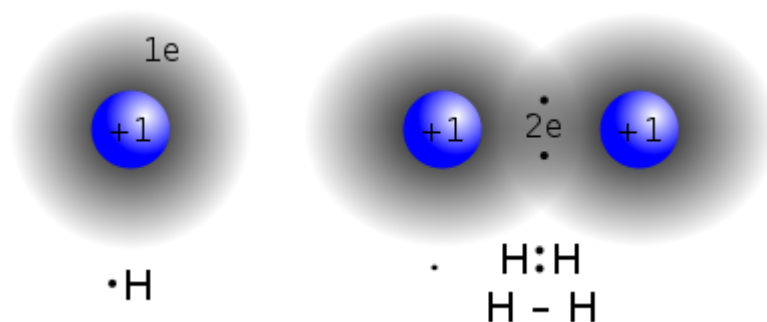
Periodic Table of Elements

1	2																	3	4	5	6	7	8	9	10
IA																		IIIA	IVA	VA	VIA	VIIA	0		
1 H																									2 He
3 Li	4 Be																	5 B	6 C	7 N	8 O	9 F	10 Ne		
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar																		
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr								
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe								
55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn								
87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110																

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



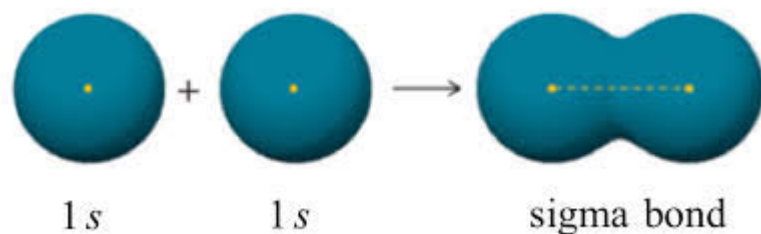
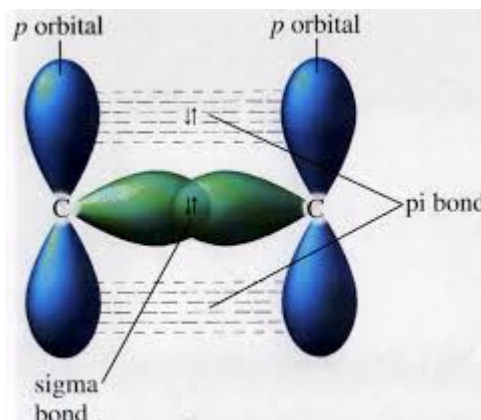
Covalent bonds: sharing electrons



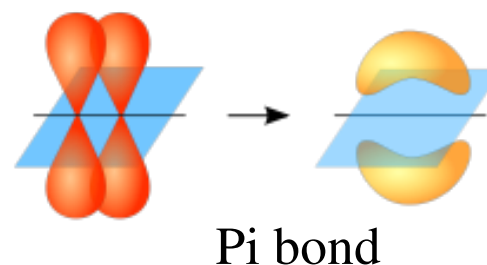
T (kinetic energy) : lower energy by delocalizing electrons

V (potential energy): lower energy by localizing electrons near ions

Types of molecular bonds

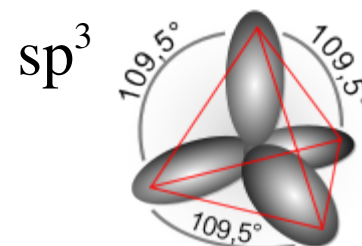
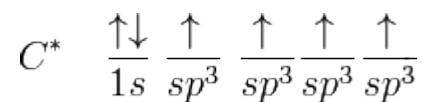
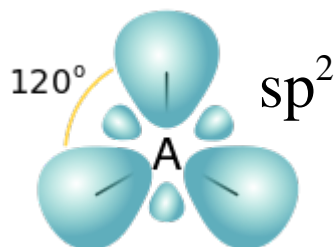
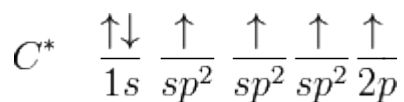
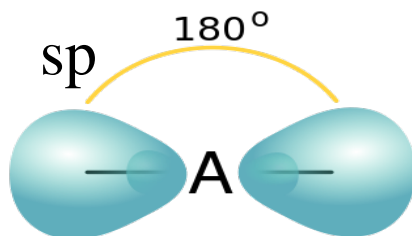
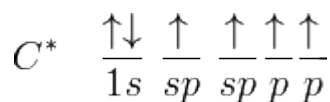
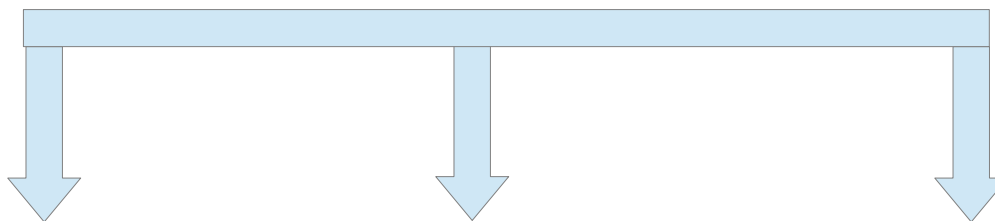
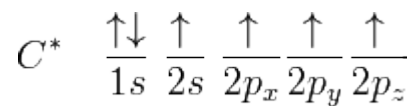
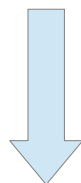
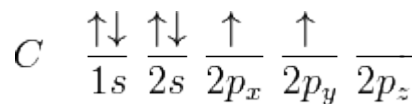


Sigma bond



T (kinetic energy) : lower energy by delocalizing electrons
V (potential energy): lower energy by localizing electrons near ions

Hybridization



SP Hybridization

$$\begin{aligned}|sp_a\rangle &= C_1|s\rangle + C_2|p_x\rangle \\ |sp_b\rangle &= C_3|s\rangle + C_4|p_x\rangle\end{aligned}$$

Orthonormality:

$$\langle sp_i | sp_j \rangle = \delta_{ij}$$



$$C_1^2 + C_2^2 = 1$$

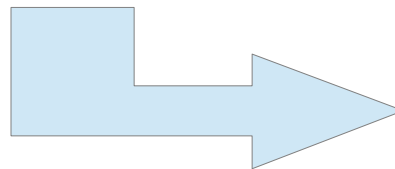
$$C_3^2 + C_4^2 = 1$$

$$C_1 C_3 + C_2 C_4 = 0$$



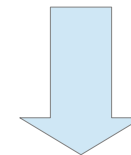
$$C_4 = \pm C_1$$

$$C_3 = \mp C_2 = \mp \sqrt{1 - C_1^2}$$



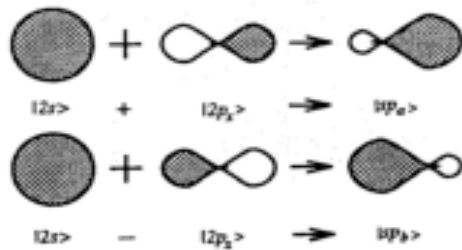
$$\begin{aligned}E_a &= C_1^2 E_s + C_2^2 E_p \\ &= C_1^2 \underbrace{(E_s - E_p)}_{<0} + E_p\end{aligned}$$

$$\begin{aligned}E_b &= C_3^2 E_s + C_4^2 E_p \\ &= E_s + C_1^2 (E_p - E_s) \\ &= E_a + (1 - 2C_1^2)(E_s - E_p)\end{aligned}$$



$$|sp_a\rangle = \frac{1}{\sqrt{2}}(|s\rangle + |p_x\rangle)$$

$$|sp_b\rangle = \frac{1}{\sqrt{2}}(|s\rangle - |p_x\rangle)$$



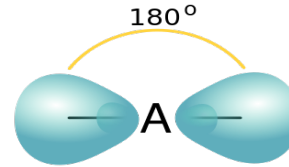
Orbitals and hybridizations for C

Structure électronique d'un atome de carbone = $1s^2 2s^2 2p^2$
 coeur = $1s^2$ 4 électrons de valence = $2s^2 2p^2$

Hybridation sp : $2s+2p_x, 2p_y, 2p_z$

Exemple : acétylène: HCCH liaison triple: 2 lien σ + 2 liens π

$$|sp_{a,b}\rangle = \frac{1}{\sqrt{2}}(|2s\rangle \pm |2p_x\rangle)$$

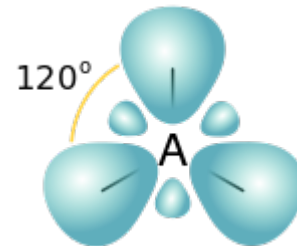


Hybridation sp^2 : $2s + 2p_x + 2p_y, 2p_z$

Exemple : polyacétylène: $(\text{HCCH})_n$ liaison double: 3 liens σ + 1 lien π

$$|sp_a^2\rangle = \frac{1}{\sqrt{3}}|2s\rangle - \sqrt{\frac{2}{3}}|2p_x\rangle$$

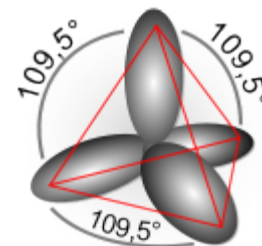
$$|sp_{b,c}^2\rangle = \pm \frac{1}{\sqrt{3}}|2s\rangle \pm \frac{1}{\sqrt{2}}|2p_x\rangle + \frac{1}{\sqrt{6}}|2p_z\rangle$$



Hybridation sp^3 : $2s + 2p_x + 2p_y + 2p_z$

Exemple : méthane: CH_4 liaison simple: 4 liens σ

$$|sp_a^3\rangle = \frac{1}{2}(|2s\rangle \pm |2p_x\rangle \pm |2p_y\rangle \pm |2p_z\rangle)$$



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Tight-binding method

1. Théorème de Bloch: Donné d'un potentiel qui est périodique sur un réseau de Bravais, $U(\mathbf{r}+\mathbf{R})=U(\mathbf{r})$, la solution de l'équation Schrodinger d'un électron est

$$\psi(\mathbf{r}) \text{ avec } \psi(\mathbf{r}+\mathbf{R})=e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r}) \forall \mathbf{R} \text{ dans le reseau.}$$

Preuve: Soit $T_{\mathbf{R}}$ etre l'opérateur de translation. Puis,

$$T_{\mathbf{R}} H \psi(\mathbf{r}) = H(\mathbf{r}+\mathbf{R}) \psi(\mathbf{r}+\mathbf{R}) = H(\mathbf{r}) \psi(\mathbf{r}+\mathbf{R}) = H(\mathbf{r}) T_{\mathbf{R}} \psi(\mathbf{r}) \rightarrow [H, T_{\mathbf{R}}] = 0$$

Alors, il ya vecteurs propres simultanés:

$$\begin{aligned} H \psi &= E \psi \\ T_{\mathbf{R}} \psi &= c(\mathbf{R}) \psi \end{aligned}$$

C'est evident que $T_{\mathbf{R}_1} T_{\mathbf{R}_2} = T_{\mathbf{R}_2} T_{\mathbf{R}_1} = T_{\mathbf{R}_1+\mathbf{R}_2}$

donc $c(\mathbf{R}_1) c(\mathbf{R}_2) = c(\mathbf{R}_1 + \mathbf{R}_2)$

$$\begin{aligned} c(\mathbf{R}_n) &= c(n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3) = c(\mathbf{a}_1)^{n_1} c(\mathbf{a}_2)^{n_2} c(\mathbf{a}_3)^{n_3} = e^{2\pi i (n_1 x_1 + n_2 x_2 + n_3 x_3)}, \quad x_j = \frac{\ln c(\mathbf{a}_j)}{2\pi i} \\ &= e^{i(x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2 + x_3 \mathbf{b}_3) \cdot \mathbf{R}_n}, \quad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \end{aligned}$$

Conditions à la limite periodique

$$\begin{aligned} \psi(\mathbf{r} + N_i \mathbf{a}_i) &= \psi(\mathbf{r}), \quad i=1,2,3 \\ \rightarrow x_i &= \frac{m_i}{N_i}, \quad m_i \text{ nombre entier } \leq N_i \end{aligned}$$

Tight-binding method

2. Tight-binding fonctions de base

$$\Phi_{jk}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n \in B} e^{i\mathbf{k} \cdot \mathbf{R}_n} \phi_j(\mathbf{r} - \mathbf{R}_n), \text{ où } \phi_j \text{ sont les fonctions atomique est } \mathbf{k} \in \tilde{B}$$

Vérification:

$$\begin{aligned} \Phi_{jk}(\mathbf{r} + \mathbf{R}_m) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n \in B} e^{i\mathbf{k} \cdot \mathbf{R}_n} \phi_j(\mathbf{r} + \mathbf{R}_m - \mathbf{R}_n) \\ &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_l \in B} e^{i\mathbf{k} \cdot (\mathbf{R}_l + \mathbf{R}_m)} \phi_j(\mathbf{r} - \mathbf{R}_l) \\ &= \Phi_{jk}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{R}_m} \end{aligned}$$

3. Tight-binding fonction d'onde

$$\psi(\mathbf{r}; \mathbf{k}) = \sum_{j=1}^n C_j(\mathbf{k}) \Phi_{jk}(\mathbf{r})$$

4. Tight-binding éléments de matrice

$$\begin{aligned} H_{jj'}(\mathbf{k}) &= \langle \Phi_{jk} | H | \Phi_{j'k} \rangle && \text{transfer integral matrix} \\ S_{jj'}(\mathbf{k}) &= \langle \Phi_{jk} | \Phi_{j'k} \rangle && \text{overlap integral matrix} \end{aligned}$$

Principe de variation pour l'équation de Schrodinger.

Theorem: La fonctionnelle $E[\psi] \equiv \frac{\int d\mathbf{r} \frac{h^2}{2m} (\nabla \psi(\mathbf{r}))^2 + V(\mathbf{r}) |\psi(\mathbf{r})|^2}{\int d\mathbf{r} |\psi(\mathbf{r})|^2}$

est minimisé pour tous fonction d'onde qui satisfie l'équation de Schrodinger.

D'après Ashcroft et Mermin,
"Solid State Physics", HRW, 1976

Preuve: Définir $F[\psi, \phi] = \int d\mathbf{r} \left(\frac{h^2}{2m} (\nabla \psi(\mathbf{r})) \cdot (\nabla \phi^*(\mathbf{r})) + V(\mathbf{r}) \psi(\mathbf{r}) \phi^*(\mathbf{r}) \right)$
 $(\psi, \phi) = \int d\mathbf{r} (\psi(\mathbf{r}) \phi^*(\mathbf{r}))$

Soit $H\psi = E\psi$ il s'ensuit que

$$F[\psi + \delta\psi, \psi + \delta\psi] = E((\psi, \psi) + (\psi, \delta\psi) + (\delta\psi, \psi)) + O(\delta\psi)^2$$

$$(\psi + \delta\psi, \psi + \delta\psi) = (\psi, \psi) + (\psi, \delta\psi) + (\delta\psi, \psi) + O(\delta\psi)^2$$

$$E[\psi + \delta\psi] \equiv \frac{F[\psi + \delta\psi, \psi + \delta\psi]}{(\psi + \delta\psi, \psi + \delta\psi)} = E + O(\delta\psi)^2$$

Tight-binding method

5. Tight-binding energies

Parce-que le calcul “tight-binding” est faite avec un ensemble restreint de fonctions de base, il s'agit d'un ansatz et non un calcul complet. Alors, on emploi le principe de variation:

$$E_0(\mathbf{k}) \leq E_{TB}(\mathbf{k}) = \frac{\langle \Psi_{\mathbf{k}} | H | \Psi_{\mathbf{k}} \rangle}{\langle \Psi_{\mathbf{k}} | \Psi_{\mathbf{k}} \rangle} = \frac{\sum_{j,j'} \bar{C}_j H_{jj'}(\mathbf{k}) C_{j'}}{\sum_{j,j'} \bar{C}_j S_{jj'}(\mathbf{k}) C_{j'}}$$

Minimizer:

$$\frac{\partial E_{TB}(\mathbf{k})}{\partial \bar{C}_j} = 0 = \frac{\sum_{j'} H_{jj'}(\mathbf{k}) C_{j'}}{\sum_{j,j'} \bar{C}_j S_{jj'}(\mathbf{k}) C_{j'}} - \frac{\sum_{j,j'} \bar{C}_j H_{jj'}(\mathbf{k}) C_{j'}}{\sum_{j,j'} \bar{C}_j S_{jj'}(\mathbf{k}) C_{j'}} \frac{\sum_{j'} S_{jj'}(\mathbf{k}) C_{j'}}{\sum_{j,j'} \bar{C}_j S_{jj'}(\mathbf{k}) C_{j'}}$$

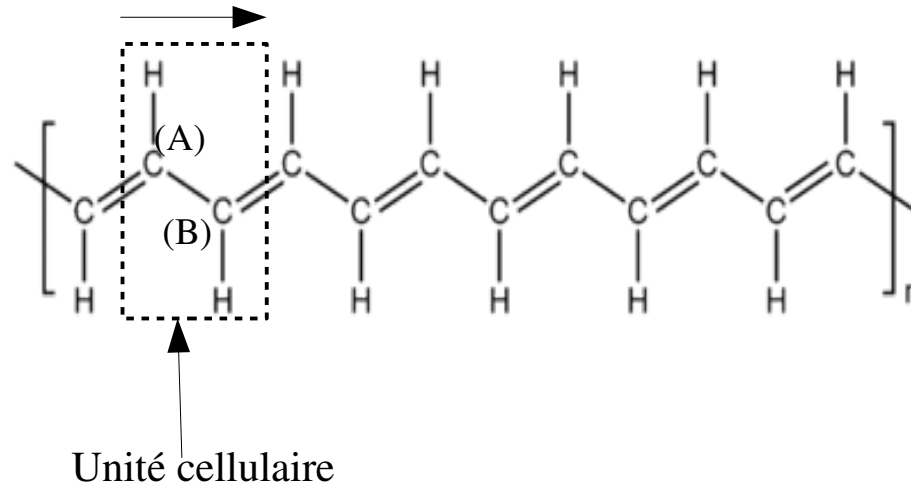
$$\rightarrow \sum_{j'} H_{jj'}(\mathbf{k}) C_{j'} = \lambda(\mathbf{k}) \sum_{j'} S_{jj'}(\mathbf{k}) C_{j'}$$

$$C_j \neq 0 \rightarrow \det(H(\mathbf{k}) - \lambda(\mathbf{k}) S(\mathbf{k})) = 0$$

Tight-binding method

Example: *trans*-polyacétylène

Vecteur de reseau: $\mathbf{a} = a \hat{x}$



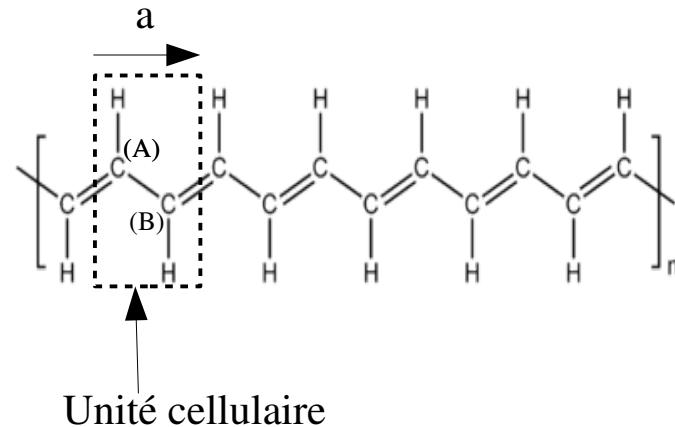
Vecteur de reseau reciproque: $\mathbf{b} = \frac{2\pi}{a} \hat{x}$

Tight-binding method

Example: *trans*-polyacétylène

Vecteur de reseau: $\mathbf{a} = a \hat{\mathbf{x}}$

Vecteur de reseau reciproque: $\mathbf{b} = \frac{2\pi}{a} \hat{\mathbf{x}}$



sp^2 hybridization \rightarrow σ -liens dans le plan, π -lien (p-p) dehors le plan

On cherche les niveau pour les π -electrons:

$$\Phi_A(\mathbf{r}; \mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n \in B} e^{i\mathbf{k} \cdot \mathbf{R}_n} \phi_{2p_z}(\mathbf{r} - \mathbf{R}_n) = \frac{1}{\sqrt{N}} \sum_{n=0}^N e^{ikna} \phi_{2p_z}(\mathbf{r} - na \hat{\mathbf{x}})$$

$$\Phi_B(\mathbf{r}; \mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n \in B} e^{i\mathbf{k} \cdot (\mathbf{R}_n + \mathbf{r}_{AB})} \phi_{2p_z}(\mathbf{r} - \mathbf{R}_n + \mathbf{r}_{AB}) = \frac{1}{\sqrt{N}} \sum_{n=0}^N e^{ikna + i\mathbf{k} \cdot \mathbf{r}_{AB}} \phi_{2p_z}(\mathbf{r} - \mathbf{r}_{AB} - na \hat{\mathbf{x}})$$

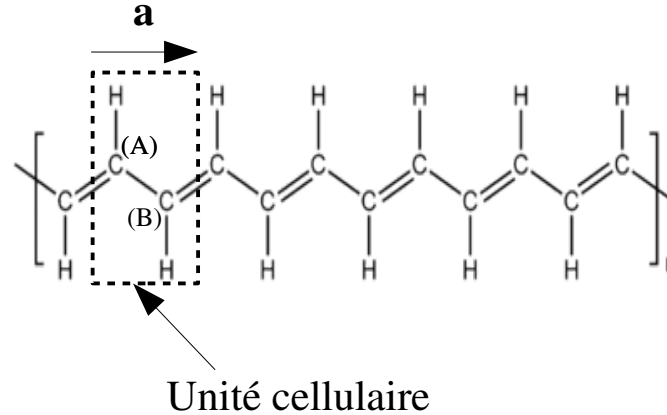
$$\mathbf{k} = \frac{2\pi}{a} \frac{p_i}{N} \hat{\mathbf{x}}, \quad 0 \leq p_i < N \quad \longrightarrow \quad 0 \leq k \leq 2\pi/a$$

Tight-binding method

Example: *trans*-polyacétylène

Vecteur de reseau: $\mathbf{a} = a \hat{\mathbf{x}}$

Vecteur de reseau reciproque: $\mathbf{b} = \frac{2\pi}{a} \hat{\mathbf{x}}$



$$\Phi_A(\mathbf{r}; \mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n \in B} e^{i\mathbf{k} \cdot \mathbf{R}_n} \phi_{2p_z}(\mathbf{r} - \mathbf{R}_n) = \frac{1}{\sqrt{N}} \sum_{n=0}^N e^{ikna} \phi_{2p_z}(\mathbf{r} - na \hat{\mathbf{x}})$$

$$\Phi_B(\mathbf{r}; \mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n \in B} e^{i\mathbf{k} \cdot (\mathbf{R}_n + \mathbf{r}_{AB})} \phi_{2p_z}(\mathbf{r} - \mathbf{R}_n + \mathbf{r}_{AB}) = \frac{1}{\sqrt{N}} \sum_{n=0}^N e^{ikna + ikR_x} \phi_{2p_z}(\mathbf{r} - \mathbf{r}_{AB} - na \hat{\mathbf{x}})$$

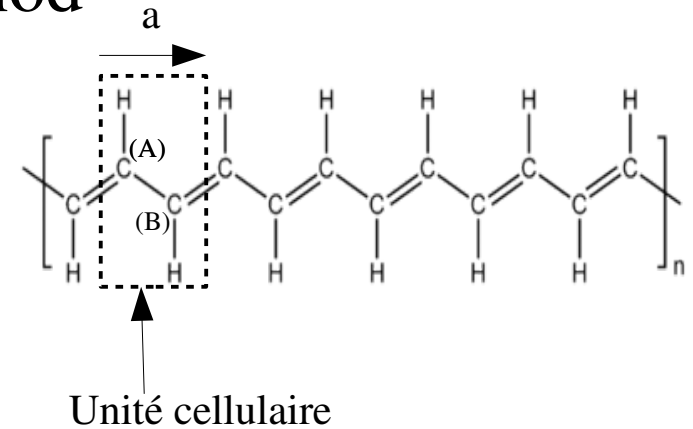
$$\begin{aligned} H_{AA}(\mathbf{k}) &= \langle \Phi_A | H | \Phi_A \rangle = \frac{1}{N} \sum_{n,m=0}^N e^{ik(n-m)a} \langle \phi_{2p_z}(\mathbf{r} - ma \hat{\mathbf{x}}) | H | \phi_{2p_z}(\mathbf{r} - na \hat{\mathbf{x}}) \rangle \\ &= \underbrace{\langle \phi_{p_z}(\mathbf{r}) | H | \phi_{p_z}(\mathbf{r}) \rangle + \frac{1}{N} \sum_{n \neq m}^N e^{ik(n-m)a} \langle \phi_{2p_z}(\mathbf{r} - ma \hat{\mathbf{x}}) | H | \phi_{2p_z}(\mathbf{r} - na \hat{\mathbf{x}}) \rangle}_{\text{faible}} \\ &\approx \epsilon_{2p} \end{aligned}$$

Tight-binding method

Example: *trans*-polyacétylène

Vecteur de reseau: $\mathbf{a} = a \hat{x}$

Vecteur de reseau reciproque: $\mathbf{b} = \frac{2\pi}{a} \hat{x}$



$$\begin{aligned}
 H_{AB}(k \hat{x}) &= \langle \Phi_{Ak} | H | \Phi_{Bk} \rangle = \frac{1}{N} \sum_{n,m=0}^N e^{ik(n-m) + ik r_{AB,x}} \langle \phi_{2p_z}(\mathbf{r} - m\mathbf{a} \hat{x}) | H | \phi_{2p_z}(\mathbf{r} - \mathbf{r}_{AB} - n\mathbf{a} \hat{x}) \rangle \\
 &= e^{ik R_x} \langle \phi_{2p_z}(\mathbf{r}) | H | \phi_{2p_z}(\mathbf{r} - \mathbf{r}_{AB}) \rangle + e^{ik(r_{AB,x} - a)} \langle \phi_{2p_z}(\mathbf{r}) | H | \phi_{2p_z}(\mathbf{r} - \mathbf{r}_{AB} + \mathbf{a}) \rangle \\
 &\quad + \underbrace{\frac{1}{N} \sum_{m=0; n \neq 0, -1}^N e^{ik r_{AB,x} + ik(n-m)} \langle \phi_{2p_z}(\mathbf{r} - m\mathbf{a} \hat{x}) | H | \phi_{2p_z}(\mathbf{r} - \mathbf{r}_{AB} - n\mathbf{a} \hat{x}) \rangle}_{\text{faible}}
 \end{aligned}$$

if $r_{ABx} = a/2$

$$\approx 2t \cos(ka/2), \quad t \equiv \langle \phi_{2p_z}(\mathbf{r}) | H | \phi_{2p_z}(\mathbf{r} - \mathbf{a}/2) \rangle$$

Tight-binding method

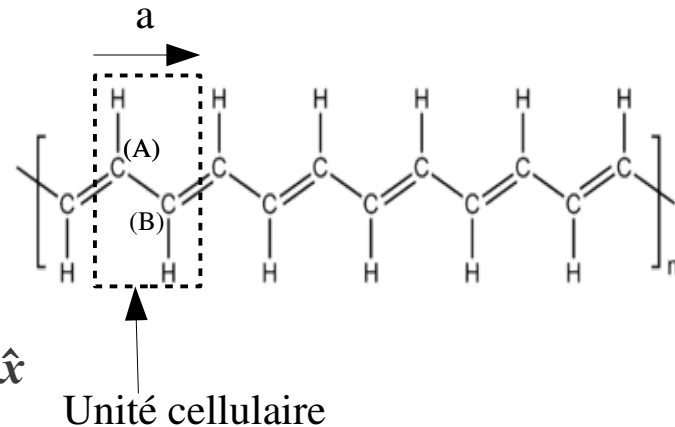
Example: *trans*-polyacétylène

Vecteur de reseau:

$$\mathbf{a} = a \hat{x}$$

Vecteur de reseau reciproque:

$$\mathbf{b} = \frac{2\pi}{a} \hat{x}$$

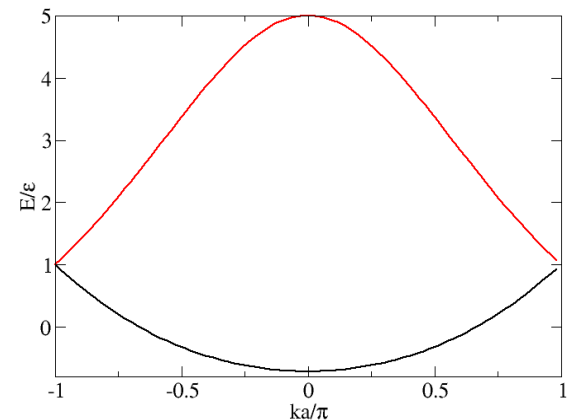


$$H_{ij} = \begin{pmatrix} \epsilon_{2p} & 2t \cos(ka/2) \\ 2t \cos(ka/2) & \epsilon_{2p} \end{pmatrix} \quad S_{ij} = \begin{pmatrix} 1 & 2s \cos(ka/2) \\ 2s \cos(ka/2) & 1 \end{pmatrix}$$

$$0 = \det \begin{pmatrix} \epsilon_{2p} - E & 2(t - sE) \cos(ka/2) \\ 2(t - sE) \cos(ka/2) & \epsilon_{2p} - E \end{pmatrix}$$

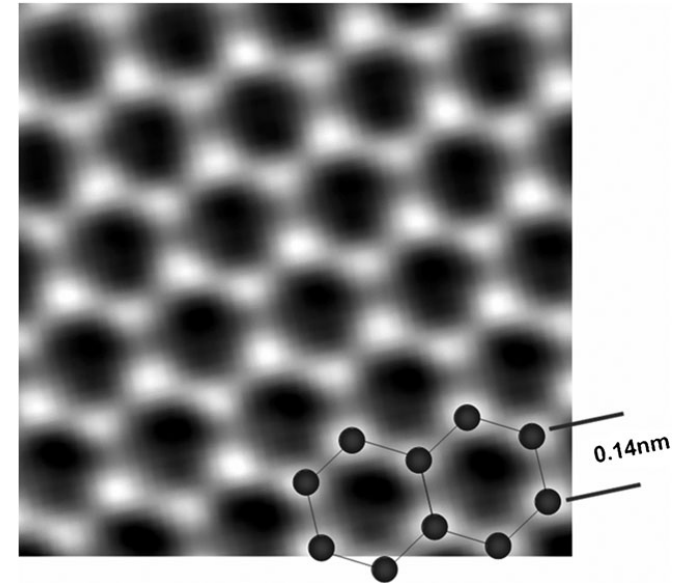
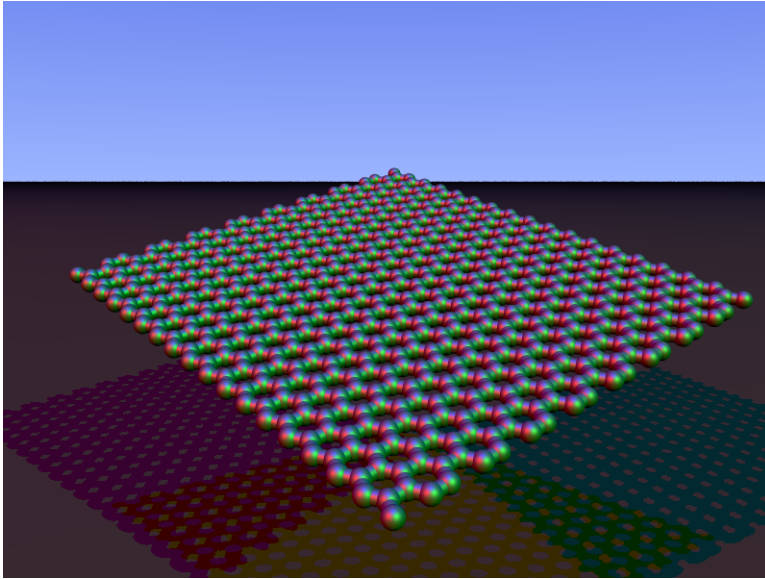
$$= (\epsilon_{2p} - E)^2 - 4(t - sE)^2 \cos^2(ka/2)$$

$$E_{\pm}(k) = \frac{\epsilon_{2p} \pm 2t \cos(ka/2)}{1 \pm 2s \cos(ka/2)}, \quad -\frac{\pi}{a} < k < \frac{\pi}{a}$$



Graphene 1

graphène = un seul feuillet de graphite



Structure électronique d'un atome de carbone = $1s^2 2s^2 2p^2$

coeur = $1s^2$

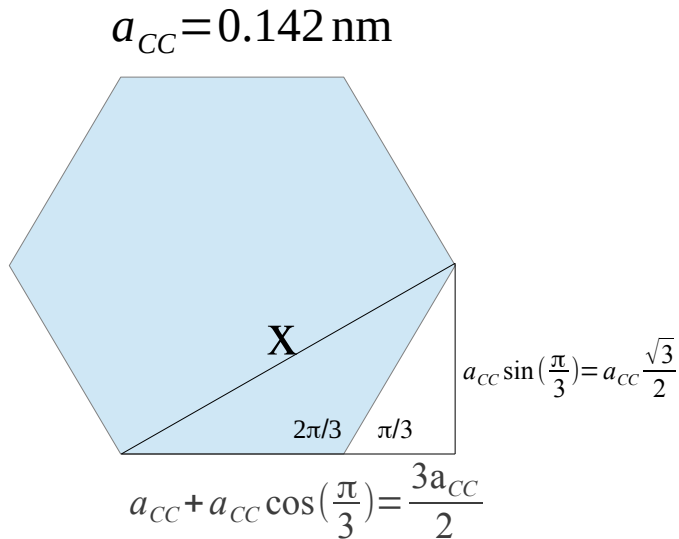
4 électrons de valence = $2s^2 2p^2$

Chaque atome de carbone offre 3 orbitales atomiques sp^2 et une orbitale $2p_z$

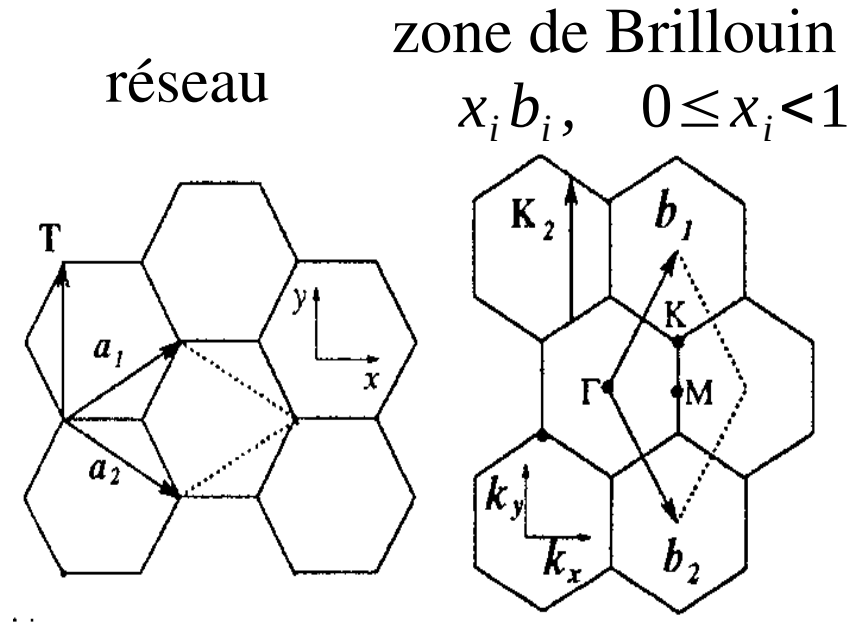
Les orbitales atomiques sp^2 forment les liens σ

Les orbitales atomiques $2p_z$ forment les liens π

Graphene 2



$$x = \sqrt{\frac{9a_{CC}^2}{4} + \frac{3a_{CC}^2}{4}} = \sqrt{3} a_{CC}$$



$$\mathbf{a}_{1,2} = \left(\frac{\sqrt{3}}{2} a, \pm \frac{a}{2} \right) \quad \mathbf{b}_{1,2} = \left(\frac{2\pi}{\sqrt{3}a}, \pm \frac{2\pi}{a} \right)$$

$$a = \|\mathbf{a}_1\| = \|\mathbf{a}_2\| = 0.246 \text{ nm}$$

Graphene Tight-binding : π -bands

réseau

zone de Brillouin

$$H_{AA} = H_{BB} = \epsilon_{2p}$$

$$H_{AB} = t(e^{ik \cdot R_1} + e^{ik \cdot R_2} + e^{ik \cdot R_3})$$

$$\equiv t f(\mathbf{k})$$

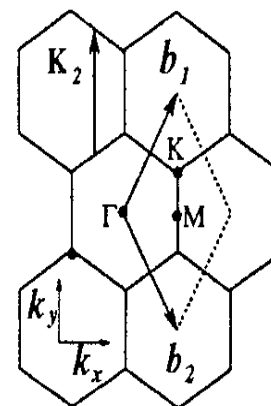
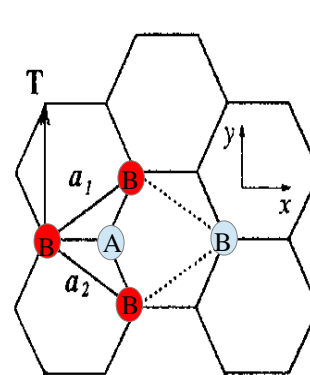
$$f(\mathbf{k}) = e^{-ik_x a / \sqrt{3}} + 2e^{ik_x a / 2\sqrt{3}} \cos\left(\frac{k_y a}{2}\right)$$

$$S_{AB} = s f(\mathbf{k})$$

$$E_{\pi\pi} = \frac{\epsilon_{2p} \pm t w(\mathbf{k})}{1 \pm s w(\mathbf{k})}$$

$$w(\mathbf{k}) = \sqrt{[f(\mathbf{k})]^2} = \sqrt{1 + 4 \cos\left(\frac{\sqrt{3} k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right)}$$

$s=0 \Leftrightarrow$ "Slater-Koster approximation"



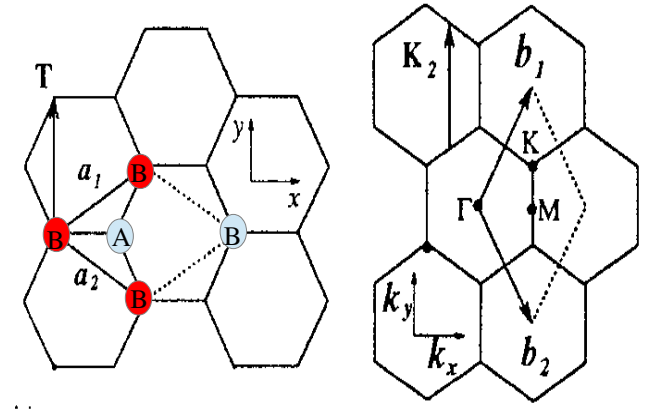
$$\mathbf{a}_{1,2} = \left(\frac{\sqrt{3}}{2} a, \pm \frac{a}{2} \right)$$

$$\mathbf{b}_{1,2} = \left(\frac{2\pi}{\sqrt{3}a}, \pm \frac{2\pi}{a} \right)$$

Graphene Tight-binding : σ -bands

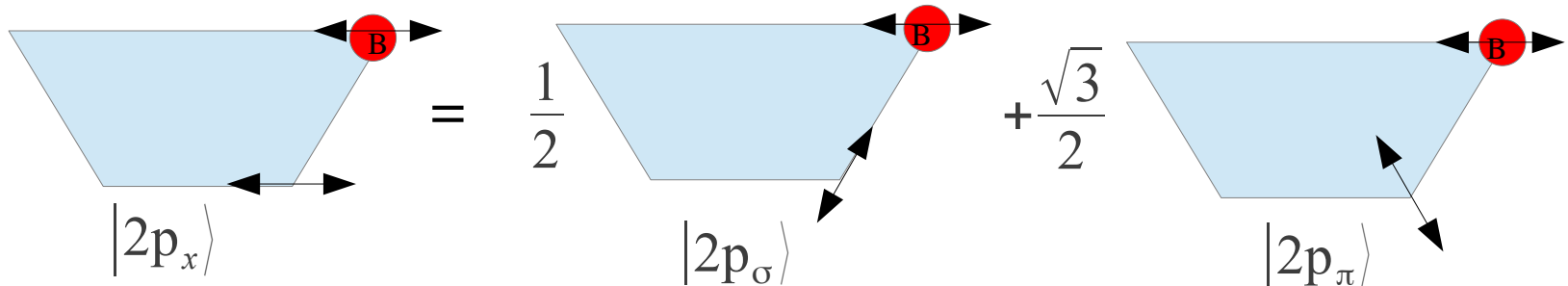
Basis: $(2s^A, 2p_x^A, 2p_y^A, 2s^B, 2p_x^B, 2p_y^B)$

$$H_{AA} = \begin{pmatrix} \epsilon_{2s} & 0 & 0 \\ 0 & \epsilon_{2p} & 0 \\ 0 & 0 & \epsilon_{2p} \end{pmatrix}, \quad S_{AA} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



Alors, $|2p_x\rangle = \cos\left(\frac{\pi}{3}\right)|2p_\sigma\rangle + \cos\left(\frac{2\pi}{3}\right)|2p_\pi\rangle = \frac{1}{2}|2p_\sigma\rangle + \frac{\sqrt{3}}{2}|2p_\pi\rangle$

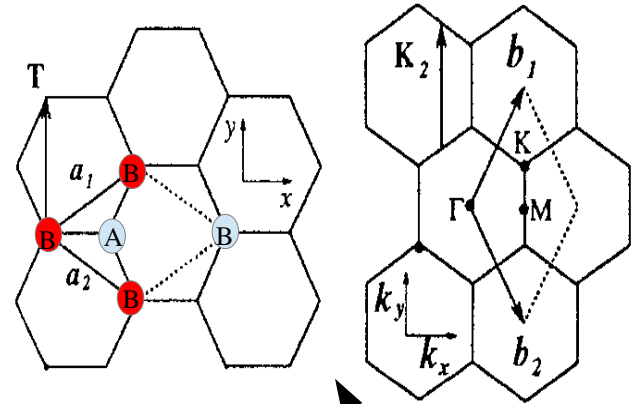
Car l'état de $l = 1$ se transforme comme un vecteur sous rotations.



Graphene Tight-binding : σ -bands

Basis: $(2s^A, 2p_x^A, 2p_y^A, 2s^B, 2p_x^B, 2p_y^B)$

$$|2p_x\rangle = \frac{1}{2}|2p_\sigma\rangle + \frac{\sqrt{3}}{2}|2p_\pi\rangle$$

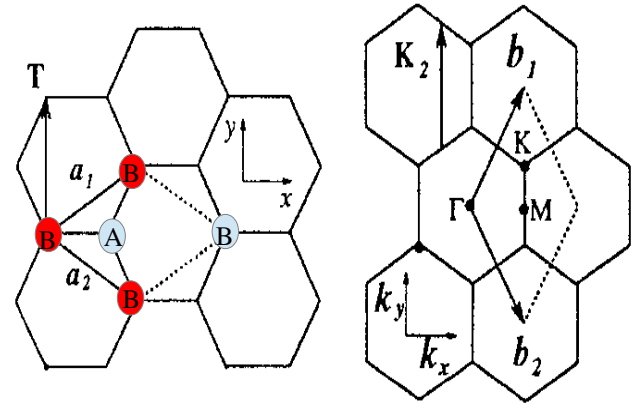
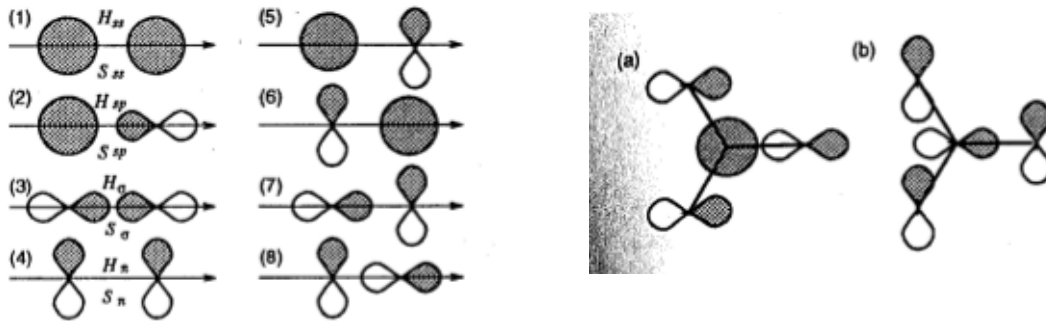


$$\begin{aligned} \langle 2p_x^B | H | 2p_x^A \rangle &= \left(\frac{1}{2}\right)^2 \langle 2p_\sigma^B | H | 2p_\sigma^A \rangle + \left(\frac{\sqrt{3}}{2}\right)^2 \langle 2p_\pi^B | H | 2p_\pi^A \rangle \\ &+ \left(\frac{1}{2}\right)\left(\frac{\sqrt{3}}{2}\right) \langle 2p_\pi^B | H | 2p_\sigma^A \rangle + \left(\frac{1}{2}\right)\left(\frac{\sqrt{3}}{2}\right) \langle 2p_\sigma^B | H | 2p_\pi^A \rangle \end{aligned}$$

$$= \left(\frac{1}{4}H_{\sigma\sigma} + \frac{3}{4}H_{\pi\pi}\right) e^{i(k_x R_x + k_y R_y)} = \left(\frac{1}{4}H_{\sigma\sigma} + \frac{3}{4}H_{\pi\pi}\right) e^{i\left(\frac{k_x a}{2\sqrt{3}} + \frac{k_y a}{2}\right)}, \quad H_{\sigma\pi} = 0$$

Graphene Tight-binding : σ -bands

Basis: $(2s^A, 2p_x^A, 2p_y^A, 2s^B, 2p_x^B, 2p_y^B)$



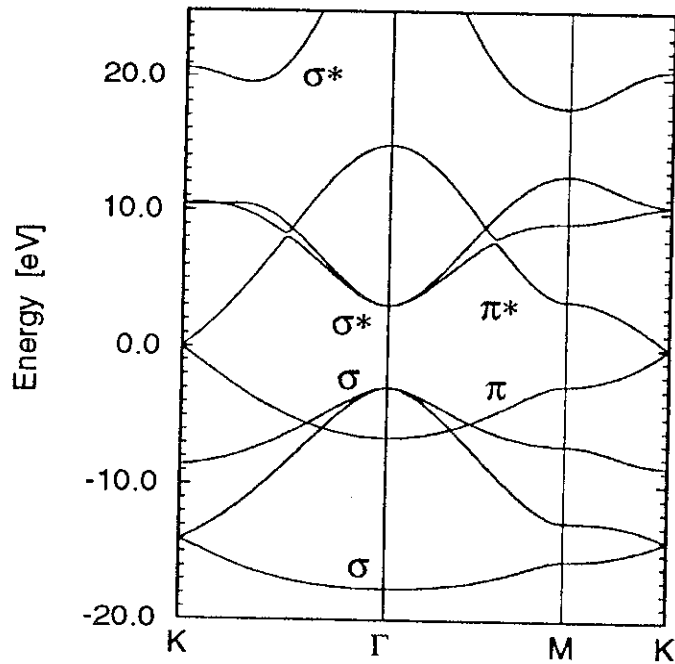
R. Saito, G. Dresselhaus & M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998)

$$\langle 2p_x^B | H | 2p_x^A \rangle = \frac{1}{4} (H_{\sigma\sigma} + 3H_{\pi\pi}) e^{i\left(\frac{k_x a}{2\sqrt{3}} + \frac{k_y a}{2}\right)}$$

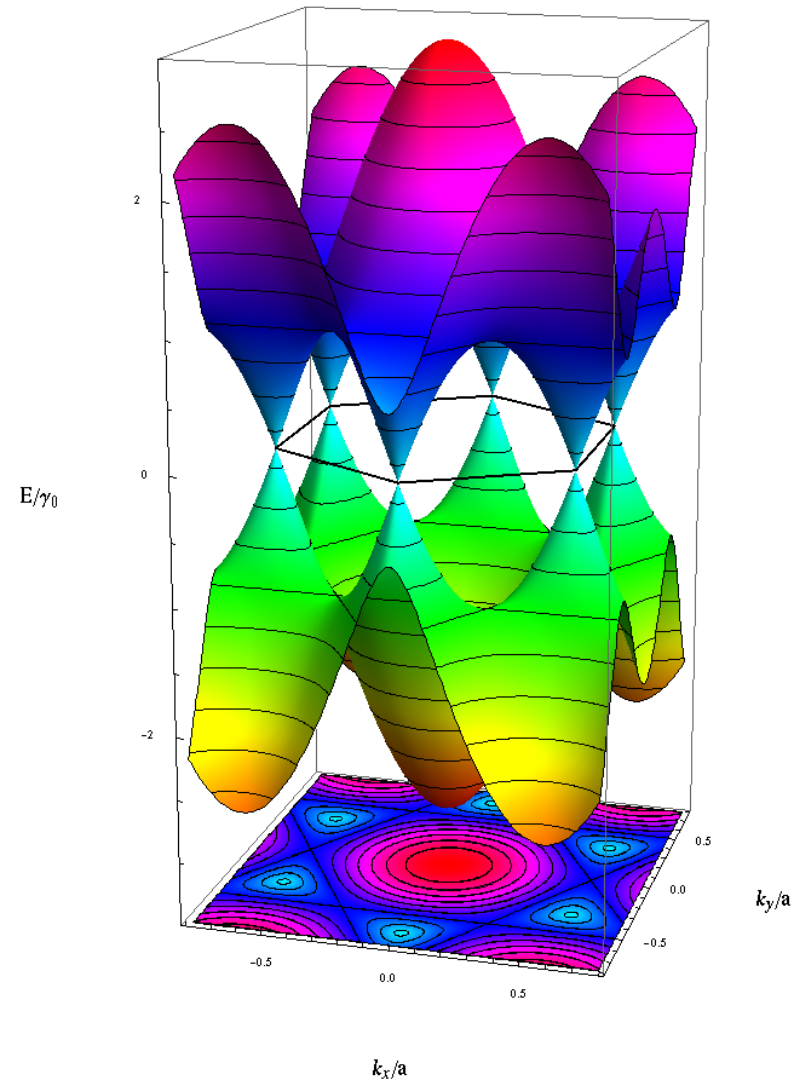
$$\langle 2p_x^B | H | 2p_y^A \rangle = \frac{i\sqrt{3}}{2} (H_{\sigma\sigma} + H_{\pi\pi}) e^{-ik_x a / 2\sqrt{3}} \sin \frac{k_y a}{2}$$

$$\langle 2s^B | H | 2p_x^A \rangle = H_{sp} \left(-e^{ik_x a / \sqrt{3}} + e^{ik_x a / (2\sqrt{3})} \right)$$

Graphene



component	H (eV)	S
ss	-6.7969	0.212
sp	-5.580	0.102
$\sigma\sigma$	-5.037	0.146
$\pi\pi$	-3.033	0.129
$\epsilon_s - \epsilon_p$	-8.868	



R. Saito, G. Dresselhaus & M. S. Dresselhaus,
Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998)

Carbon Structures

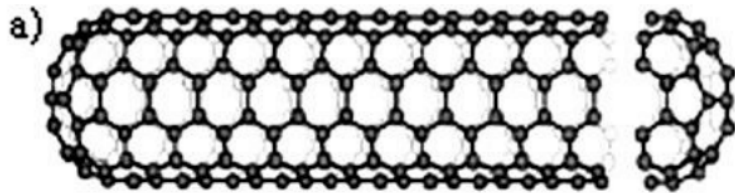
- Introduction
 - Histoire
 - Carbone
 - Hybridization
- Tight-binding calculations
 - Principe
 - Example: trans
 - Graphene π -liens
 - Graphene σ -liens
- Structure de carbone nanotubes
- Structure Electronique
- Synthesis
- Transport
- Multi-walled nanotubes

Nanotube structure

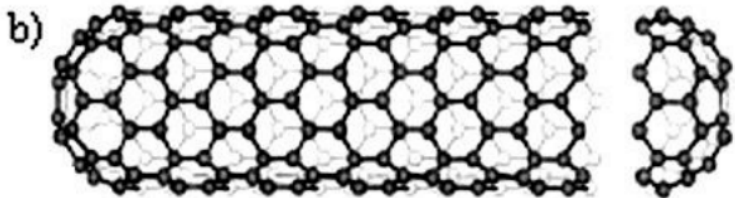
Rayon: 0.7-10 nm (pour la plupart $< 2\text{nm}$)

Longueur: 1-100 μm

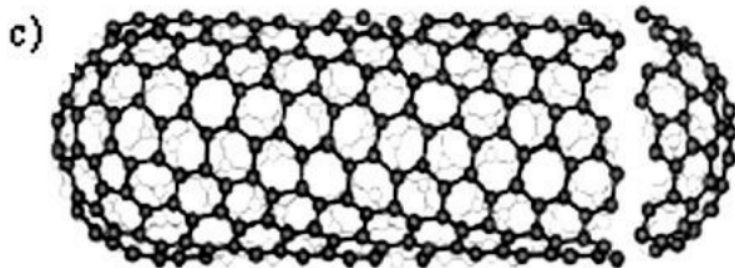
Chapeau (“cap”): fullerene avec
6 pentagons +plusieurs hexagon



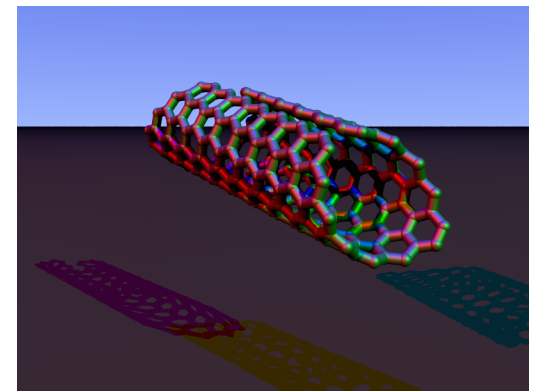
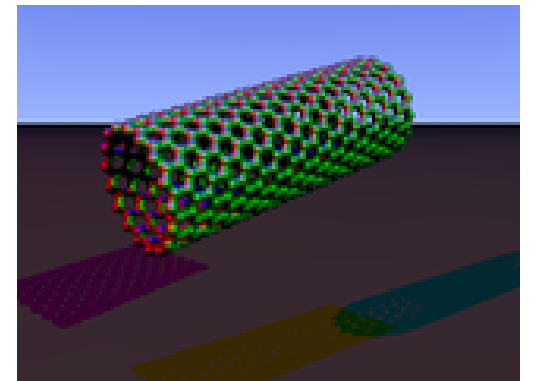
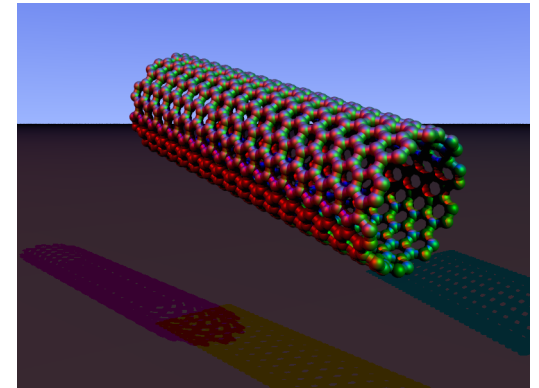
“armchair”



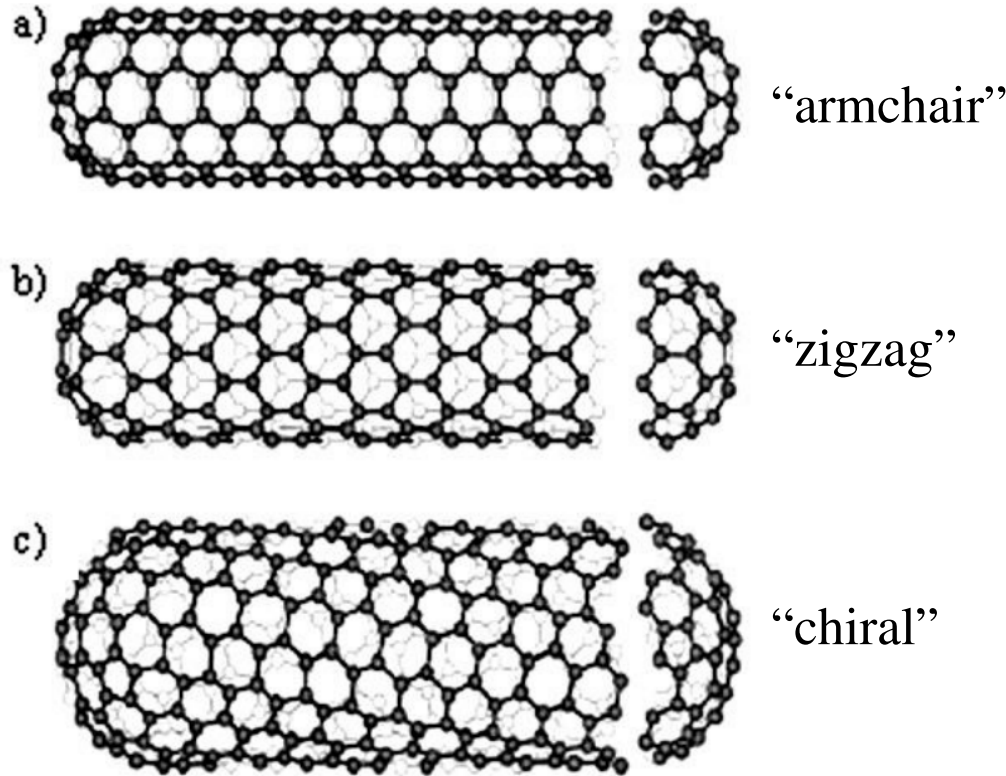
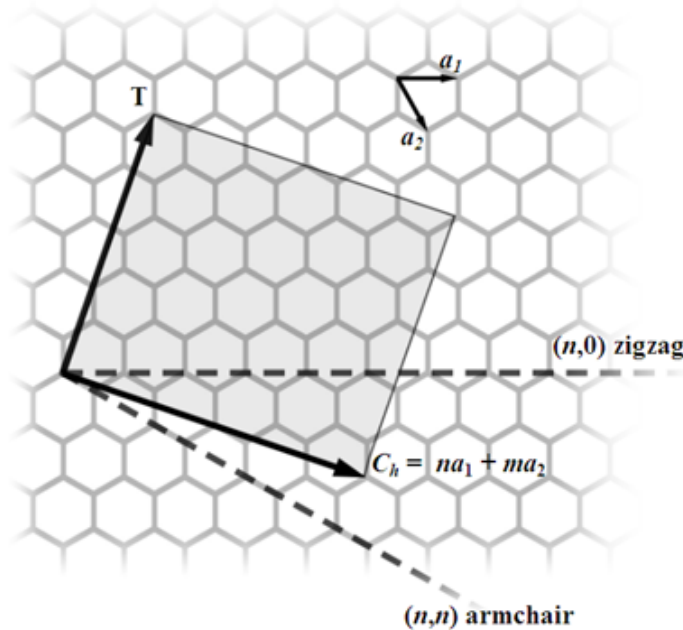
“zigzag”



“chiral”



Nanotube structure

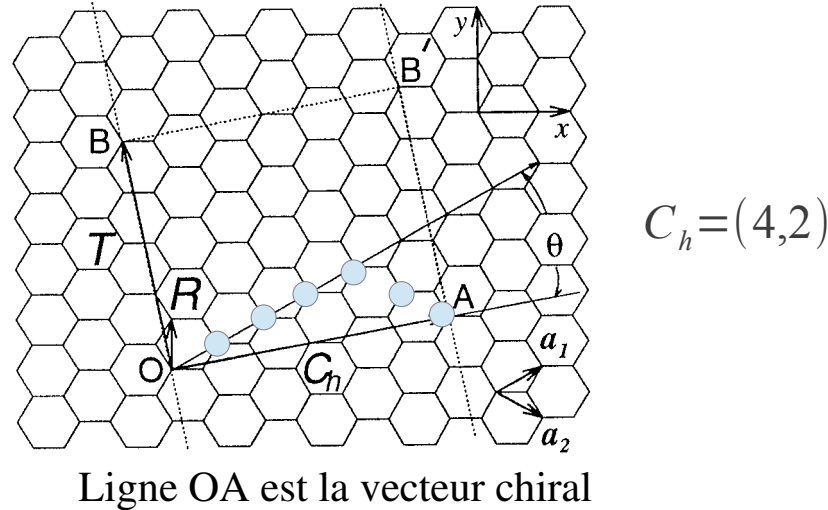


Division fondamentale:

- “achiral” : possédant une symétrie miroir (seulement la “zigzag” et la “armchair”)
- “chiral” : pas de symétrie miroir

Nanotube structure : vecteur chiral

Les points O,A et B,B' sont identifiés



Vecteur chiral: $C_h = n a_1 + m a_2 \Leftrightarrow (n, m), \quad 0 \leq |m| \leq n$

N.B.: $a_1 \cdot a_1 = a_2 \cdot a_2 = a^2, \quad a_1 \cdot a_2 = \frac{a^2}{2} \quad a = 0.144 \text{ nm} \times \sqrt{3} = 0.249 \text{ nm}$

Diamètre: $d_t = L/\pi = \|C_h\|/\pi = \sqrt{n^2 + m^2 + nm} \times 0.079 \text{ nm}$

Angle chiral: $\cos \theta \equiv \frac{C_h \cdot a_1}{\|C_h\| \|a_1\|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$

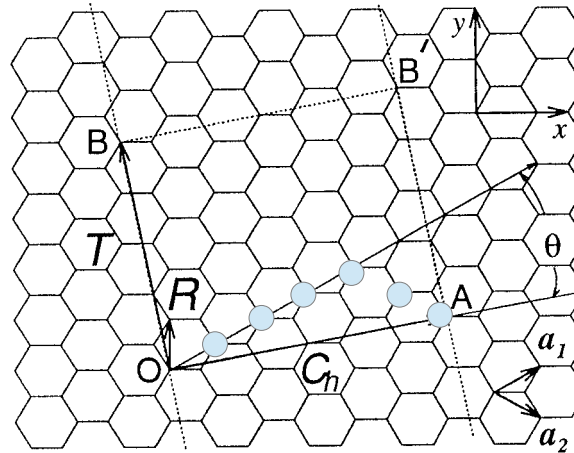
Nanotube structure : vecteur de translation

Les points O,A et B,B' sont identifiés

R. Saito, G. Dresselhaus & M. S. Dresselhaus,
Physical Properties of Carbon Nanotubes
(Imperial College Press, London, 1998)

$$C_h = (4, 2)$$

Ligne OB est la vecteur de translation



La vecteur de translation
définit le unité cellulaire
le long de la nanotube.

Vecteur de translation: $T = t_1 a_1 + t_2 a_2 \Leftrightarrow (n, m)$

$$C_h \cdot T = 0 \Leftrightarrow t_1 (2n + m) + t_2 (n + 2m) = 0 \Leftrightarrow t_1 = \frac{2m + n}{\gcd(2m + n, m + 2n)}, \quad t_2 = -\frac{m + 2n}{\gcd(2m + n, m + 2n)}$$

Dans l'exemple: $\gcd(8, 10) = 2 \Leftrightarrow t_1 = \frac{8}{2} = 4, \quad t_2 = -\frac{10}{2} = -5$

Le nombre d'hexagônes par unite cellulaire est: $N = \frac{2L^2}{a^2 \gcd(2m + n, m + 2n)}$
(exercice)

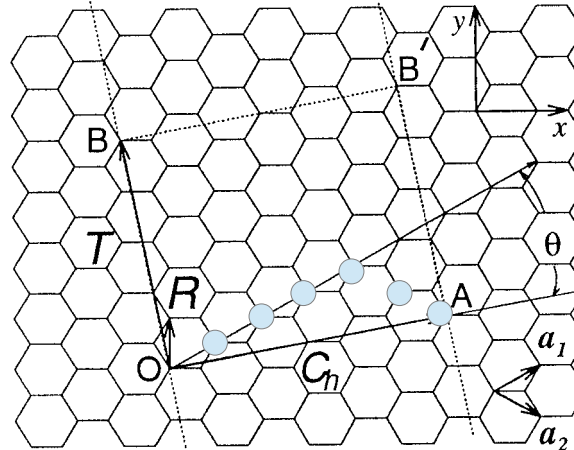
Le nombre d'atoms par unite cellulaire est: $2N$

Nanotube structure : vecteur de symétrie

Les points O,A et B,B' sont identifiés

R. Saito, G. Dresselhaus & M. S. Dresselhaus,
Physical Properties of Carbon Nanotubes
(Imperial College Press, London, 1998)

$$C_h = (4,2)$$



Les positions de tous les atomes dans la maille élémentaire peut être représenté en tant que $n\mathbf{R}$ avec les bords periodique.

Ligne OR est la vecteur de symétrie.

R est la site d'atom avec la plus petite non-zero projection sur C.

$$\mathbf{R} = p\mathbf{a}_1 + q\mathbf{a}_2 \Leftrightarrow (p, q) \quad \mathbf{R} \cdot \frac{\mathbf{C}_h}{|\mathbf{C}_h|} = \frac{p(m + \frac{n}{2}) + q(\frac{m}{2} + n)}{\sqrt{m^2 + n^2 + mn}} = \frac{p(2m + n) + q(m + n2)}{2\sqrt{m^2 + n^2 + mn}}$$

La valeur minimale possible pour le numérateur est

$$p(2m + n) + q(m + n2) = \gcd(2m + n, 2n + m)$$

Aussi

$$0 < \frac{\mathbf{R} \cdot \mathbf{T}}{|\mathbf{T}|} < T \Leftrightarrow 0 < (p(t_1 + t_2/2) + q(t_2 + t_1/2)) < t_1^2 + t_2^2 + t_1 t_2$$

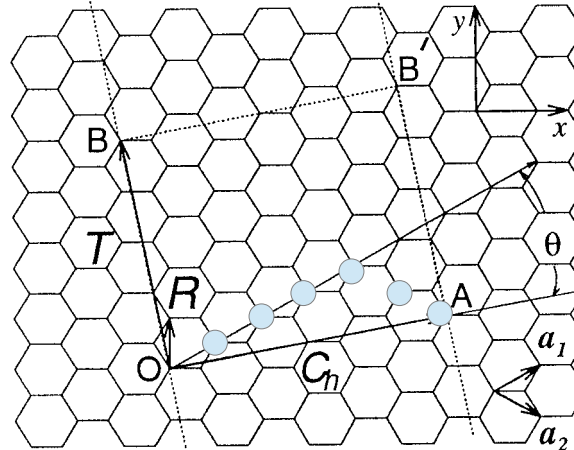
$$\Leftrightarrow 0 < mp - nq \leq N$$

Nanotube structure : vecteur de symétrie

Les points O,A et B,B' sont identifiés

R. Saito, G. Dresselhaus & M. S. Dresselhaus,
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$$C_h = (4,2)$$



Ligne OR est la vecteur de symétrie.

R est la site d'atom avec la plus petite non-zero projection sur C.

$$\mathbf{R} = p \mathbf{a}_1 + q \mathbf{a}_2 \Leftrightarrow (p, q) \quad \frac{\mathbf{R} \cdot \mathbf{C}_h}{|\mathbf{C}_h|} = \frac{|\mathbf{R} \times \mathbf{T}|}{|\mathbf{T}|} = \frac{(t_1 q - t_2 p)(\mathbf{a}_1 \times \mathbf{a}_2)}{|\mathbf{T}|} \Rightarrow t_1 q - t_2 p = 1$$

Aussi

$$0 < \frac{\mathbf{R} \cdot \mathbf{T}}{|\mathbf{T}|^2} = \frac{|\mathbf{C}_h \times \mathbf{R}|}{|\mathbf{C}| |\mathbf{T}|} = \frac{mp - nq}{N} < 1$$

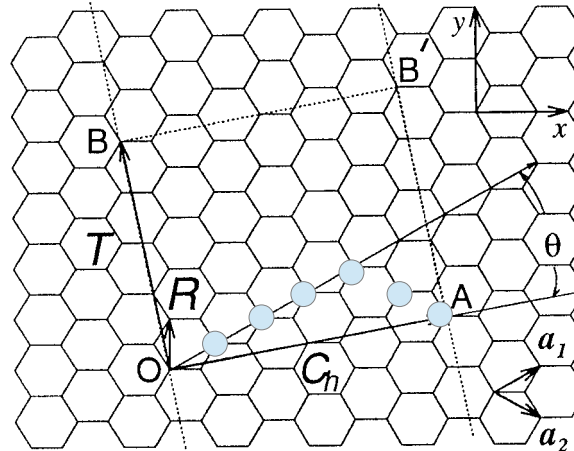
$$\Leftrightarrow 0 < mp - nq \leq N$$

Nanotube structure : vecteur de symétrie

Les points O,A et B,B' sont identifiés

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$$C_h = (4, 2)$$



Ligne OR est la vecteur de symétrie.

$$\mathbf{R} = p \mathbf{a}_1 + q \mathbf{a}_2 \Leftrightarrow (p, q)$$

$$t_1q-t_2p=1$$

$$0 < mp - nq \leq N$$

Les positions de tous les atomes dans la maille élémentaire peut être représenté en tant que $n\mathbf{R}$ avec les bords periodique car

$$N \mathbf{R} \cdot \frac{\mathbf{C}_h}{|\mathbf{C}_h|} = N \frac{|\mathbf{R} \times \mathbf{T}|}{|\mathbf{T}|} = N \frac{|\mathbf{a}_1 \times \mathbf{a}_2|}{|\mathbf{T}|} = |\mathbf{C}_h|$$

Structure

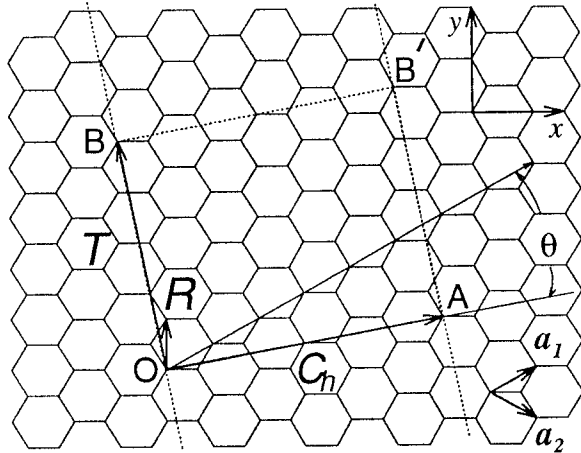
	zigzag	armchair	chiral
C	(n,0)	(n,n)	(n,m)
T	(1,-2)	(1,-1)	$(\frac{2m+n}{d_R}, -\frac{2n+m}{d_R})$
R	(1,-1)	(1,0)	
L/a	n	$\sqrt{3} n$	$\sqrt{m^2+n^2+nm}$
T	$\sqrt{3}$	1	$\sqrt{3} L/d_R$
N	2n	2n	$2L^2/(a^2 d_R)$

$$d_R = \gcd(2m+n, 2n+m)$$

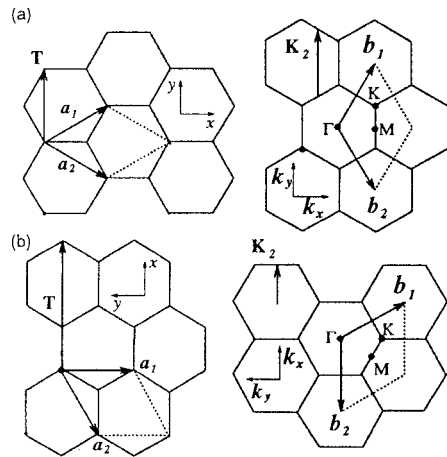
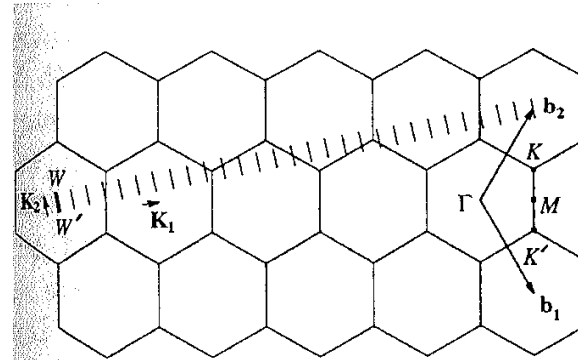
$$= \begin{cases} d & \text{if } n-m \text{ is not a multiple of } 3d \\ 3d & \text{if } n-m \text{ is a multiple of } 3d \end{cases}, \quad d = \gcd(n, m)$$

Nanotube structure

réseau



zone de Brillouin



« armchair » (n,n)

« zigzag » $(n,0)$

