

# NANOPHYSIQUE

## INTRODUCTION PHYSIQUE AUX NANOSCIENCES

### *Ch 5. Carbon Structures*

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Lecture 6, 2020-2021

# Carbon Structures

- Introduction
  - Histoire
  - Carbone
  - Hybridization
- Tight-binding calculations
  - Principe
  - Example: trans
  - Graphene  $\pi$ -liens
  - Graphene  $\sigma$ -liens
- Structure de carbone nanotubes
- Structure Electronique
- Synthesis
- Transport
- Multi-walled nanotubes

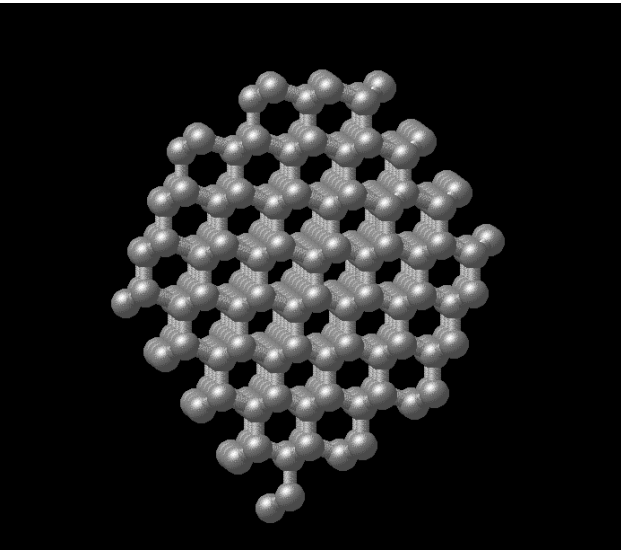
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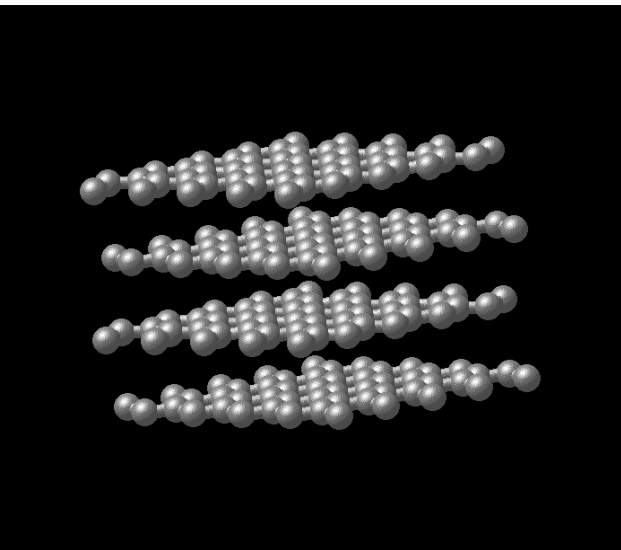
# Une petite histoire

- 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).

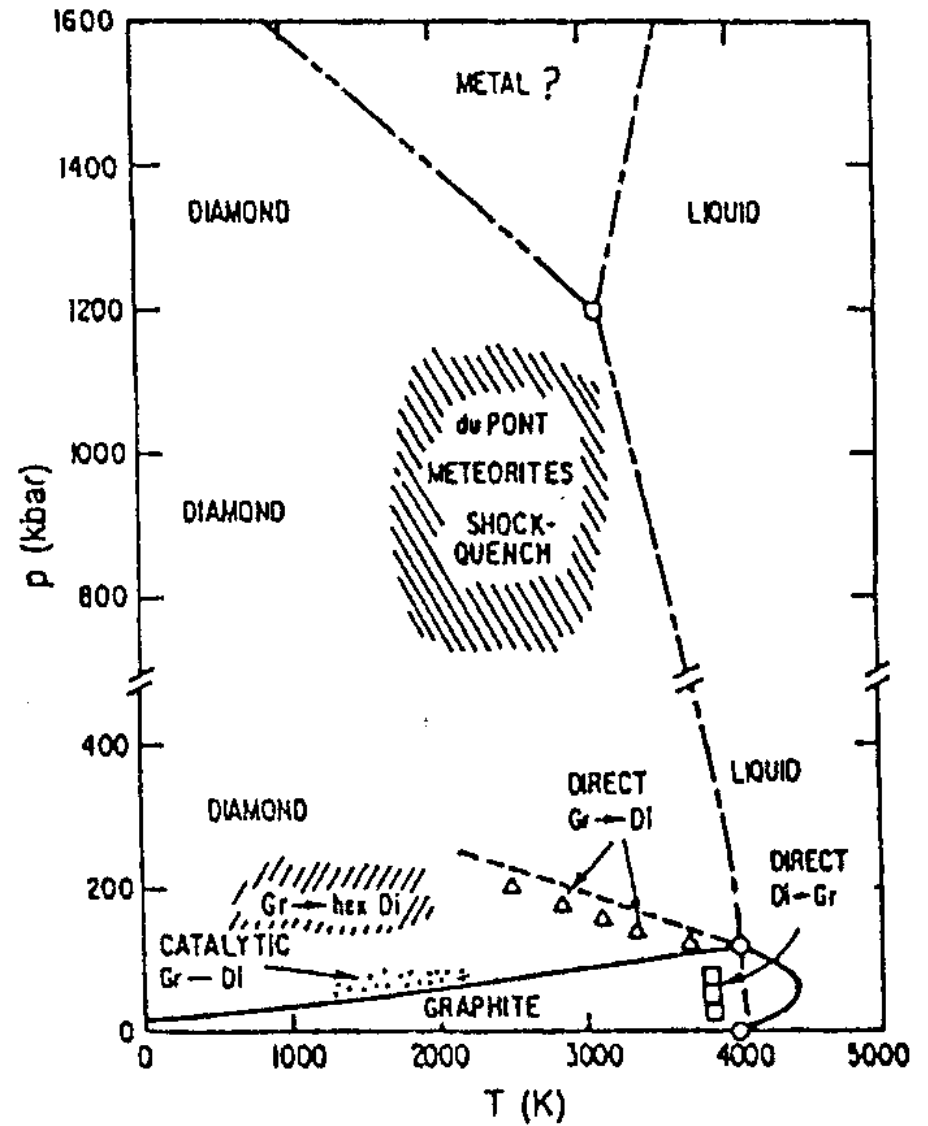
# Propriétés du carbone



diamant

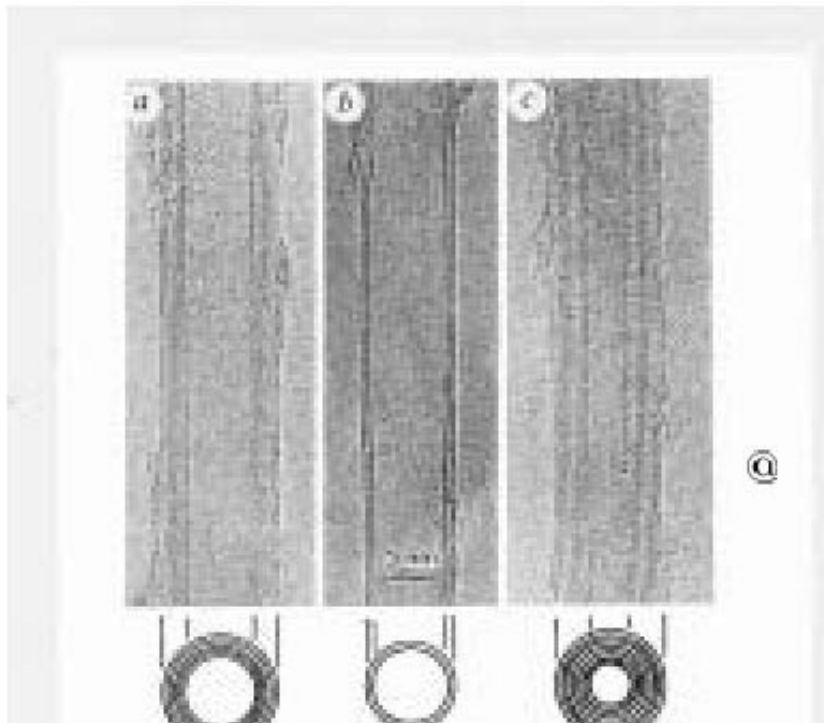


graphite

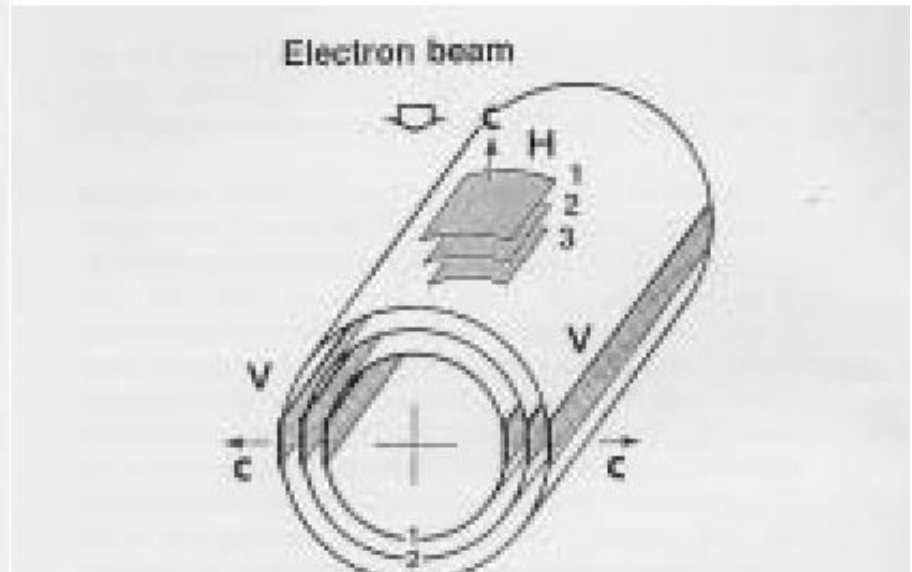


# Discovery of Carbon Nanotubes

Iijima, Nature 354, 56 (1992)



Electron microscope image

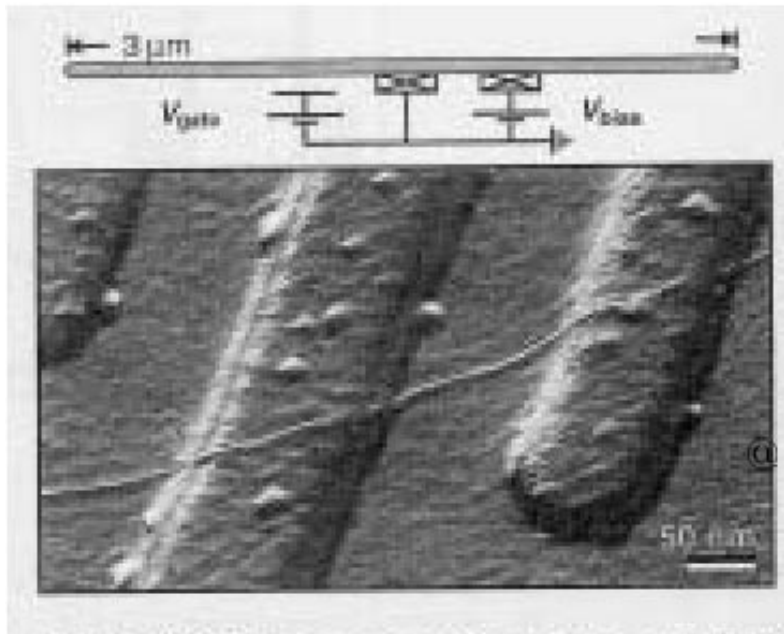


Interpretation of the images

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

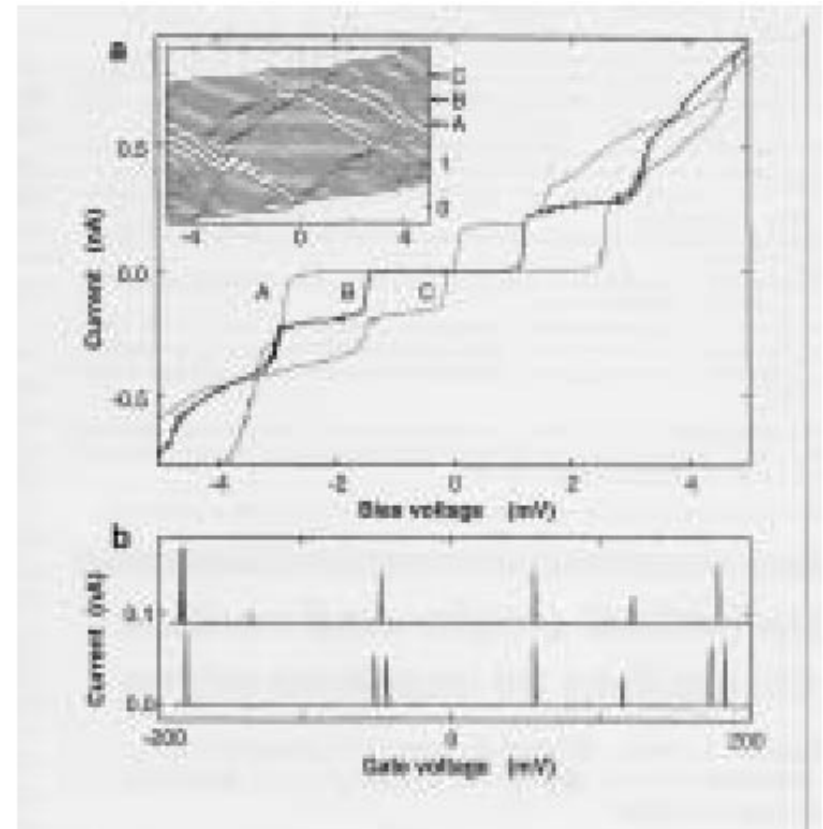
# Current-voltage characteristics of CNT

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

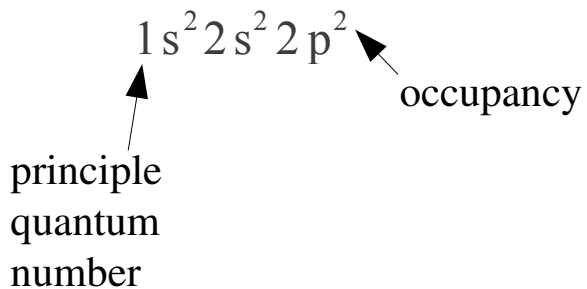
# Carbone:

$$Z = 6$$

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

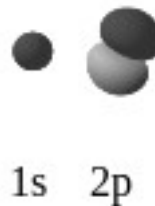
$^{14}\text{C}$  --> half-life = 5,730 an  
(carbon dating)

## Configuration Electronique:



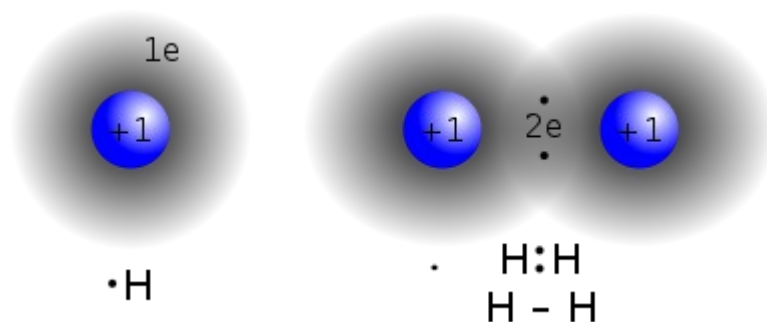
# Periodic Table of Elements

* 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





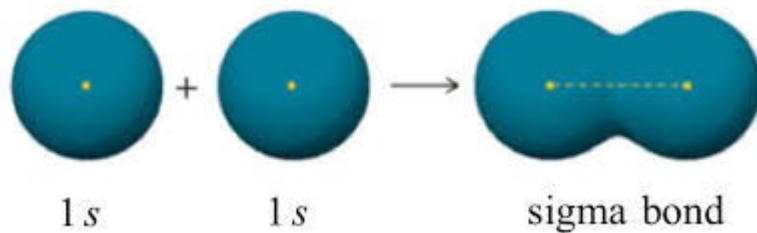
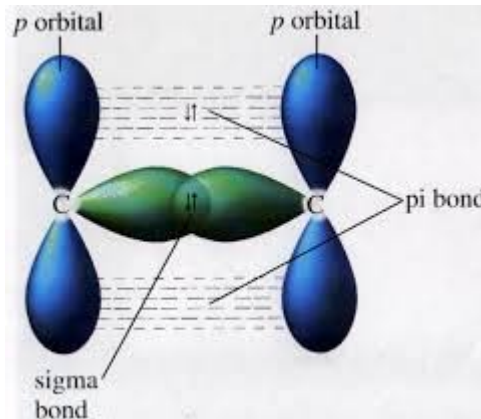
# Covalent bonds: sharing electrons



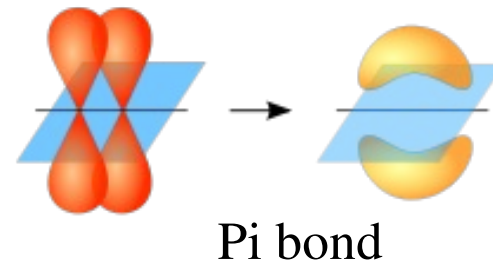
T (kinetic energy) : lower energy by delocalizing electrons

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

# Types of molecular bonds

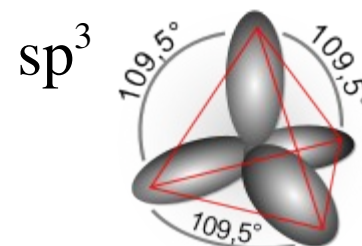
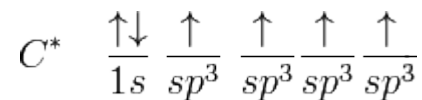
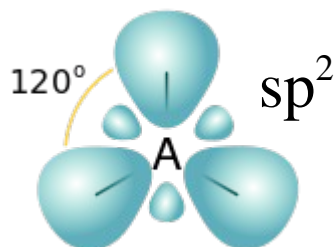
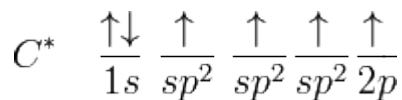
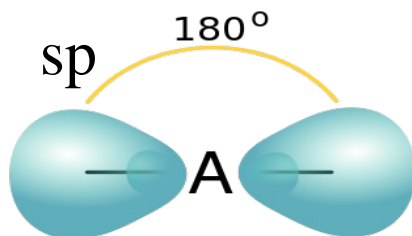
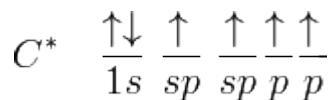
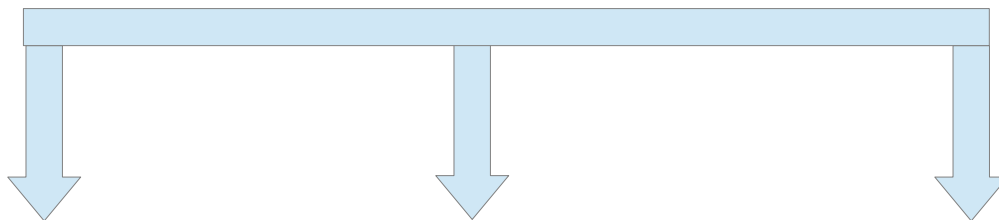
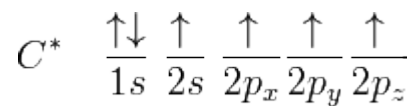
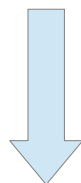
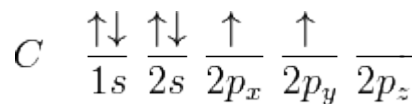


Sigma bond



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:

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



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

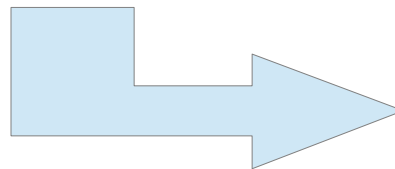
$$C_3^2 + C_4^2 = 1$$

$$C_1 C_3 + C_2 C_4 = 0$$



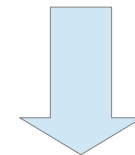
$$C_4 = \pm C_1$$

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



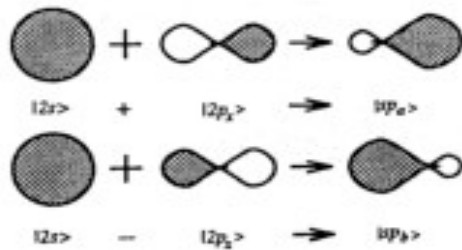
$$\begin{aligned}E_a &= C_1^2 E_s + C_2^2 E_p \\ &= C_1^2 \underbrace{(E_s - E_p)}_{<0} + E_p\end{aligned}$$

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



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

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



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

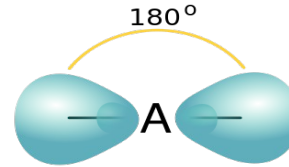
# Orbitals and hybridizations for C

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:  $\text{HCCH}$  liaison triple: 2 lien  $\sigma$  + 2 liens  $\pi$

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

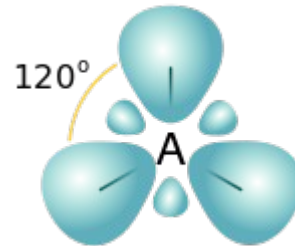


## Hybridation $sp^2$ : $2s + 2p_x + 2p_y, 2p_z$

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

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

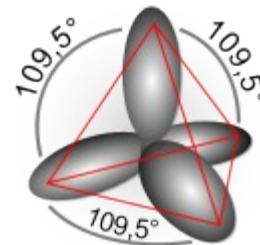
$$|sp_{b,c}^2\rangle = \pm \frac{1}{\sqrt{3}}|2s\rangle \pm \frac{1}{\sqrt{2}}|2p_x\rangle + \frac{1}{\sqrt{6}}|2p_z\rangle$$



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

Exemple : méthane:  $\text{CH}_4$  liaison simple: 4 liens  $\sigma$

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



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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:

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

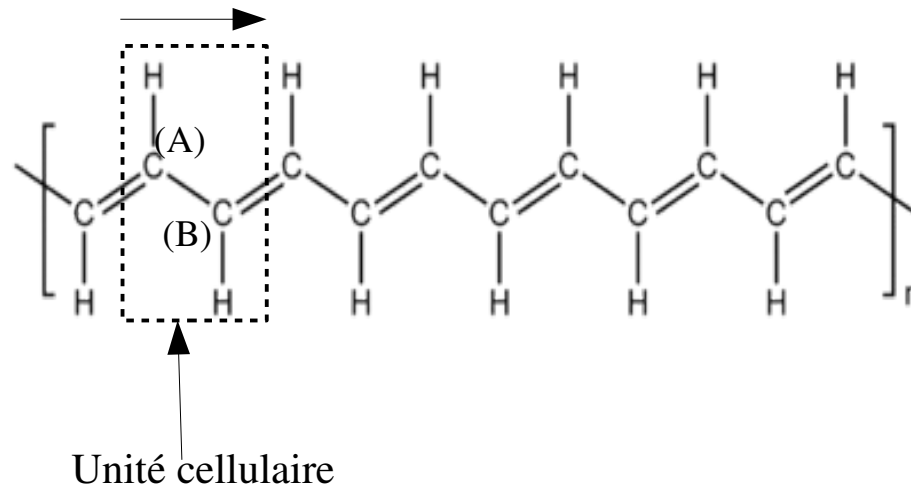
$$\rightarrow \sum_{j'} H_{jj'}(\mathbf{k}) C_{j'} = \lambda(\mathbf{k}) \sum_{j'} S_{jj'}(\mathbf{k}) C_{j'}$$

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

# Tight-binding method

## Example: *trans*-polyacétylène

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



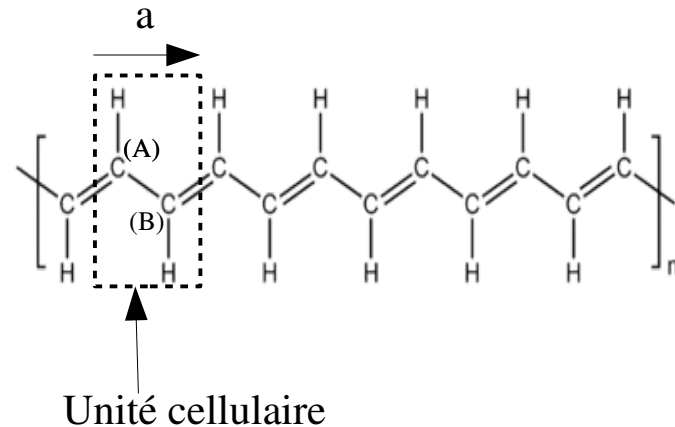
Vecteur de reseau reciproque:  $\mathbf{b} = \frac{2\pi}{a} \hat{x}$

# 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  $\rightarrow$   $\sigma$ -liens dans le plan,  $\pi$ -lien (p-p) dehors le plan

***On cherche les niveau pour les  $\pi$ -electrons:***

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

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

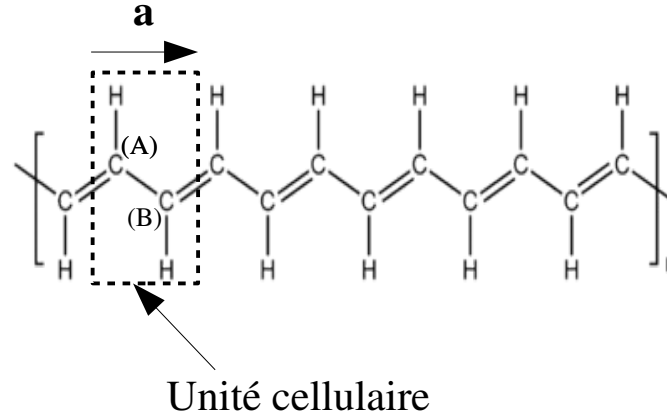
$$\mathbf{k} = \frac{2\pi}{a} \frac{p_i}{N} \hat{\mathbf{x}}, \quad 0 \leq p_i < N \quad \longrightarrow \quad 0 \leq k \leq 2\pi/a$$

# Tight-binding method

Example: *trans*-polyacétylène

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

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



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

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

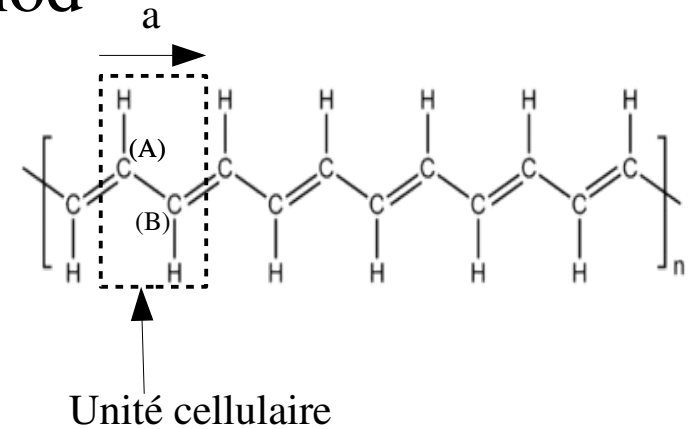
$$\begin{aligned} H_{AA}(\mathbf{k}) &= \langle \Phi_A | H | \Phi_A \rangle = \frac{1}{N} \sum_{n,m=0}^N e^{ik(n-m)a} \langle \phi_{2p_z}(\mathbf{r} - ma \hat{\mathbf{x}}) | H | \phi_{2p_z}(\mathbf{r} - na \hat{\mathbf{x}}) \rangle \\ &= \underbrace{\langle \phi_{p_z}(\mathbf{r}) | H | \phi_{p_z}(\mathbf{r})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

# Tight-binding method

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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  $R_x = a/2$

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

# Tight-binding method

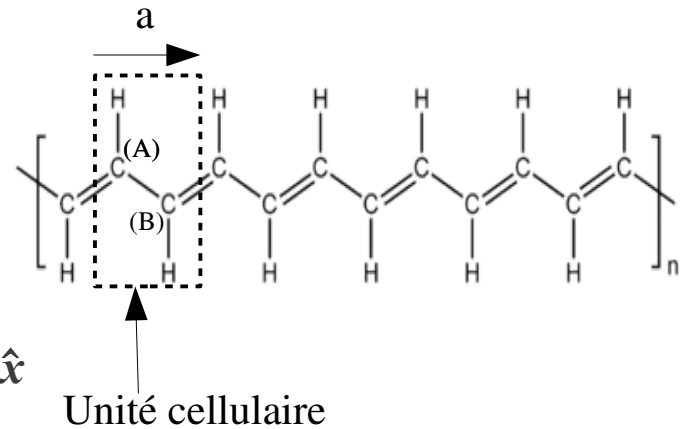
Example: *trans*-polyacétylène

Vecteur de reseau:

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

Vecteur de reseau reciproque:

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

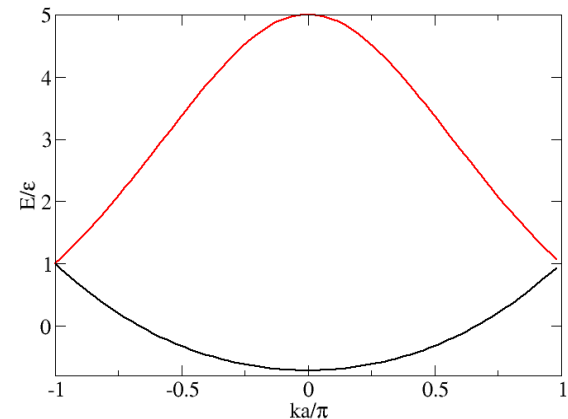


$$H_{ij} = \begin{pmatrix} \epsilon_{2p} & 2t \cos(ka/2) \\ 2t \cos(ka/2) & \epsilon_{2p} \end{pmatrix} \quad S_{ij} = \begin{pmatrix} 1 & 2s \cos(ka/2) \\ 2s \cos(ka/2) & 1 \end{pmatrix}$$

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

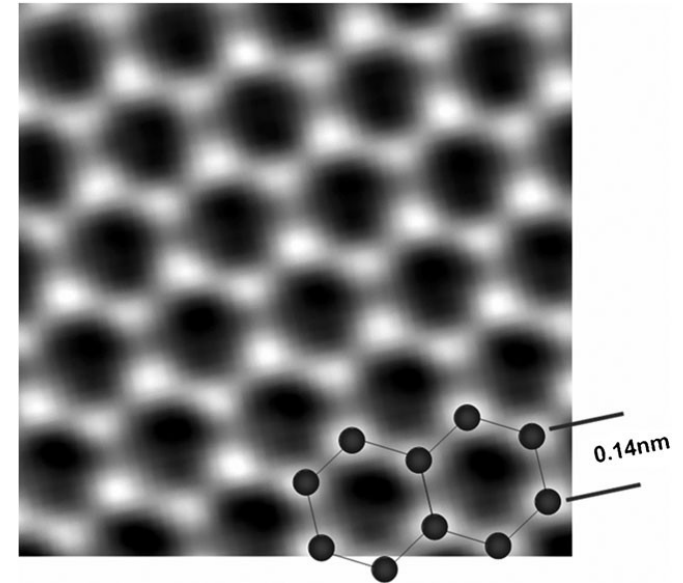
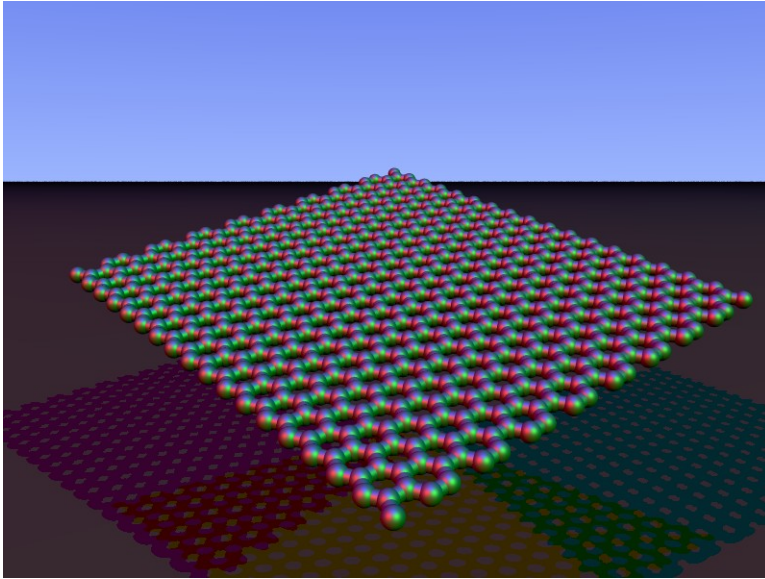
$$= (\epsilon_{2p} - E)^2 - 4(t - sE)^2 \cos^2(ka/2)$$

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



# 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 =  $2s^2 2p^2$

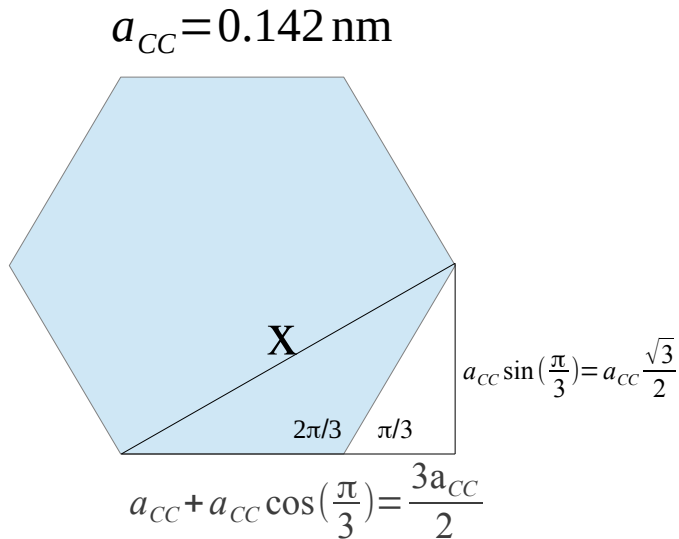
Chaque atome de carbone offre 3 orbitales atomiques  $sp^2$  et une orbitale  $2p_z$

Les orbitales atomiques  $sp^2$  forment les liens  $\sigma$

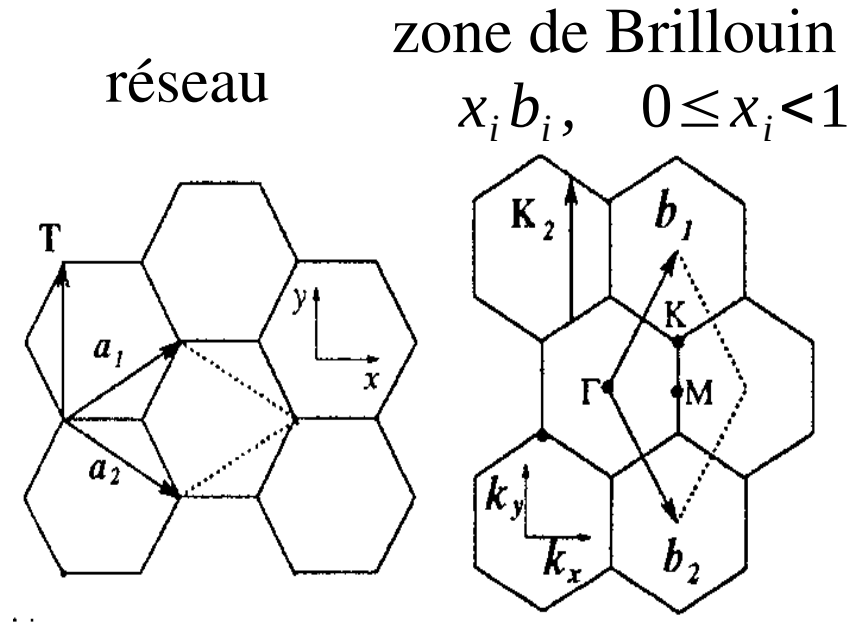
Les orbitales atomiques  $2p_z$  forment les liens  $\pi$



# Graphene 2



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



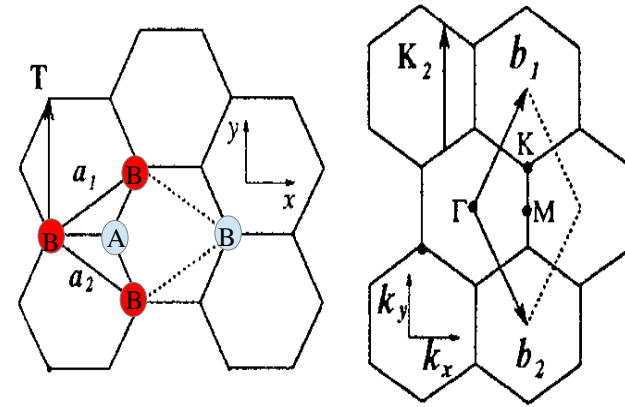
$$\mathbf{a}_{1,2} = \left( \frac{\sqrt{3}}{2} a, \pm \frac{a}{2} \right) \quad \mathbf{b}_{1,2} = \left( \frac{2\pi}{\sqrt{3}a}, \pm \frac{2\pi}{a} \right)$$

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

# Graphene Tight-binding : $\pi$ -bands

réseau

zone de Brillouin



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

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

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

$$H_{AB} = t \left( e^{i\mathbf{k} \cdot \mathbf{R}_1} + e^{i\mathbf{k} \cdot \mathbf{R}_2} + e^{i\mathbf{k} \cdot \mathbf{R}_3} \right) \equiv t f(\mathbf{k})$$

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

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

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

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

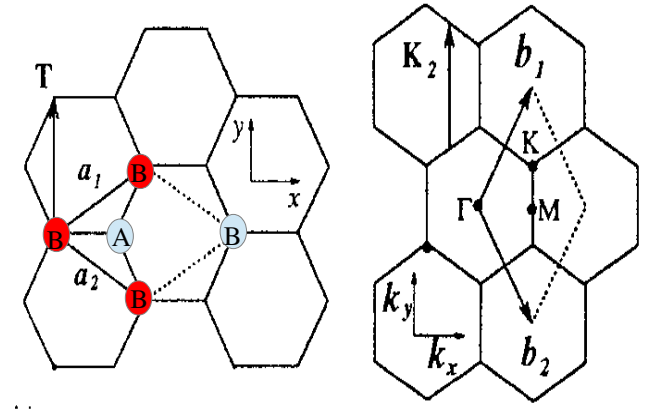
$s=0 \Leftrightarrow$  "Slater-Koster approximation"

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

# Graphene Tight-binding : $\sigma$ -bands

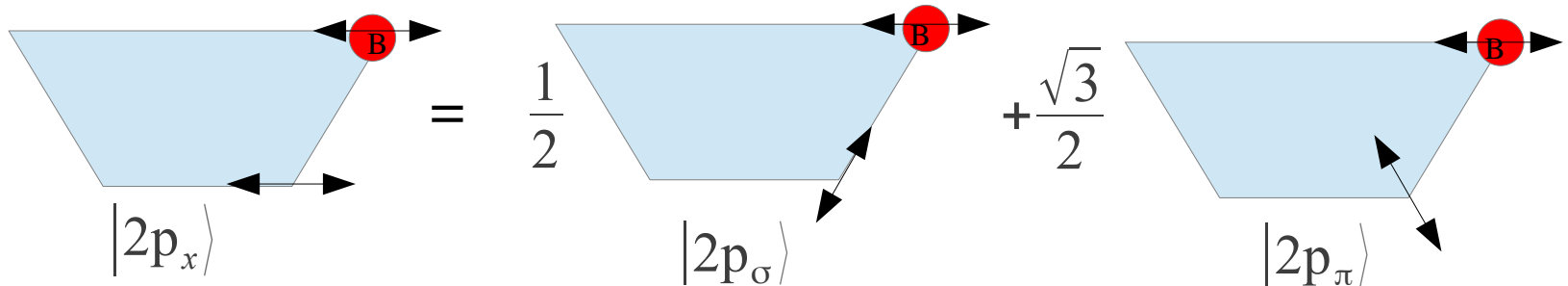
Basis:  $(2s^A, 2p_x^A, 2p_y^A, 2s^B, 2p_x^B, 2p_y^B)$

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



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

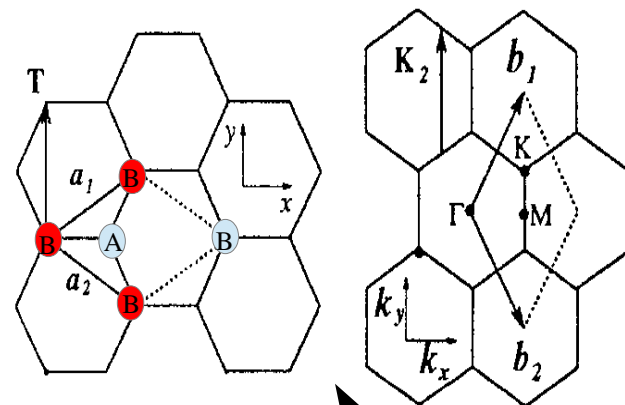
Car l'état de  $l = 1$  se transforme comme un vecteur sous rotations.



# Graphene Tight-binding : $\sigma$ -bands

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

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

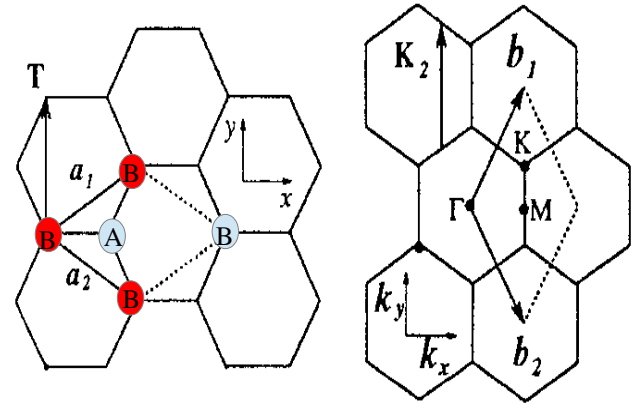
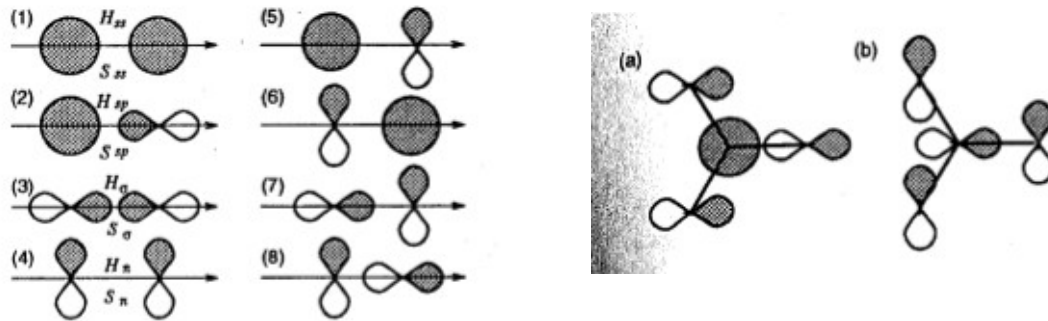


$$\begin{aligned} \langle 2p_x^B | H | 2p_x^A \rangle &= \left( \frac{1}{2} \right)^2 \langle 2p_\sigma^B | H | 2p_\sigma^A \rangle + \left( \frac{\sqrt{3}}{2} \right)^2 \langle 2p_\pi^B | H | 2p_\pi^A \rangle \\ &+ \left( \frac{1}{2} \right) \left( \frac{\sqrt{3}}{2} \right) \langle 2p_\pi^B | H | 2p_\sigma^A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

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

# Graphene Tight-binding : $\sigma$ -bands

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



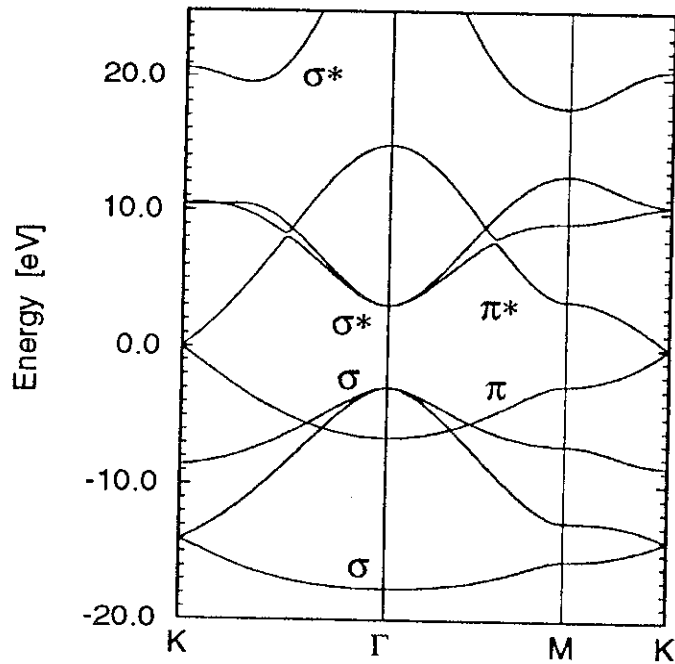
R. Saito, G. Dresselhaus & M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998)

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

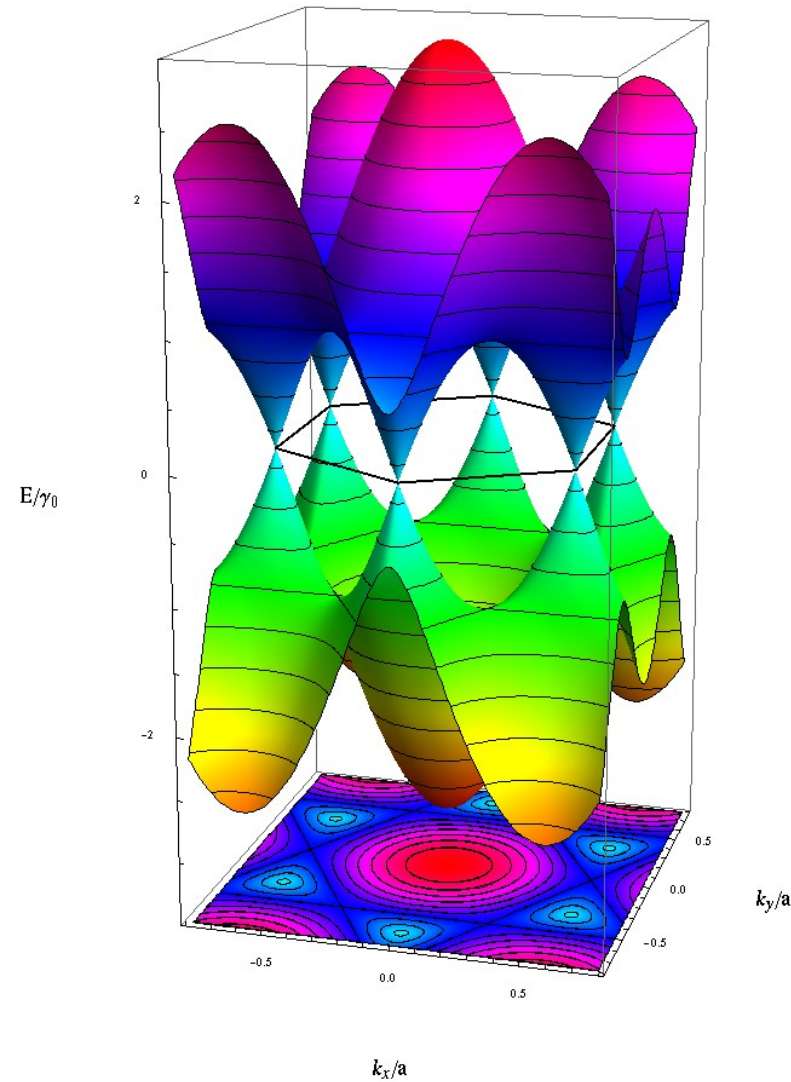
$$\langle 2p_x^B | H | 2p_y^A \rangle = \frac{i\sqrt{3}}{2} (H_{\sigma\sigma} + H_{\pi\pi}) e^{-ik_x a / 2\sqrt{3}} \sin \frac{k_y a}{2}$$

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

# 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

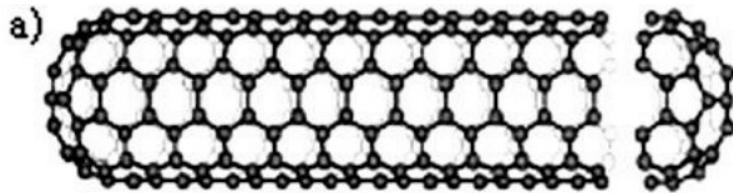
- Introduction
  - Histoire
  - Carbone
  - Hybridization
- Tight-binding calculations
  - Principe
  - Example: trans
  - Graphene  $\pi$ -liens
  - Graphene  $\sigma$ -liens
- Structure de carbone nanotubes
- Structure Electronique
- Synthesis
- Transport
- Multi-walled nanotubes

# Nanotube structure

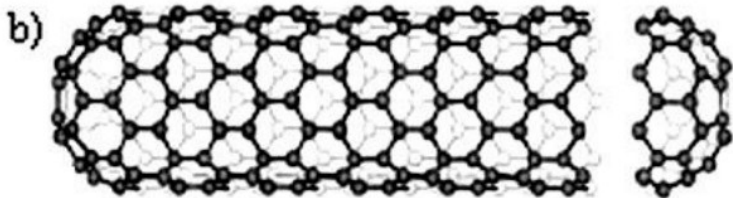
Rayon: 0.7-10 nm (pour la plupart  $< 2\text{nm}$ )

Longueur: 1-100  $\mu\text{m}$

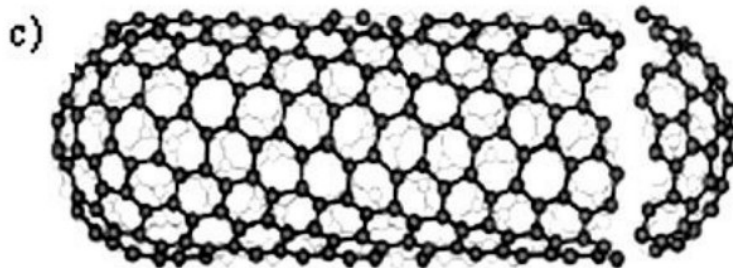
Chapeau (“cap”): fullerene avec  
6 pentagons +plusieurs hexagon



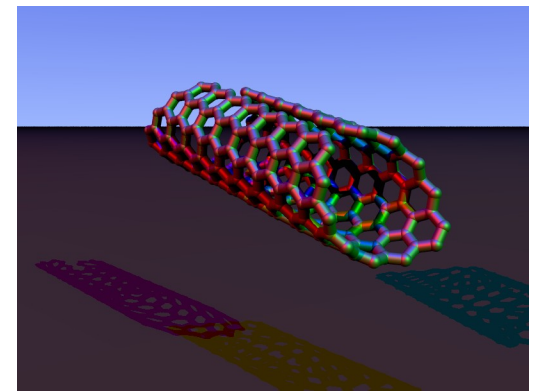
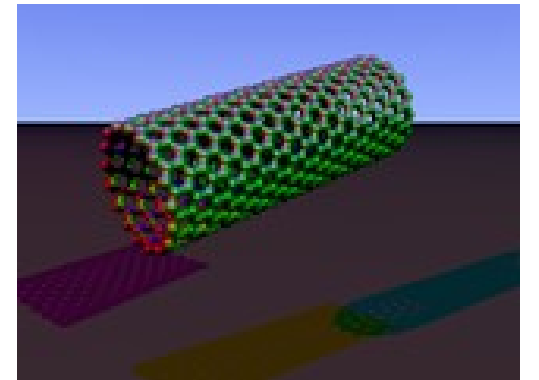
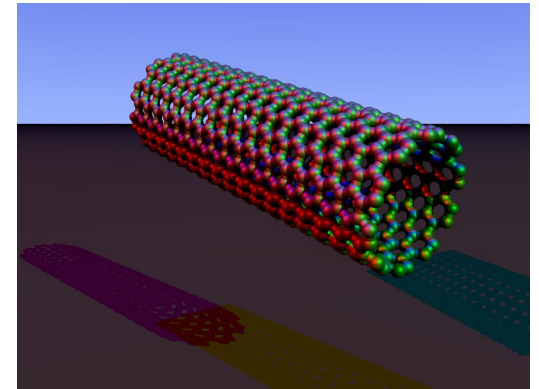
“armchair”



“zigzag”

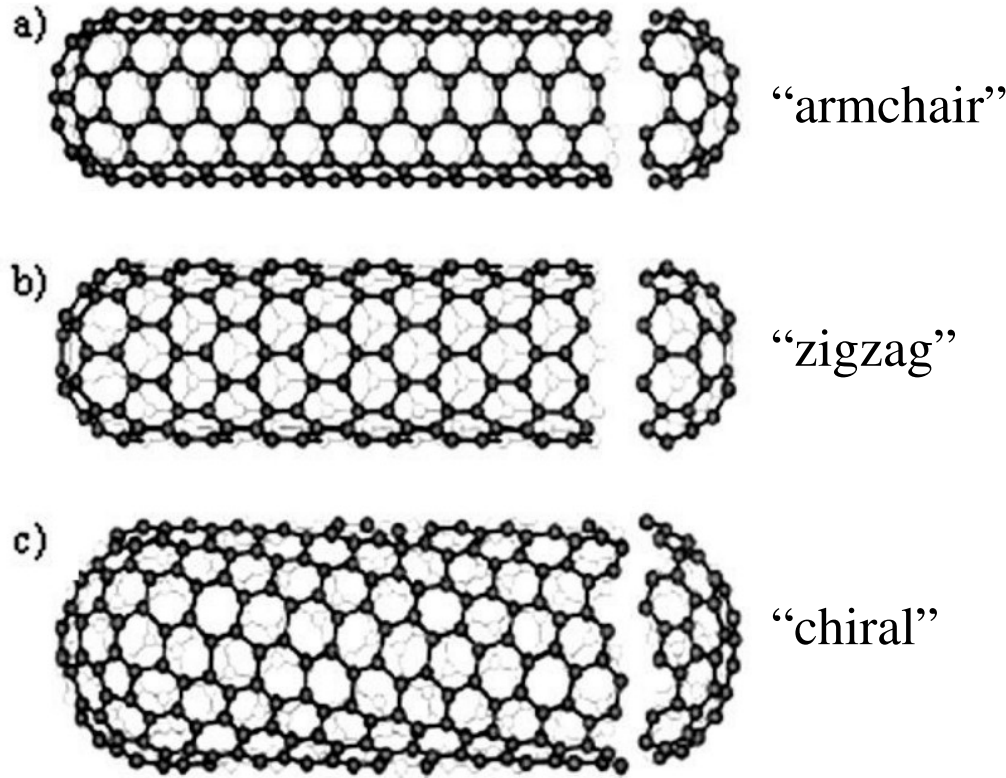
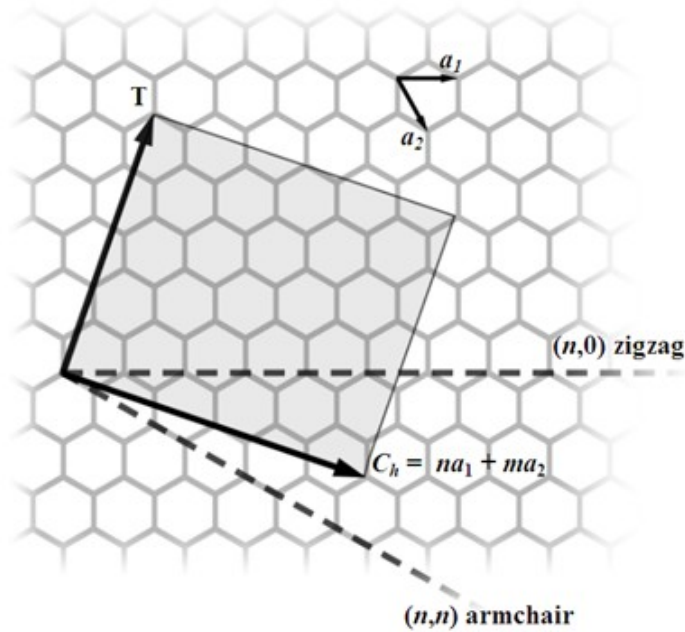


“chiral”





# Nanotube structure

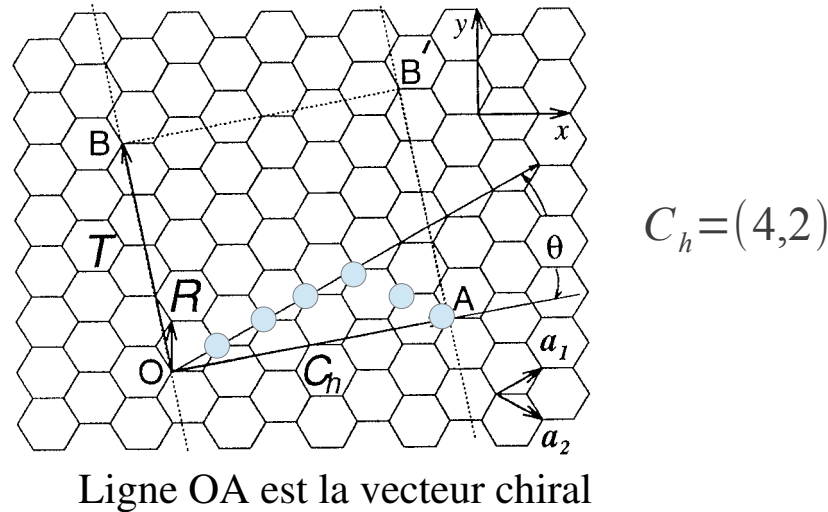


Division fondamentale:

- “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:  $\mathbf{C}_h = n \mathbf{a}_1 + m \mathbf{a}_2 \Leftrightarrow (n, m), \quad 0 \leq |m| \leq n$

N.B.:  $\mathbf{a}_1 \cdot \mathbf{a}_1 = \mathbf{a}_2 \cdot \mathbf{a}_2 = a^2$ ,  $\mathbf{a}_1 \cdot \mathbf{a}_2 = \frac{a^2}{2}$   $a = 0.144 \text{ nm} \times \sqrt{3} = 0.249 \text{ nm}$

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

Angle chiral:  $\cos \theta \equiv \frac{\mathbf{C}_h \cdot \mathbf{a}_1}{|\mathbf{C}_h| |\mathbf{a}_1|} = \frac{2n+m}{2\sqrt{n^2+m^2+nm}}$

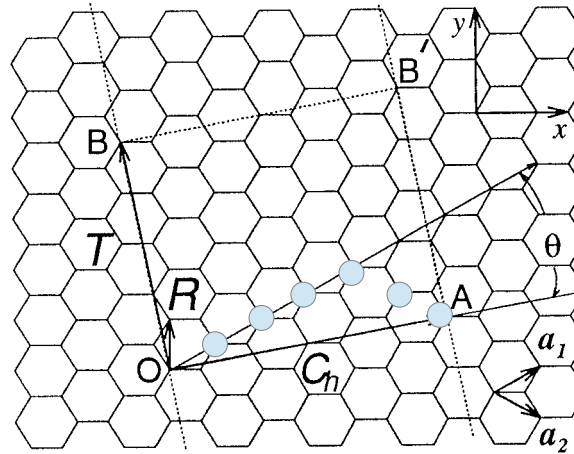
# Nanotube structure : vecteur de translation

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:  $\mathbf{T} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2 \Leftrightarrow (n, m)$

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

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:  $N = \frac{2L^2}{a^2 \gcd(2m + n, m + 2n)}$   
(exercise)

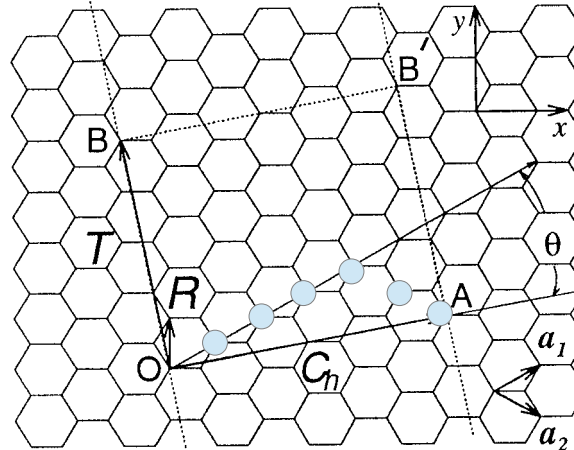
Le nombre d'atoms par unite cellulaire est:  $2N$

# 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

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

Aussi

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

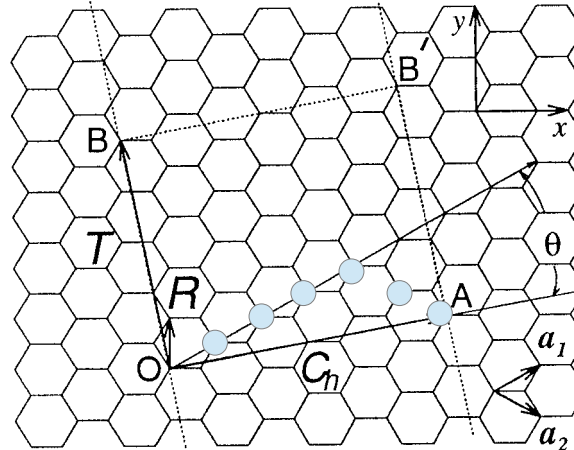
$$\Leftrightarrow 0 < mp - nq \leq N$$

# Nanotube structure : vecteur de symétrie

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

R. Saito, G. Dresselhaus & M. S. Dresselhaus,  
*Physical Properties of Carbon Nanotubes*  
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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

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

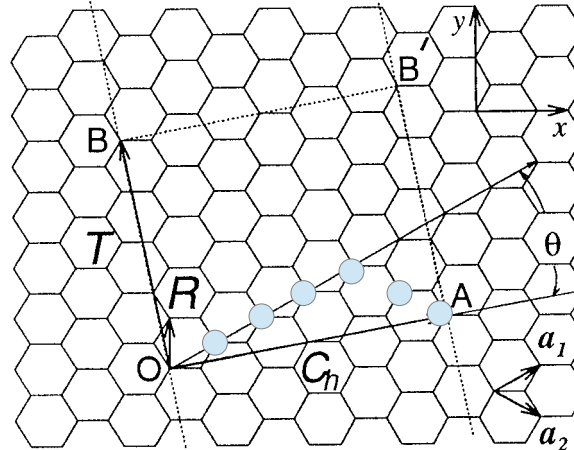
$$\Leftrightarrow 0 < mp - nq \leq N$$

# Nanotube structure : vecteur de symétrie

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$$C_h = (4, 2)$$



Ligne OR est la vecteur de symétrie.

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

$$t_1 q - t_2 p = 1$$

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

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

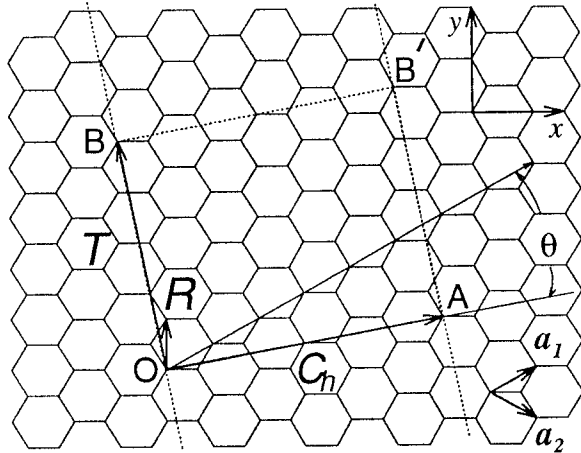
	<b>zigzag</b>	<b>armchair</b>	<b>chiral</b>
<b>C</b>	(n,0)	(n,n)	(n,m)
<b>T</b>	(1,-2)	(1,-1)	$(\frac{2m+n}{d_R}, -\frac{2n+m}{d_R})$
<b>R</b>	(1,-1)	(1,0)	
<b>L/a</b>	n	$\sqrt{3} n$	$\sqrt{m^2+n^2+nm}$
<b>T</b>	$\sqrt{3}$	1	$\sqrt{3} L/d_R$
<b>N</b>	2n	2n	$2L^2/(a^2 d_R)$

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

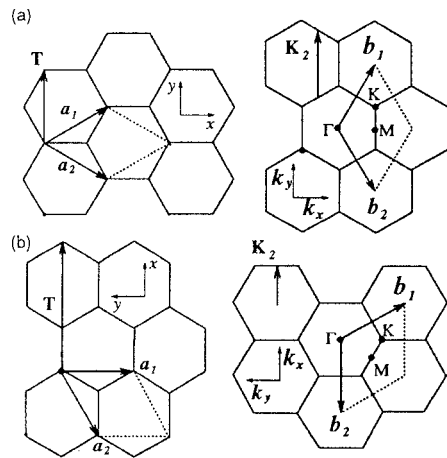
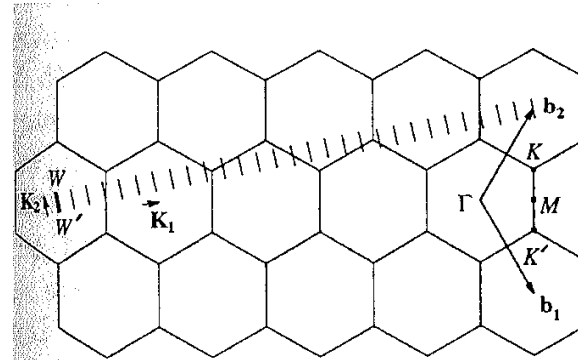
$$= \begin{cases} d & \text{if } n-m \text{ is not a multiple of } 3d \\ 3d & \text{if } n-m \text{ is a multiple of } 3d \end{cases}, \quad d = \gcd(n, m)$$

# Nanotube structure

réseau



zone de Brillouin



« armchair »  $(n,n)$

« zigzag »  $(n,0)$

