NANOPHYSIQUE
INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch 5. Carbon Structres

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Lecture 6, 2022-2023

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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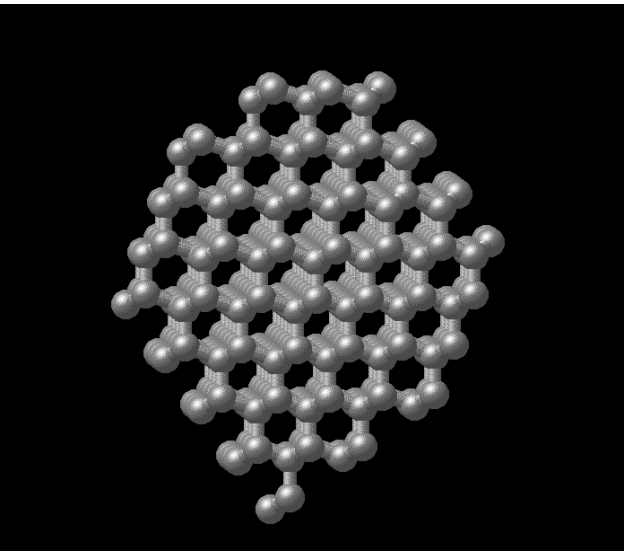
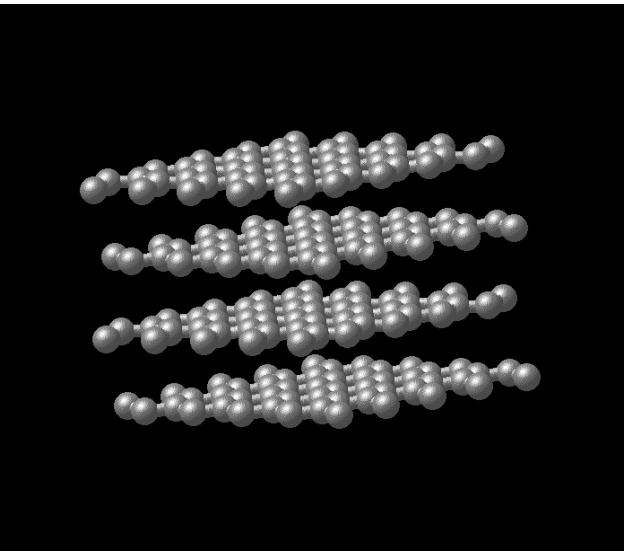
Une petite histoire

- 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 invité 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).

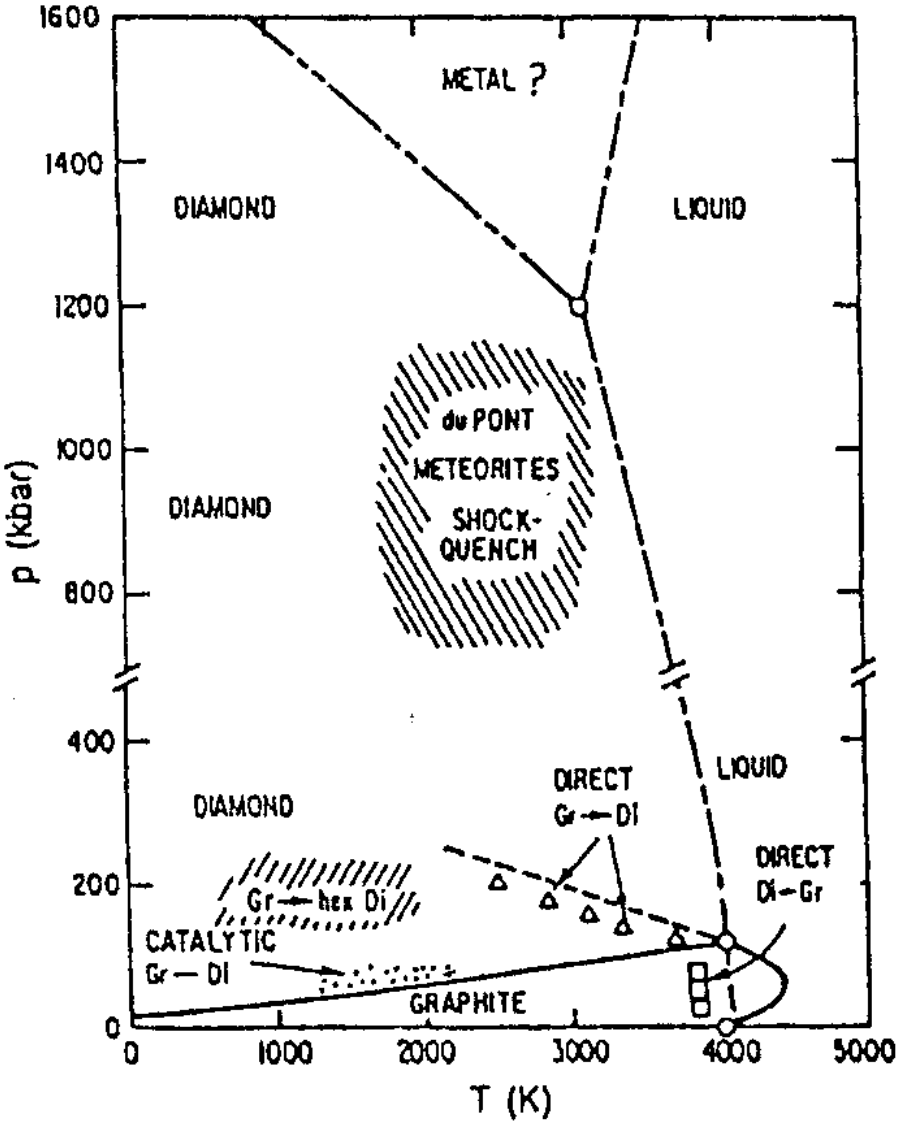
Propriétés du carbone



diamant

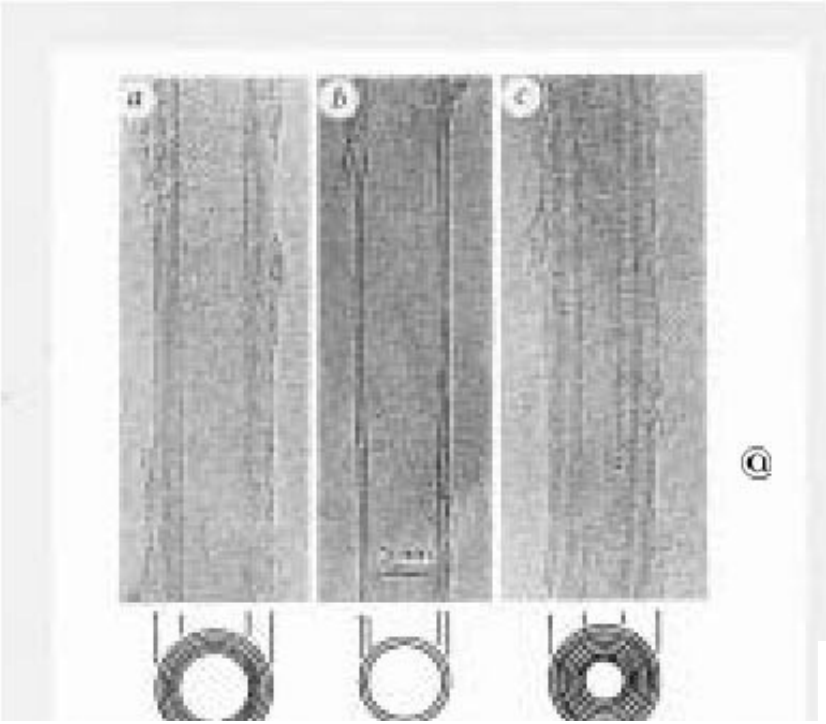


graphite

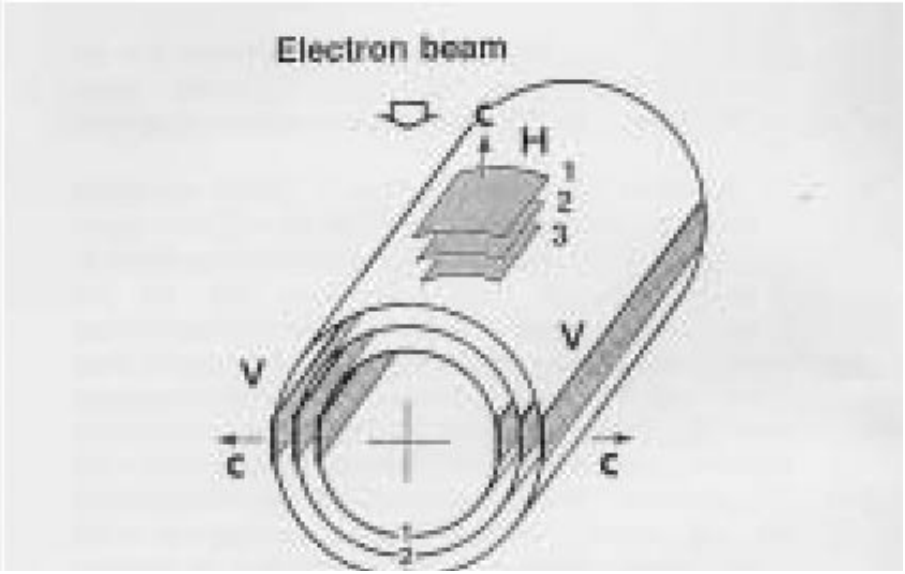


Discovery of Carbon Nanotubes

Iijima, Nature 354, 56 (1992)



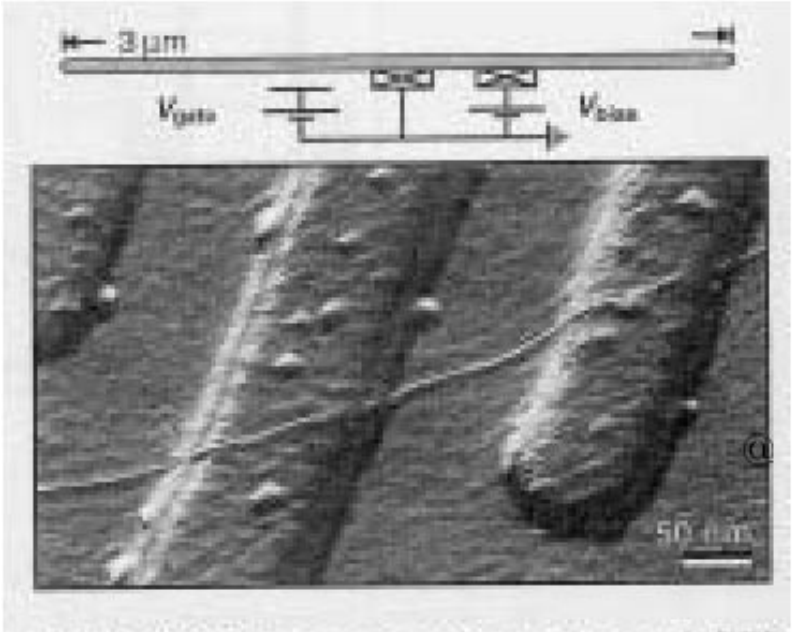
Electron microscope image



Interpretation of the images

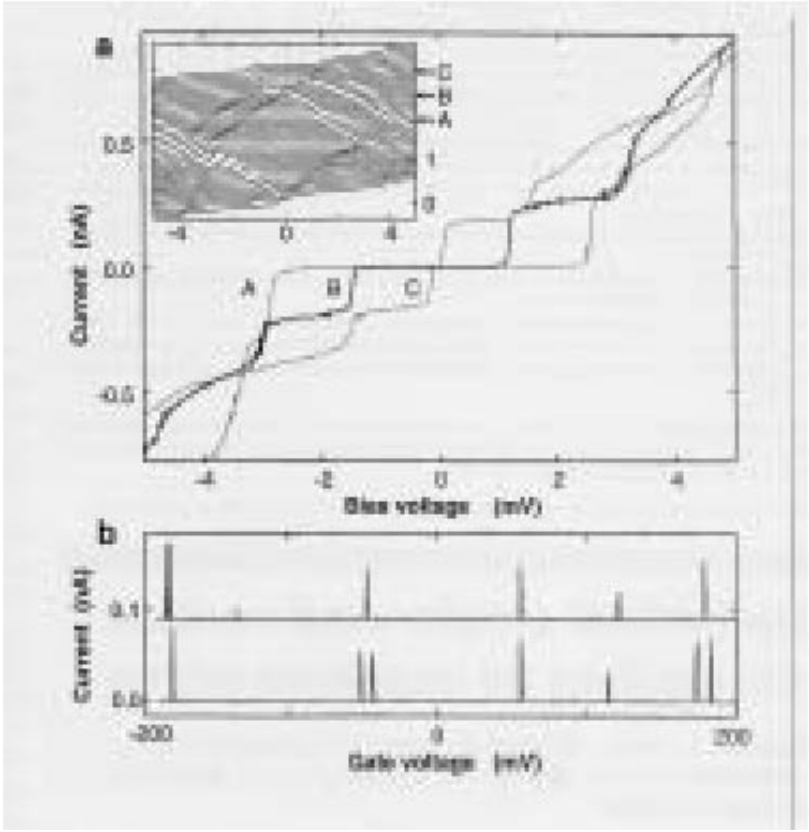
Current-voltage characteristics of CNT

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

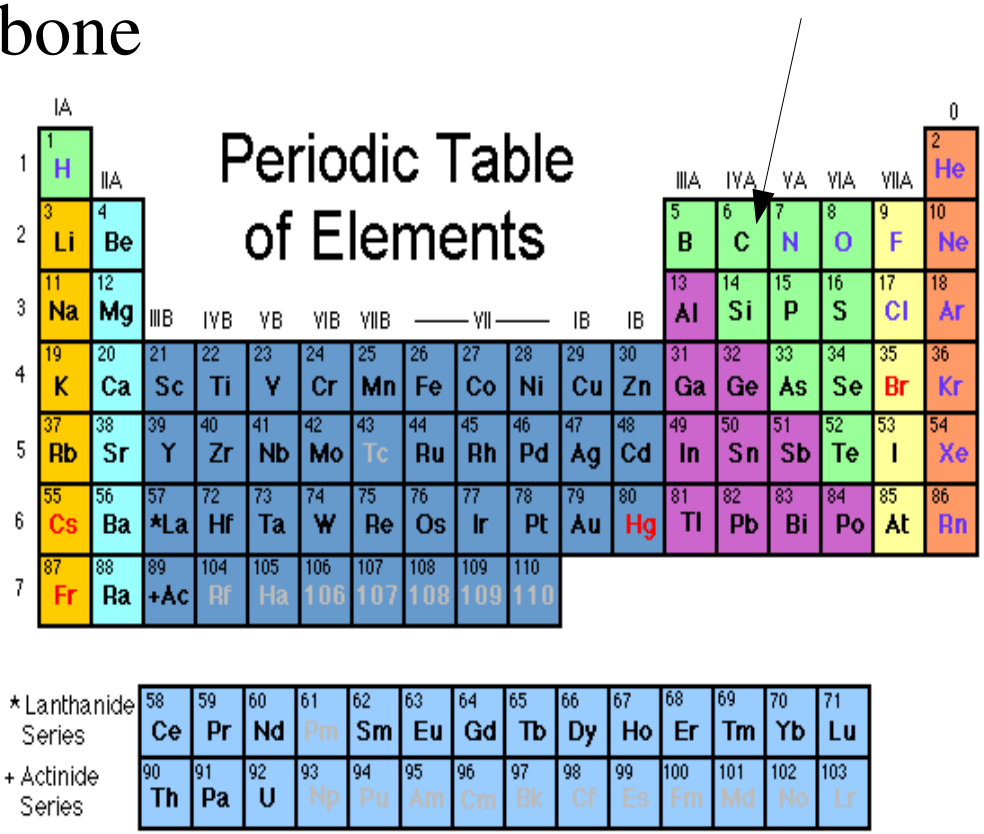
Carbone:

$Z = 6$

$^{12}C, ^{13}C$--> stable

^{14}C--> half-life = 5,730 an

(carbon dating)



Configuration Electronique:

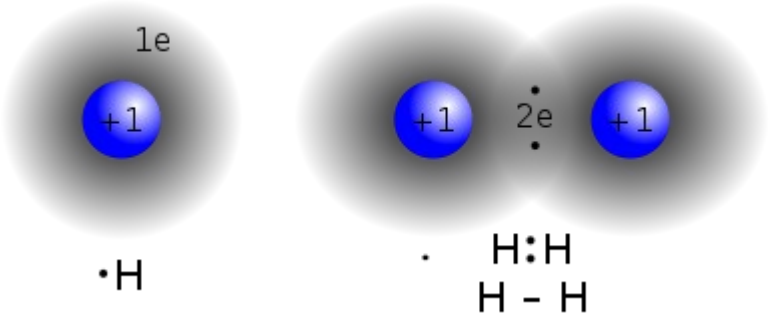
$1s^2 2s^2 2p^2$

principle quantum number

occupancy

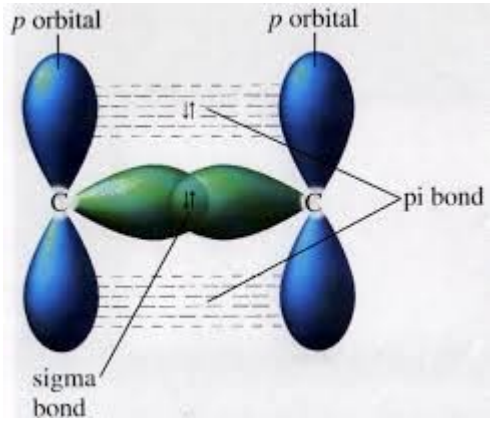
1s 2p

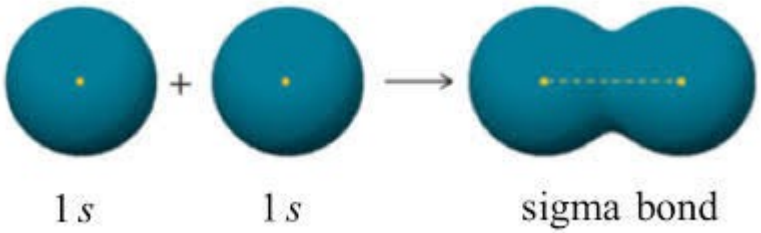
Covalent bonds: sharing electrons



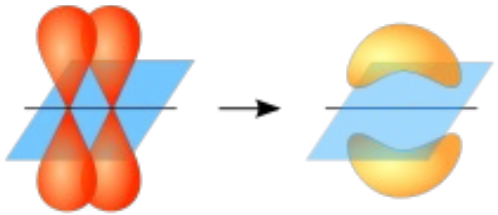
T (kinetic energy) : lower energy by delocalizing electrons
V (potential energy): lower energy by localizing electrons near ions

Types of molecular bonds





Sigma bond



Pi bond

T (kinetic energy) : lower energy by delocalizing electrons

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

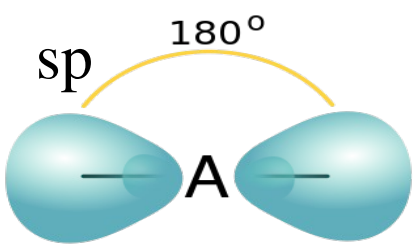
Hybridization

C $\underset{1s}{\uparrow\downarrow}$ $\underset{2s}{\uparrow\downarrow}$ $\underset{2p_x}{\uparrow}$ $\underset{2p_y}{\uparrow}$ $\underset{2p_z}{}$

C^* $\underset{1s}{\uparrow\downarrow}$ $\underset{2s}{\uparrow}$ $\underset{2p_x}{\uparrow}$ $\underset{2p_y}{\uparrow}$ $\underset{2p_z}{\uparrow}$

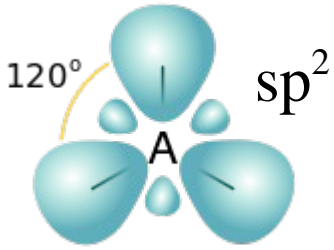
C^* $\underset{1s}{\uparrow\downarrow}$ $\underset{sp}{\uparrow}$ $\underset{sp}{\uparrow}$ $\underset{p}{\uparrow}$ $\underset{p}{\uparrow}$

sp



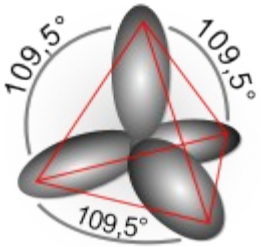
C^* $\underset{1s}{\uparrow\downarrow}$ $\underset{sp^2}{\uparrow}$ $\underset{sp^2}{\uparrow}$ $\underset{sp^2}{\uparrow}$ $\underset{2p}{\uparrow}$

sp^2



C^* $\underset{1s}{\uparrow\downarrow}$ $\underset{sp^3}{\uparrow}$ $\underset{sp^3}{\uparrow}$ $\underset{sp^3}{\uparrow}$ $\underset{sp^3}{\uparrow}$

sp^3



SP Hybridization

$$|sp_a\rangle = C_1|s\rangle + C_2|p_x\rangle$$
$$|sp_b\rangle = C_3|s\rangle + C_4|p_x\rangle$$

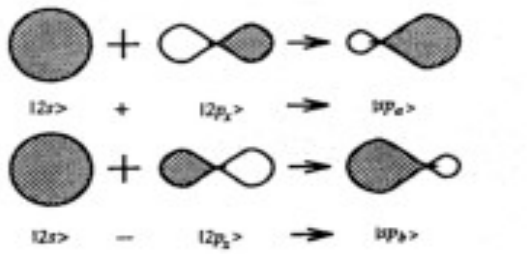
Orthonormality: $\langle sp_i | sp_j \rangle = \delta_{ij}$

$$C_1^2 + C_2^2 = 1$$
$$C_3^2 + C_4^2 = 1$$
$$C_1 C_3 + C_2 C_4 = 0$$

$$C_4 = \pm C_1$$
$$C_3 = \mp C_2 = \mp\sqrt{1 - C_1^2}$$

$$E_a = C_1^2 E_s + C_2^2 E_p$$
$$= C_1^2 \underbrace{(E_s - E_p)}_{<0} + E_p$$
$$E_b = C_3^2 E_s + C_4^2 E_p$$
$$= E_s + C_1^2 (E_p - E_s)$$
$$= E_a + (1 - 2C_1^2)(E_s - E_p)$$

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



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

Orbitals and hybridizations for C

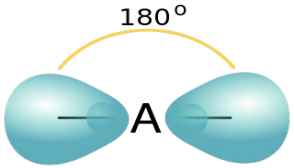
Structure électronique d'un atome de carbone = $1s^2\ 2s^2\ 2p^2$

coeur = $1s^2$ 4 électrons de valence = $2s^2\ 2p^2$

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

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

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

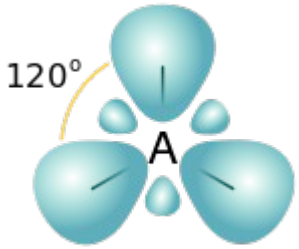


Hybridation sp^2: $2s + 2p_x + 2p_y$, $2p_z$

Example : polyacétylène: $(HCCH)_n$ liaison double: 3 liens σ + 1 lien π

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

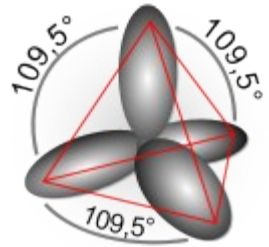
$$|sp^2_{b,c}\rangle = \pm\frac{1}{\sqrt{3}}|2s\rangle \pm \frac{1}{\sqrt{2}}|2p_x\rangle + \frac{1}{\sqrt{6}}|2p_z\rangle$$



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

Example : méthane: CH_4 liaison simple: 4 liens σ

$$|sp^3_a\rangle = \frac{1}{2}\left(|2s\rangle \pm |2p_x\rangle \pm |2p_y\rangle \pm |2p_z\rangle\right)$$



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Tight-binding method

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

$$\psi(\boldsymbol{r}) \text{ avec } \psi(\boldsymbol{r}+\boldsymbol{R}) = e^{i\,\boldsymbol{k}\cdot\boldsymbol{R}}\,\psi(\boldsymbol{r})\;\forall\;\boldsymbol{R} \text{ dans le reseaux .}$$

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

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

Alors, il ya vecteurs propres simultanés:

$$H\,\psi = E\,\psi$$
$$T_{\boldsymbol{R}}\,\psi = c(\boldsymbol{R})\,\psi$$

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

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

$$c(\boldsymbol{R}_n) = c(n_1\boldsymbol{a}_1+n_2\boldsymbol{a}_2+n_3\boldsymbol{a}_3) = c(\boldsymbol{a}_1)^{n_1} c(\boldsymbol{a}_2)^{n_2} c(\boldsymbol{a}_3)^{n_3} = e^{2\pi i(n_1 x_1+n_2 x_2+n_3 x_3)}, \qquad x_j = \frac{\ln c(\boldsymbol{a}_j)}{2\pi i}$$

$$= e^{i(x_1\boldsymbol{b}_1+x_2\boldsymbol{b}_2+x_3\boldsymbol{b}_3)\cdot\boldsymbol{R}_n}, \qquad \boldsymbol{a}_i\cdot\boldsymbol{b}_j = 2\pi\delta_{ij}$$

Conditions à la limite periodique

$$\psi(\boldsymbol{r}+N_i\boldsymbol{a}_i) = \psi(\boldsymbol{r}), \qquad i = 1,2,3$$

$$\rightarrow x_i = \frac{m_i}{N_i}, \qquad m_i \text{ nombre entier} \le N_i$$

Tight-binding method

2. **Tight-binding fonctions de base**

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

Vérification:

$$\Phi_{j\boldsymbol{k}}(\boldsymbol{r} + R_m) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}_n \in B}^{N} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_n} \phi_j(\boldsymbol{r} + \boldsymbol{R}_m - \boldsymbol{R}_n)$$

$$= \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}_l \in B}^{N} e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_l + \boldsymbol{R}_m)} \phi_j(\boldsymbol{r} - \boldsymbol{R}_l)$$

$$= \Phi_{j\boldsymbol{k}}(\boldsymbol{r}) e^{i\boldsymbol{k}\cdot\boldsymbol{R}_m}$$

3. **Tight-binding fonction d'onde**

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

4. **Tight-binding éléments de matrice**

$H_{jj'}(\boldsymbol{k}) = \langle \Phi_{j\boldsymbol{k}} | H | \Phi_{j'\boldsymbol{k}} \rangle$ transfer integral matrix

$S_{jj'}(\boldsymbol{k}) = \langle \Phi_{j\boldsymbol{k}} | \Phi_{j'\boldsymbol{k}} \rangle$ overlap integral matrix

Principe de variation pour l'équation de Schrodinger.

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

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

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

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

$(\psi,\phi) = \int d\boldsymbol{r}\left(\psi(\boldsymbol{r})\phi^*(\boldsymbol{r})\right)$

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

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

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

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

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:

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

Minimizer:

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

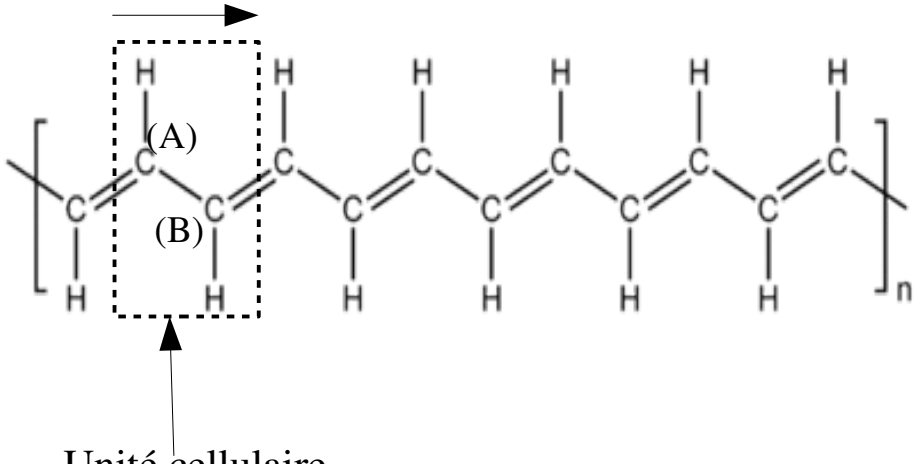
$$\rightarrow \sum_{j'} H_{jj'}(\boldsymbol{k}) C_{j'} = \lambda(\boldsymbol{k}) \sum_{j'} S_{jj'}(\boldsymbol{k}) C_{j'}$$

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

Tight-binding method

Example: *trans*-polyacétylène

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

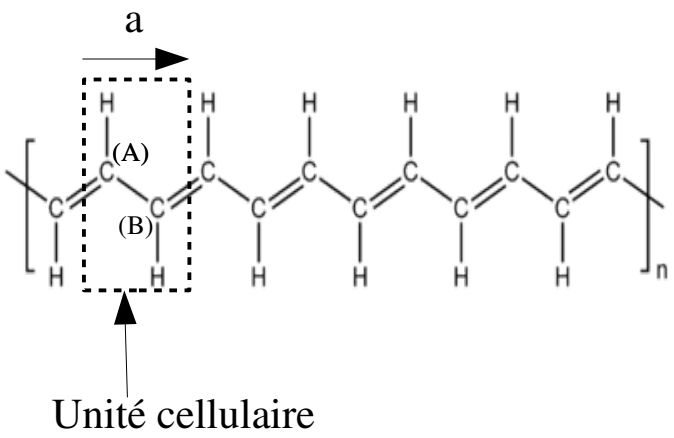


Unité cellulaire

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

Tight-binding method

Example: *trans*-polyacétylène



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

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

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

On cherche les niveau pour les π-electrons:

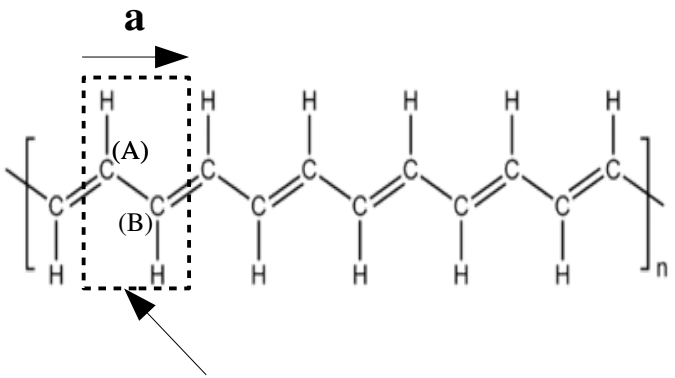
$$\Phi_A(\boldsymbol{r};\boldsymbol{k}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}_n \in B}^{N} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_n} \phi_{2p_z}(\boldsymbol{r} - \boldsymbol{R}_n) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N} e^{ikna} \phi_{2p_z}(\boldsymbol{r} - na\,\hat{\boldsymbol{x}})$$

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

$$\boldsymbol{k} = \frac{2\pi}{a}\frac{p_i}{N}\,\hat{\boldsymbol{x}}, \quad 0 \le p_i < N \quad \Longrightarrow \quad 0 \le k \le 2\pi/a$$

Tight-binding method

Example: *trans*-polyacétylène



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

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

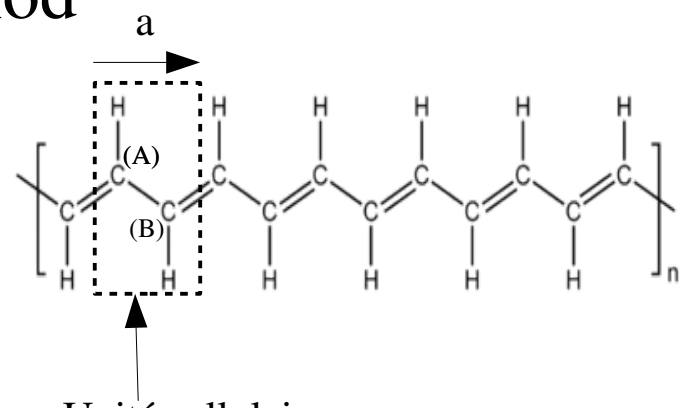
$$H_{AA}(\boldsymbol{k}) = \langle \Phi_{A\boldsymbol{k}} | H | \Phi_{A\boldsymbol{k}} \rangle = \frac{1}{N} \sum_{n,m=0}^{N} e^{ik(n-m)a} \langle \phi_{2p_z}(\boldsymbol{r} - ma\,\hat{\boldsymbol{x}}) | H | \phi_{2p_z}(\boldsymbol{r} - na\,\hat{\boldsymbol{x}}) \rangle$$

$$= \langle \phi_{p_z}(\boldsymbol{r}) | H | \phi_{p_z}(\boldsymbol{r}) \rangle + \underbrace{\frac{1}{N} \sum_{n \neq m}^{N} e^{ik(n-m)a} \langle \phi_{2p_z}(\boldsymbol{r} - ma\,\hat{\boldsymbol{x}}) | H | \phi_{2p_z}(\boldsymbol{r} - na\,\hat{\boldsymbol{x}}) \rangle}_{\text{faible}}$$

$$\approx \epsilon_{2p}$$

Tight-binding method

Example: *trans*-polyacétylène



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

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

$$H_{AB}(k\,\hat{\boldsymbol{x}}) = \langle \Phi_{A\boldsymbol{k}} | H | \Phi_{B\boldsymbol{k}} \rangle = \frac{1}{N} \sum_{n,m=0}^{N} e^{ik(n-m)+ik\,r_{AB,x}} \langle \phi_{2\,p_z}(\boldsymbol{r} - ma\,\hat{\boldsymbol{x}}) | H | \phi_{2\,p_z}(\boldsymbol{r} - \boldsymbol{r}_{AB} - na\,\hat{\boldsymbol{x}}) \rangle$$

$$= e^{ik\,R_x} \langle \phi_{2\,p_z}(\boldsymbol{r}) | H | \phi_{2\,p_z}(\boldsymbol{r} - \boldsymbol{r}_{AB}) \rangle + e^{ik(r_{AB,x}-a)} \langle \phi_{2\,p_z}(\boldsymbol{r}) | H | \phi_{2\,p_z}(\boldsymbol{r} - \boldsymbol{r}_{\boldsymbol{AB}} + \boldsymbol{a}) \rangle$$

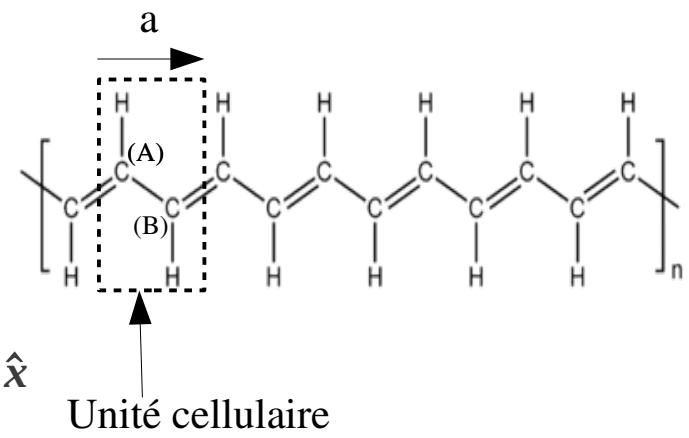
$$+ \underbrace{\frac{1}{N} \sum_{m=0;\, n\neq 0,-1}^{N} e^{ik\,r_{AB,x}+ik(n-m)} \langle \phi_{2\,p_z}(\boldsymbol{r} - ma\,\hat{\boldsymbol{x}}) | H | \phi_{2\,p_z}(\boldsymbol{r} - \boldsymbol{r}_{AB} - na\,\hat{\boldsymbol{x}}) \rangle}_{\text{faible}}$$

if $r_{ABx} = a/2$

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

Tight-binding method

Example: *trans*-polyacétylène



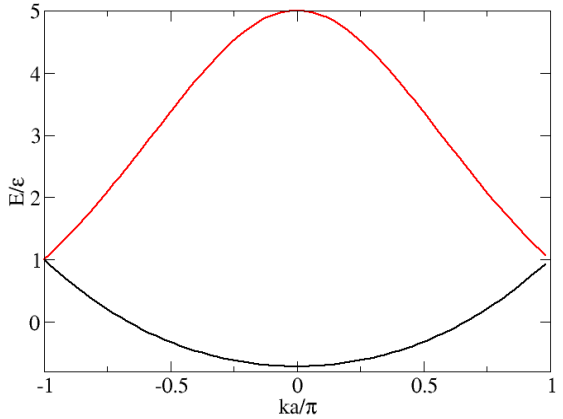
Vecteur de reseau: $\boldsymbol{a} = a\,\hat{\boldsymbol{x}}$

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

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

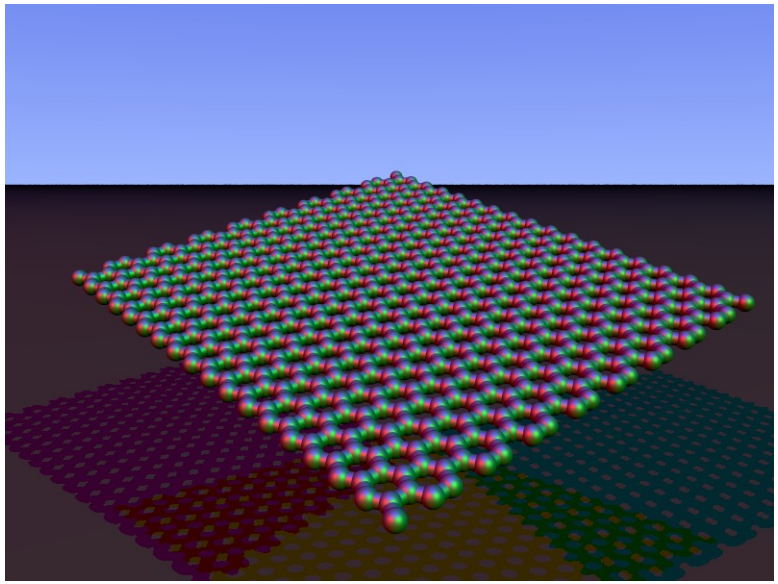
$$0 = det\begin{pmatrix} \epsilon_{2p} - E & 2(t - sE)\cos(ka/2) \\ 2(t - sE)\cos(ka/2) & \epsilon_{2p} - E \end{pmatrix}$$
$$= (\epsilon_{2p} - E)^2 - 4(t - sE)^2\cos^2(ka/2)$$

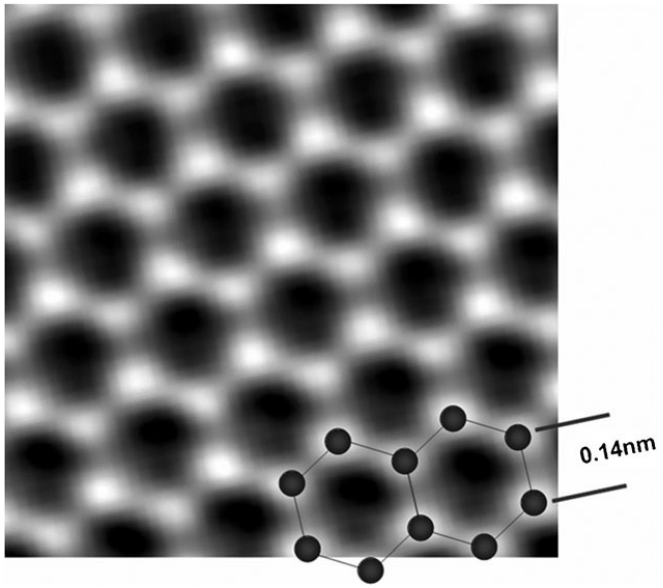
$$E_{\pm}(k) = \frac{\epsilon_{2p} \pm 2t\cos(ka/2)}{1 \pm 2s\cos(ka/2)}, -\frac{\pi}{a} < k < \frac{\pi}{a}$$



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 = $2s^2\ 2p^2$

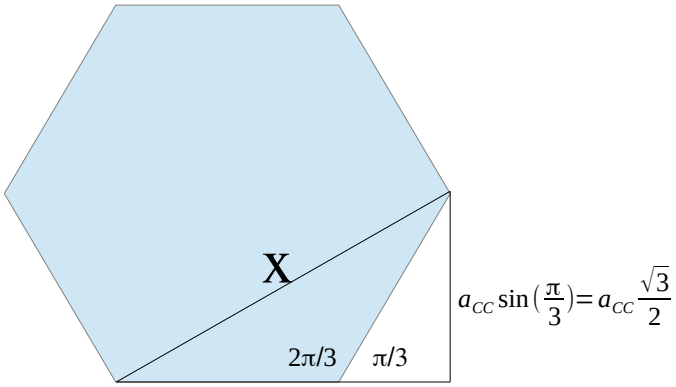
Chaque atome de carbone offre 3 orbitales atomiques sp^2 et une orbitale $2p_z$

Les orbitales atomiques sp^2 forment les liens σ

Les orbitales atomiques $2p_z$ forment les liens π

Graphene 2

$a_{CC} = 0.142\,\mathrm{nm}$



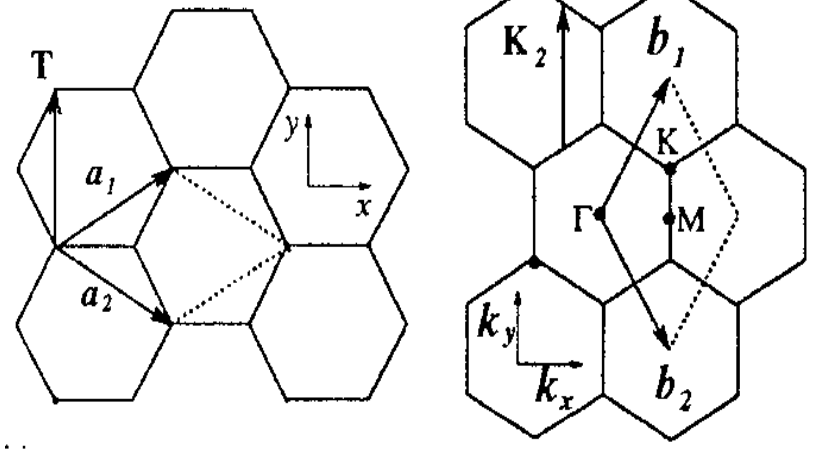
$$a_{CC} + a_{CC}\cos(\frac{\pi}{3}) = \frac{3a_{CC}}{2}$$

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

réseau

zone de Brillouin

$x_i\,b_i, \quad 0 \le x_i < 1$



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

$$a = \|\boldsymbol{a}_1\| = \|\boldsymbol{a}_2\| = 0.246\,\mathrm{nm}$$

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

Graphene Tight-binding : π-bands

réseau zone de Brillouin

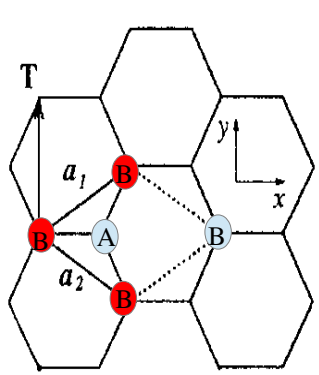
$$H_{AA} = H_{BB} = \epsilon_{2p}$$

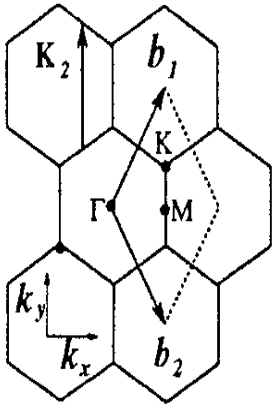
$$H_{AB} = t\left(e^{i\boldsymbol{k}\cdot\boldsymbol{R}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{R}_2} + e^{i\boldsymbol{k}\cdot\boldsymbol{R}_3}\right) \equiv t f(\boldsymbol{k})$$

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

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

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





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

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

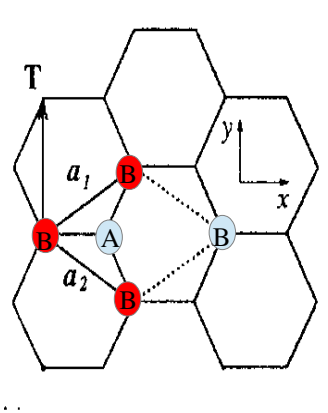
$s = 0 \Leftrightarrow$ "Slater-Koster approximation"

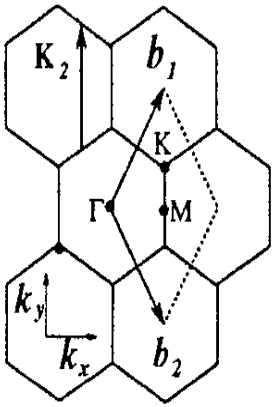
R. Saito, G. Dresselhaus & M. S. Dresselhaus,
Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998)

Graphene Tight-binding : σ-bands

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

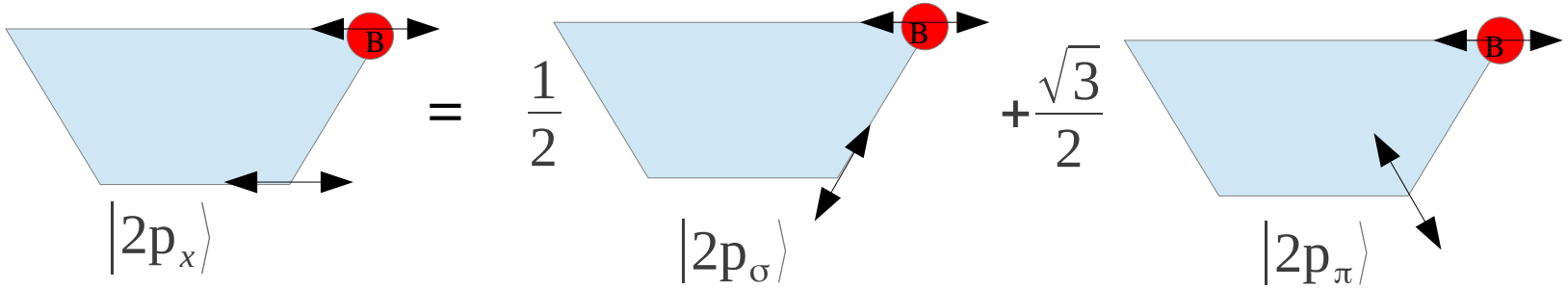
$$H_{AA}=\begin{pmatrix}\epsilon_{2s} & 0 & 0\\ 0 & \epsilon_{2p} & 0\\ 0 & 0 & \epsilon_{2p}\end{pmatrix}, \quad S_{AA}=\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}$$





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.

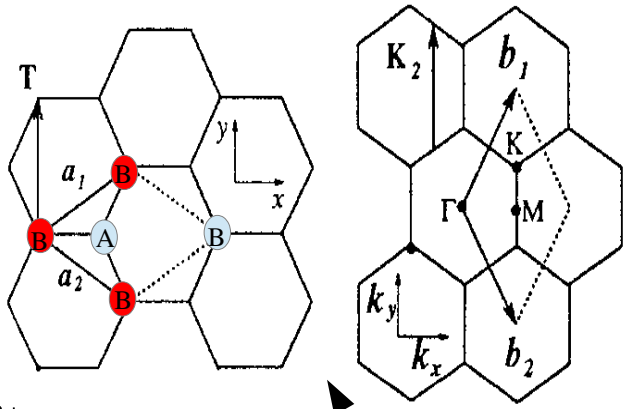


R. Saito, G. Dresselhaus & M. S. Dresselhaus,
Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998)

Graphene Tight-binding : σ-bands

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

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



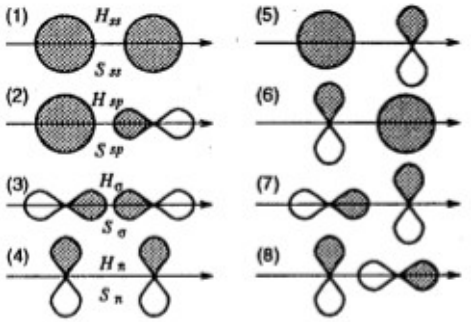
$$\left\langle 2p_x^B \middle| H \middle| 2p_x^A \right\rangle = \left(\frac{1}{2}\right)^2 \left\langle 2p_\sigma^B \middle| H \middle| 2p_\sigma^A \right\rangle + \left(\frac{\sqrt{3}}{2}\right)^2 \left\langle 2p_\pi^B \middle| H \middle| 2p_\pi^A \right\rangle$$

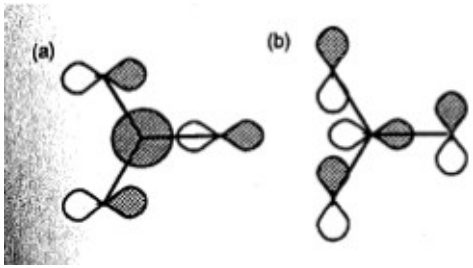
$$+\left(\frac{1}{2}\right)\left(\frac{\sqrt{3}}{2}\right)\left\langle 2p_\pi^B \middle| H \middle| 2p_\sigma^A \right\rangle + \left(\frac{1}{2}\right)\left(\frac{\sqrt{3}}{2}\right)\left\langle 2p_\sigma^B \middle| H \middle| 2p_\pi^A \right\rangle$$

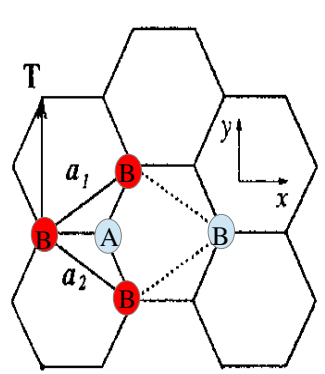
$$= \left(\frac{1}{4}H_{\sigma\sigma} + \frac{3}{4}H_{\pi\pi}\right)e^{i\left(k_x R_x + k_y R_y\right)} = \left(\frac{1}{4}H_{\sigma\sigma} + \frac{3}{4}H_{\pi\pi}\right)e^{i\left(\frac{k_x a}{2\sqrt{3}} + \frac{k_y a}{2}\right)}, \qquad H_{\sigma\pi} = 0$$

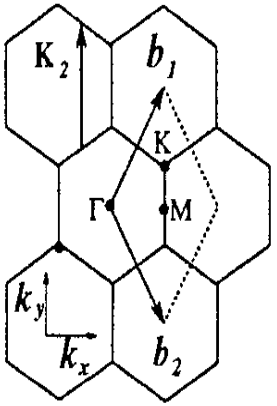
Graphene Tight-binding : σ-bands

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









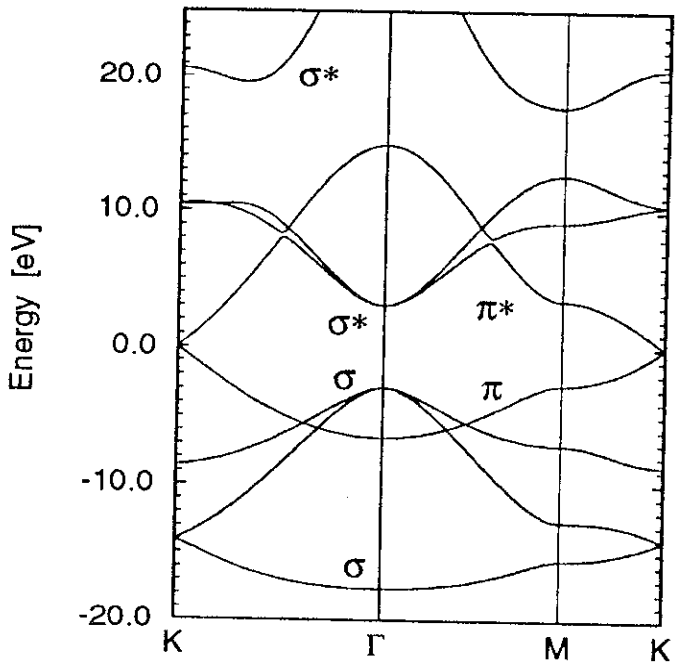
R. Saito, G. Dresselhaus & M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998)

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

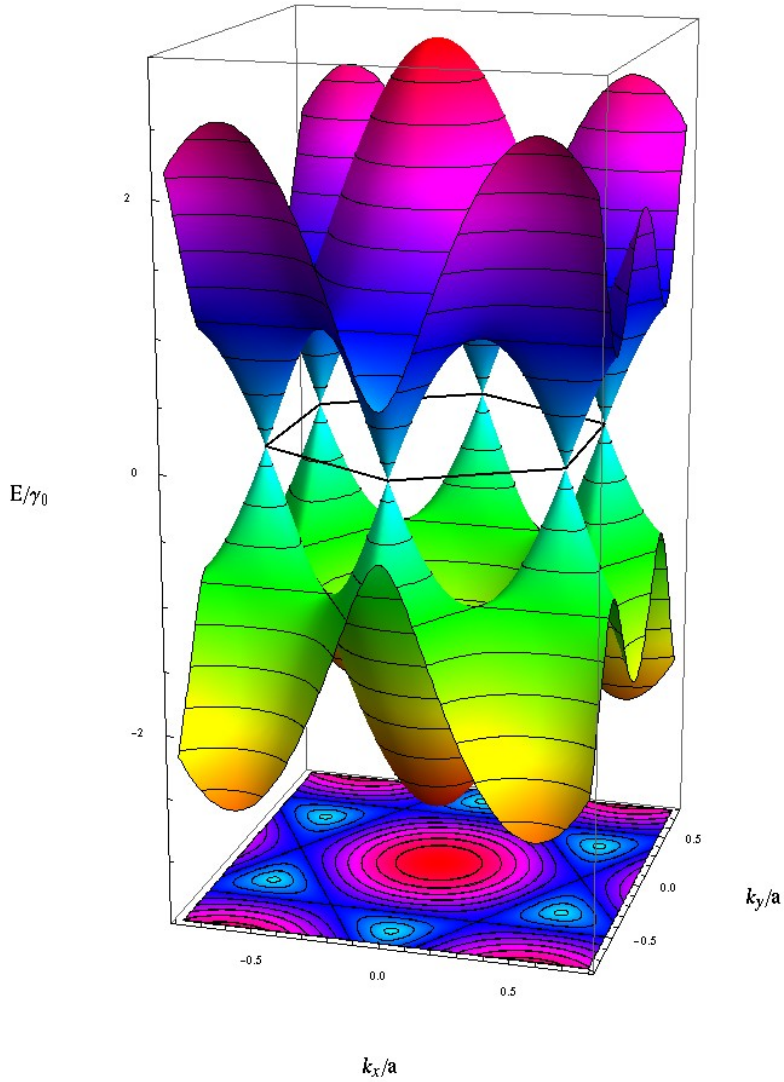
$$\left\langle 2p_x^B \middle| H \middle| 2p_y^A \right\rangle = \frac{i\sqrt{3}}{2}\left(H_{\sigma\sigma} + H_{\pi\pi}\right) e^{-ik_x a/2\sqrt{3}} \sin\frac{k_y a}{2}$$

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

Graphene



component	H (eV)	S
ss	-6.7969	0.212
sp	-5.580	0.102
σσ	-5.037	0.146
ππ	-3.033	0.129
$\varepsilon_s - \varepsilon_p$	-8.868	



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

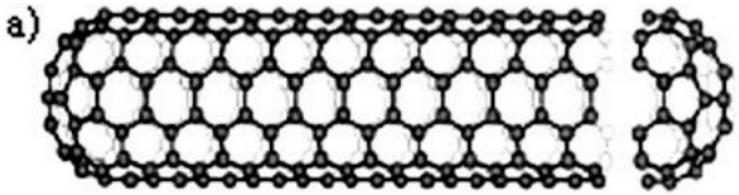
Carbon Structures

- 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

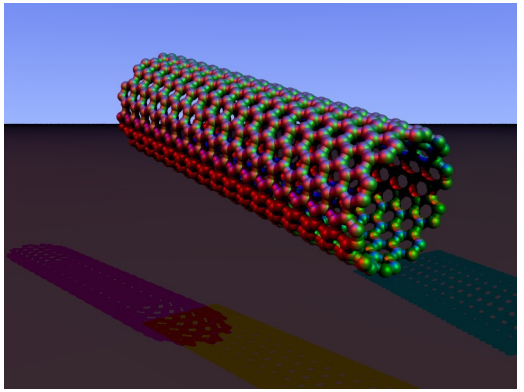
Nanotube structure

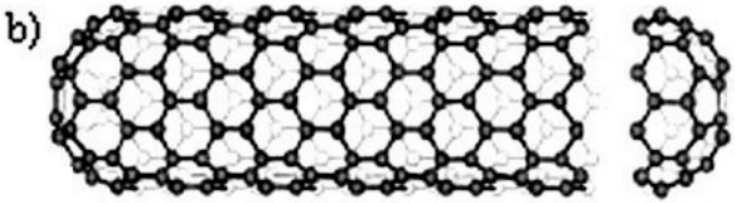
Rayon: 0.7-10 nm (pour la plupart < 2nm)
Longeur: 1-100 μm

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

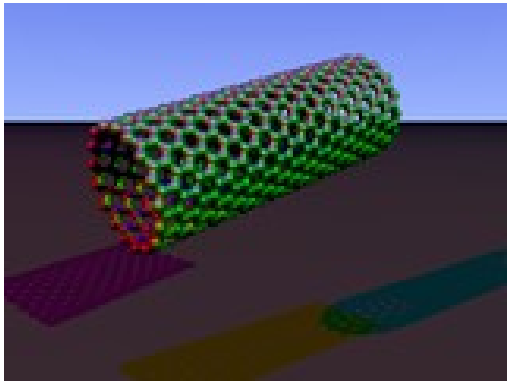


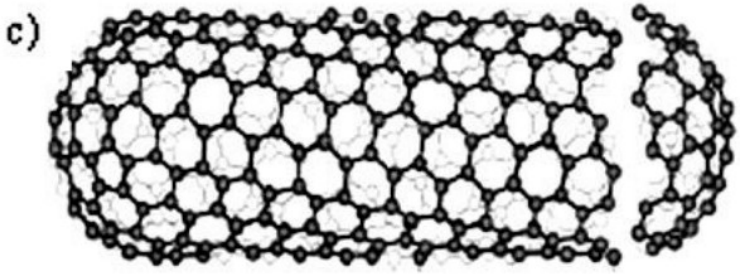
“armchair”



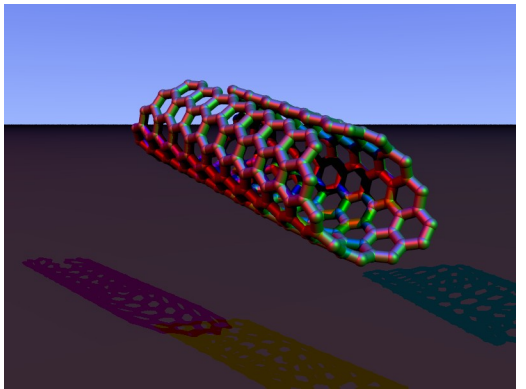


“zigzag”

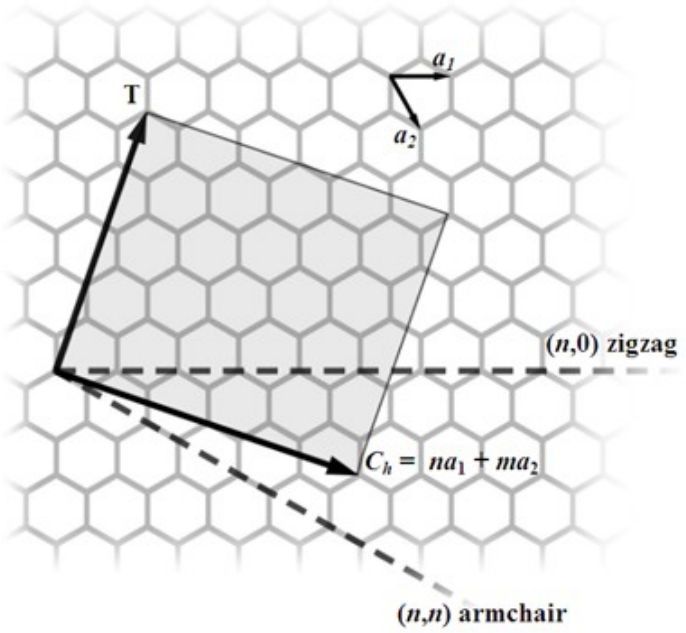


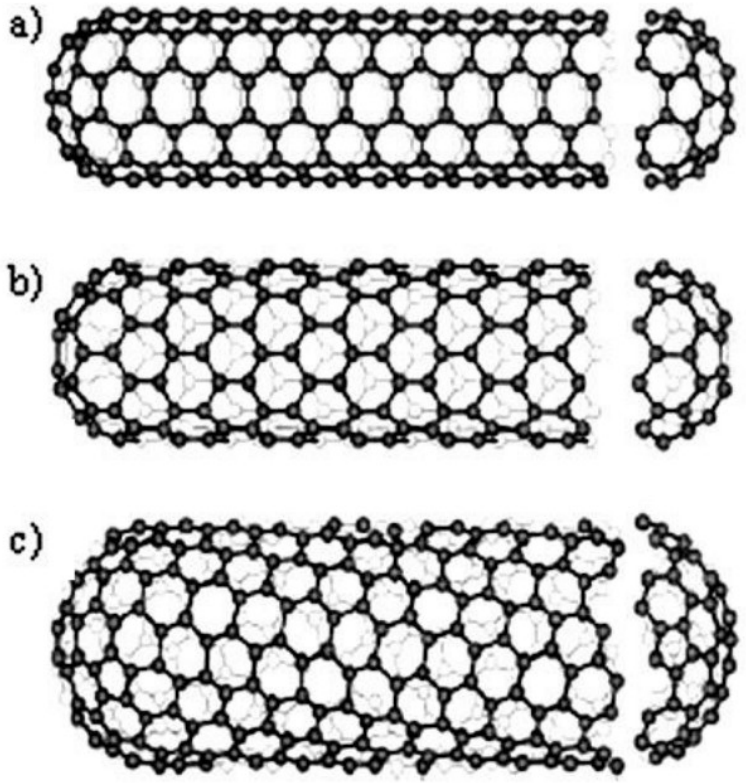


“chiral”



Nanotube structure





"armchair"

"zigzag"

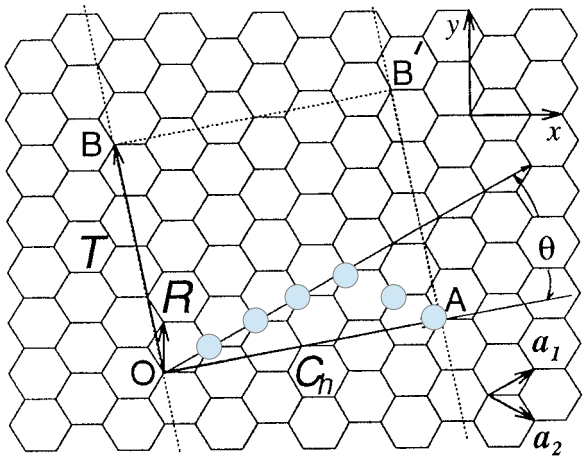
"chiral"

Division fondamentale:

- "achiral" : possédant une symétrie miroir (seulement la"zigzag" et la "armchair"
- "chiral" : pas de symétrie mirroir

Nanotube structure : vecteur chiral

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



$C_h=(4,2)$

Ligne OA est la vecteur chiral

Vecteur chiral: $\boldsymbol{C}_h=n\,\boldsymbol{a}_1+m\,\boldsymbol{a}_2\Leftrightarrow(n,m),\quad 0\le|m|\le n$

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

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

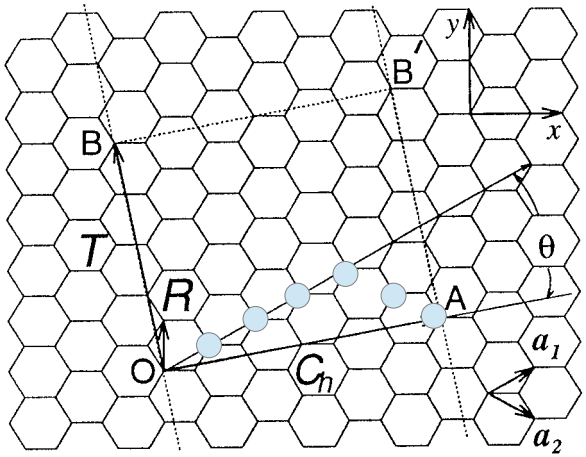
Angle chiral: $\cos\theta\equiv\frac{\boldsymbol{C}_h\cdot\boldsymbol{a}_1}{|\boldsymbol{C}_h||\boldsymbol{a}_1|}=\frac{2n+m}{2\sqrt{n^2+m^2+nm}}$

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

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)



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

$C_h = (4,2)$

Ligne OB est la vecteur de translation

Vecteur de translation: $\boldsymbol{T} = t_1 \boldsymbol{a}_1 + t_2 \boldsymbol{a}_2 \Leftrightarrow (n, m)$

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

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

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

(exercise)

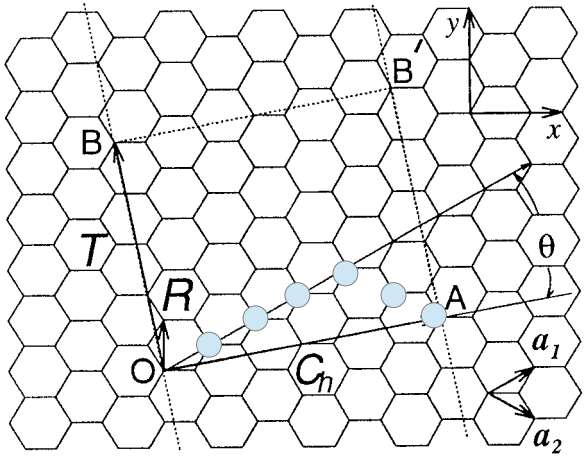
Le nombre d'atoms par unite cellulaire est: 2N

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)

$C_h = (4,2)$



Ligne OR est la vecteur de symétrie.

Les positions de tous les atomes dans la maille élémentaire peut être représenté en tant que n**R** avec les bords periodique.

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

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

La valeur minimale possible pour le numérateur est

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

Aussi $$0 < \frac{\boldsymbol{R}\cdot\boldsymbol{T}}{|\boldsymbol{T}|} < T \Leftrightarrow 0 < \left(p(t_1+t_2/2)+q(t_2+t_1/2)\right) < t_1^2+t_2^2+t_1t_2$$

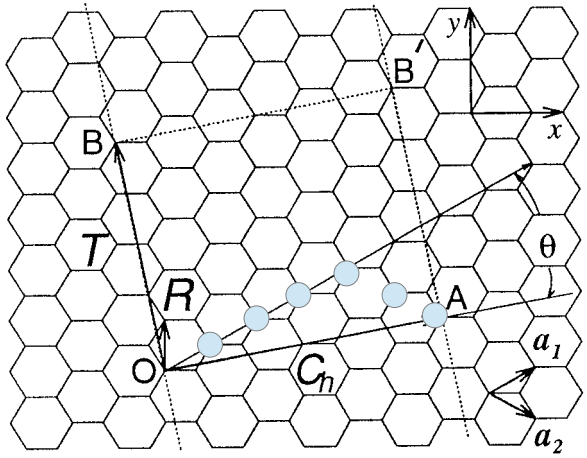
$$\Leftrightarrow 0 < mp - nq \le N$$

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
(Imperial College Press, London, 1998)

$C_h=(4,2)$



Ligne OR est la vecteur de symétrie.

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

$$\boldsymbol{R}=p\,\boldsymbol{a}_1+q\,\boldsymbol{a}_2\Leftrightarrow(p,q) \qquad \frac{\boldsymbol{R}\cdot\boldsymbol{C}_h}{|\boldsymbol{C}_h|}=\frac{|\boldsymbol{R}\times\boldsymbol{T}|}{|\boldsymbol{T}|}=\frac{(t_1q-t_2p)(\boldsymbol{a}_1\times\boldsymbol{a}_2)}{|\boldsymbol{T}|}\Rightarrow t_1q-t_2p=1$$

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

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

Nanotube structure : vecteur de symétrie

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

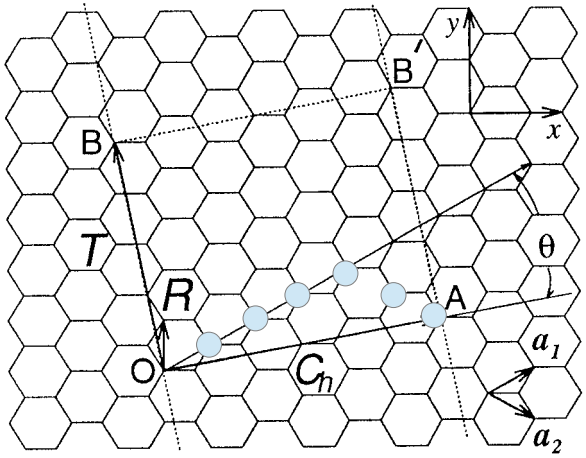
$$\boldsymbol{R} = p\,\boldsymbol{a}_1 + q\,\boldsymbol{a}_2 \Leftrightarrow (p, q)$$

$$t_1 q - t_2 p = 1$$

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

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

$C_h = (4,2)$



Ligne OR est la vecteur de symétrie.

Les positions de tous les atomes dans la maille élémentaire peut être représenté en tant que n**R** avec les bords periodique car

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

Structure

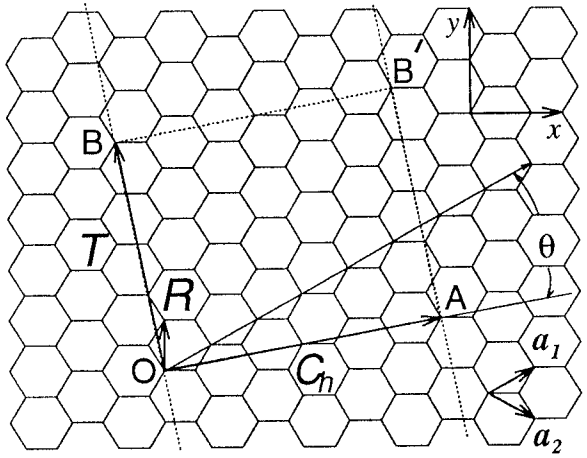
	zigzag	armchair	chiral
C	(n,0)	(n,n)	(n,m)
T	(1,-2)	(1,-1)	$(\frac{2m+n}{d_R}, -\frac{2n+m}{d_R})$
R	(1,-1)	(1,0)	
L/a	n	$\sqrt{3}n$	$\sqrt{m^2+n^2+nm}$
T	$\sqrt{3}$	1	$\sqrt{3}L/d_R$
N	2n	2n	$2L^2/(a^2 d_R)$

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

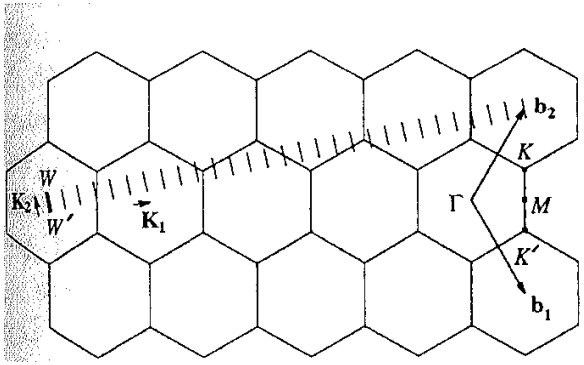
$$= \begin{pmatrix} d & \text{if } n-m \text{ is not a multiple of } 3d \\ 3d & \text{if } n-m \text{ is a multiple of } 3d \end{pmatrix}, \quad d = gcd(n, m)$$

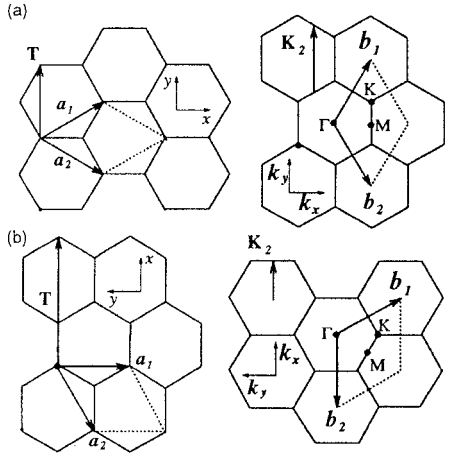
Nanotube structure

réseau



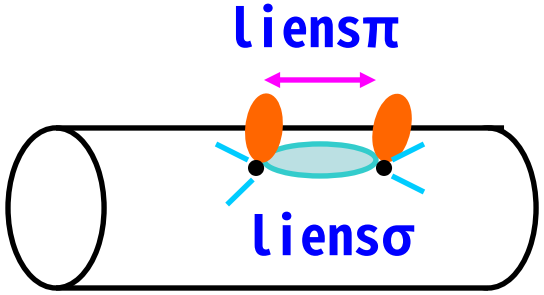
zone de Brillouin





« armchair » (n,n)

« zigzag » $(n,0)$

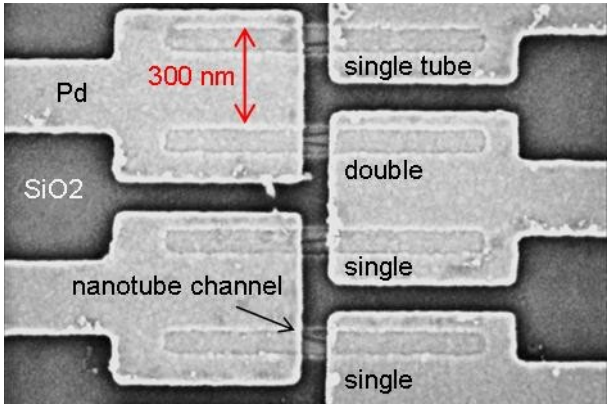


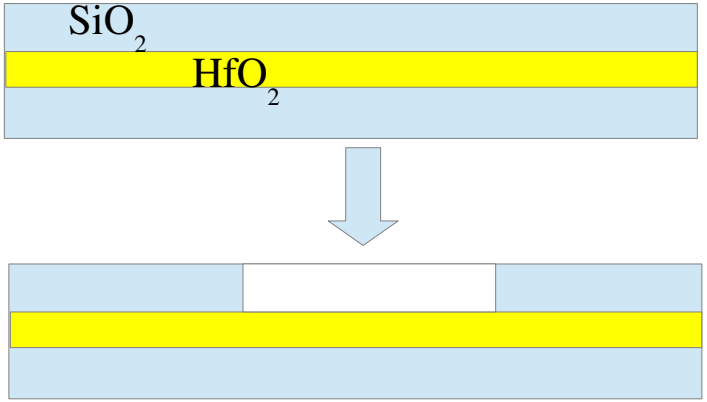
R. Saito, G. Dresselhaus & M. S. Dresselhaus,
Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998)

Nanotubes de carbone

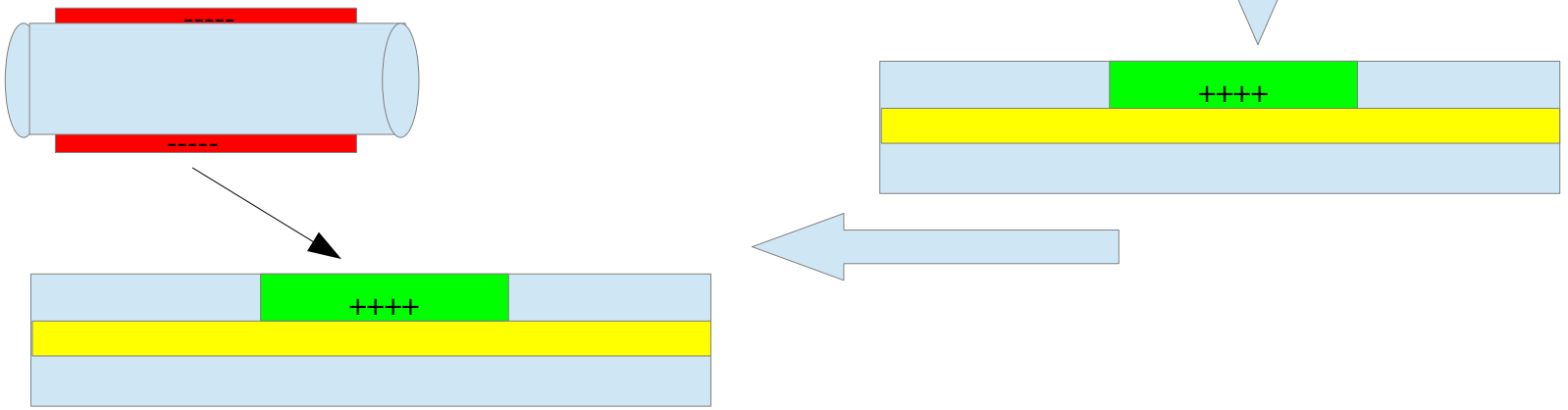
- Introduction
  - Histoire
  - Carbone
  - Hybridization
- Tight-binding calculations
  - Principe
  - Example: trans
  - Graphene π-liens
  - Graphene σ-liens
- Structure de carbone nanotubes
- Structure Electronique
- Synthesis
- Transport
- Multi-walled nanotubes

Nanotubes





"High-density integration of carbon nanotubes via chemical self-assembly",
Hongsik Park, Ali Afzali, Shu-Jen Han, George S. Tulevski, Aaron D. Franklin, Jerry Tersoff, James B. Hannon & Wilfried Haensch, Nature Nanotechnology (Oct, 2012)



Bandes d'energie du nanotube : zone folding

L'idée: La géométrie de la CN est un sous-ensemble d'une feuille infinie de graphène avec des frontières périodiques. Par conséquent, les ondes vecteurs de la CN sont un sous-ensemble de ceux pour le graphène et les bandes de l'energie sont:

$$E_{CN}\left(\boldsymbol{k}_{CN}\right)=E_{GR}\left(\boldsymbol{k}_{CN}\right)$$

C'est ce qu'on appelle "pliage de bande" car ce n'est pas necessaire que $\boldsymbol{k}_{CN}\in$ first Brillouin zone of Graphene.

Donc, nous avons besoin de les vecteurs disponible pour le CN.

Bandes d'energie du nanotube

Théorème de Bloch $\psi(\boldsymbol{r})=\sum_j e^{i\boldsymbol{k}\cdot\boldsymbol{R}_j}\phi(\boldsymbol{r}+\boldsymbol{R}_j)$, $\boldsymbol{R}_j$ dans le reseaux .

Bohr- von Karman conditions conditions à la limite

Graphene

$$\psi(\boldsymbol{r}+N_l\boldsymbol{a}_l)=e^{-i\boldsymbol{k}\cdot N_l\boldsymbol{a}_l}\sum_j e^{i\boldsymbol{k}\cdot\boldsymbol{R}_j}\phi(\boldsymbol{r}+\boldsymbol{R}_j)=\psi(\boldsymbol{r})$$

$$\rightarrow \boldsymbol{k}\cdot N_l\boldsymbol{a}_l=2n_l\pi,\quad n_l\in\mathbb{Z}$$

$$\rightarrow \boldsymbol{k}\cdot\boldsymbol{a}_l=2\pi\frac{n_l}{N_l},\quad 0\le n_l\le N_l$$

Nanotube Reseaux avec unité cellulaire ($\mathbf{C}_h$,$\mathbf{T}$) est base de 2N points.

$$\boldsymbol{K}\cdot\boldsymbol{C}_h=2n_C\pi \qquad \boldsymbol{K}\cdot N_T\boldsymbol{T}=2n_T\pi$$

(si la tube est un tore de longeur N_T)

$$\boldsymbol{K}=n_C\boldsymbol{K}_1+\frac{n_T}{N_T}\boldsymbol{K}_2,\quad 0\le n_T\le N_T$$

$$\boldsymbol{K}_1\cdot\boldsymbol{C}_h=2\pi \quad \boldsymbol{K}_1\cdot\boldsymbol{T}=0 \qquad n_c\in???$$

$$\boldsymbol{K}_2\cdot\boldsymbol{C}_h=0 \quad \boldsymbol{K}_2\cdot\boldsymbol{T}=2\pi$$

Bandes d'energie du nanotube

Graphene

Vecteurs de base du réseau

$$\boldsymbol{a}_1=\left(\frac{\sqrt{3}a}{2},\frac{a}{2}\right),\boldsymbol{a}_2=\left(\frac{\sqrt{3}a}{2},-\frac{a}{2}\right)$$

Vecteurs de base du réseau réciproque

$$\boldsymbol{b}_1=\left(\frac{2\pi}{\sqrt{3}a},\frac{2\pi}{a}\right),\boldsymbol{b}_2=\left(\frac{2\pi}{\sqrt{3}a},-\frac{2\pi}{a}\right)$$

Nanotube

Vecteurs de base du réseau

$$\boldsymbol{C}_h=n\boldsymbol{a}_1+m\boldsymbol{a}_2,\boldsymbol{T}=t_1\boldsymbol{a}_1+t_2\boldsymbol{a}_2$$

Vecteurs de base du réseau réciproque $\boldsymbol{K}_1,\boldsymbol{K}_2$

$$\boldsymbol{C}_h\cdot\boldsymbol{K}_1=2\pi \quad \boldsymbol{T}\cdot\boldsymbol{K}_1=0$$
$$\boldsymbol{C}_h\cdot\boldsymbol{K}_2=0 \quad \boldsymbol{T}\cdot\boldsymbol{K}_2=2\pi$$

$$\boldsymbol{K}_1=K_{11}\boldsymbol{b}_1+K_{12}\boldsymbol{b}_2$$

$$K_{11}n+K_{12}m=1 \quad K_{11}t_1+K_{12}t_2=0$$
$$t_1K_{11}n+t_1K_{12}m=t_1$$
$$K_{12}\left(-t_2n+t_1m\right)=t_1$$

$$K_{12}=\frac{t_1}{-t_2n+t_1m}=\frac{t_1}{N}$$

$$\boldsymbol{K}_1=\frac{1}{N}\left(-t_2\boldsymbol{b}_1+t_1\boldsymbol{b}_2\right)$$

$$\boldsymbol{K}_2=\frac{1}{N}\left(m\boldsymbol{b}_1-n\boldsymbol{b}_2\right)$$

Bandes d'energie du nanotube

$$\boldsymbol{K}_1=\frac{1}{N}\left(-t_2\boldsymbol{b}_1+t_1\boldsymbol{b}_2\right) \qquad |\boldsymbol{K}_1|=\frac{2\pi}{|\boldsymbol{C}_h|}$$

$$\boldsymbol{K}_2=\frac{1}{N}\left(m\boldsymbol{b}_1-n\boldsymbol{b}_2\right) \qquad |\boldsymbol{K}_2|=\frac{2\pi}{|\boldsymbol{T}|}$$

$$\boldsymbol{K}=n_C\boldsymbol{K}_1+\frac{n_T}{N_T}\boldsymbol{K}_2,\ \ 0\le n_T\le N_T$$

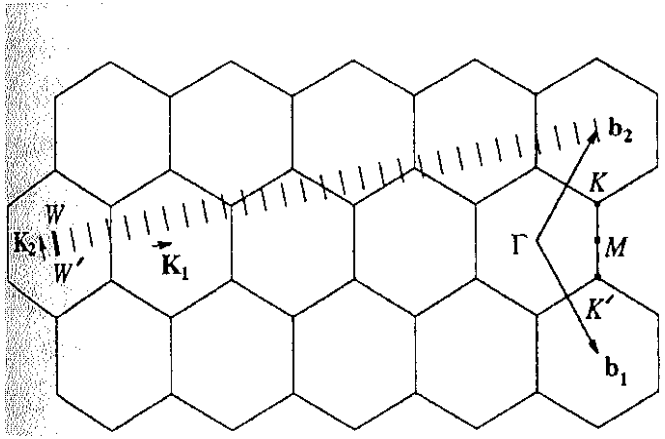
$$=n_C\boldsymbol{K}_1+k\frac{\boldsymbol{K}_2}{|\boldsymbol{K}_2|},\ \ 0\le k\le\frac{2\pi}{|\boldsymbol{T}|},\text{si } N_T\gg 1$$

$$n_C\boldsymbol{K}_1=\left(-\frac{n_C t_2}{N}\boldsymbol{b}_1+\frac{n_C t_1}{N}\boldsymbol{b}_2\right)$$

$$\frac{n_C t_2}{N}=r\in\mathbb{Z} \text{ et } \frac{n_C t_1}{N}=s\in\mathbb{Z}\rightarrow n_C t_2=rN,\ \ n_C t_1=sN$$

mais $gcd(t_1,t_2)=1\rightarrow N$ divise n_C

$$\rightarrow 0\le n_C<N$$



$$\boldsymbol{C}_h=(4,2),\ \ \boldsymbol{T}=(4,-5),\ \ N=28$$

$$\boldsymbol{K}_1=(5\boldsymbol{b}_1+4\boldsymbol{b}_2)/28$$

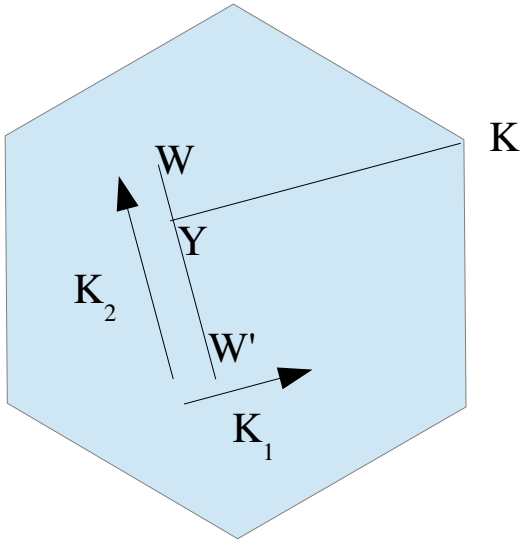
$$\boldsymbol{K}_2=(4\boldsymbol{b}_1-2\boldsymbol{b}_2)/28$$

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

Bandes d'energie du nanotube

vecteurs de base du réseau réciproque: $\boldsymbol{K}_1 = \frac{1}{N}\left(-t_2\boldsymbol{b}_1 + t_1\boldsymbol{b}_2\right)$

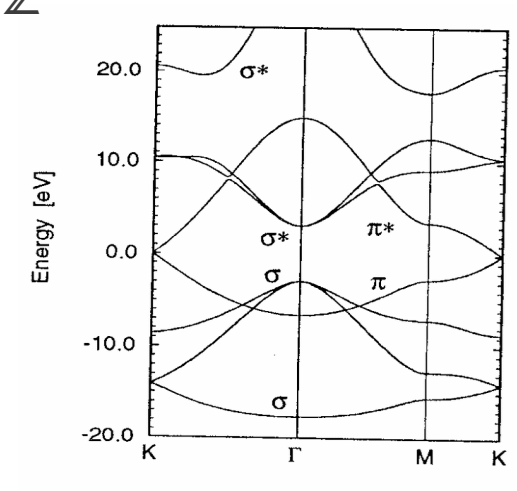
$\boldsymbol{K}_2 = \frac{1}{N}\left(m\boldsymbol{b}_1 - n\boldsymbol{b}_2\right)$



métallique si la point “K”est permi:

$\bar{YK} = n\boldsymbol{K}_1, \quad n \in \mathbb{Z}$

Mais: $\bar{YK} = \frac{2n+m}{3}\boldsymbol{K}_1$

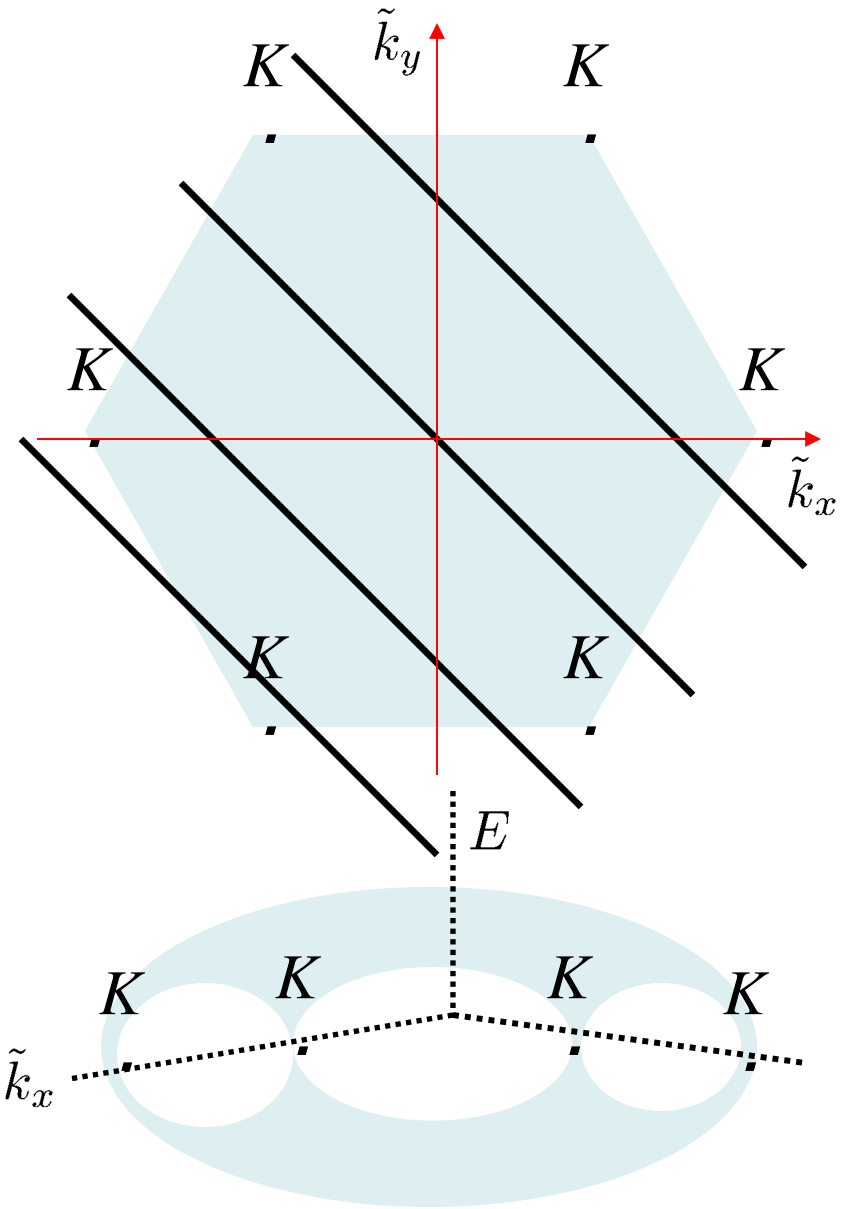


Alors, métallique si $\frac{2n+m}{3} \in \mathbb{Z} \Leftrightarrow \frac{n-m}{3} \in \mathbb{Z}$

Notez: “armchair” (n,n) toujour métallique.

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

Nanotubes Semiconducteurs



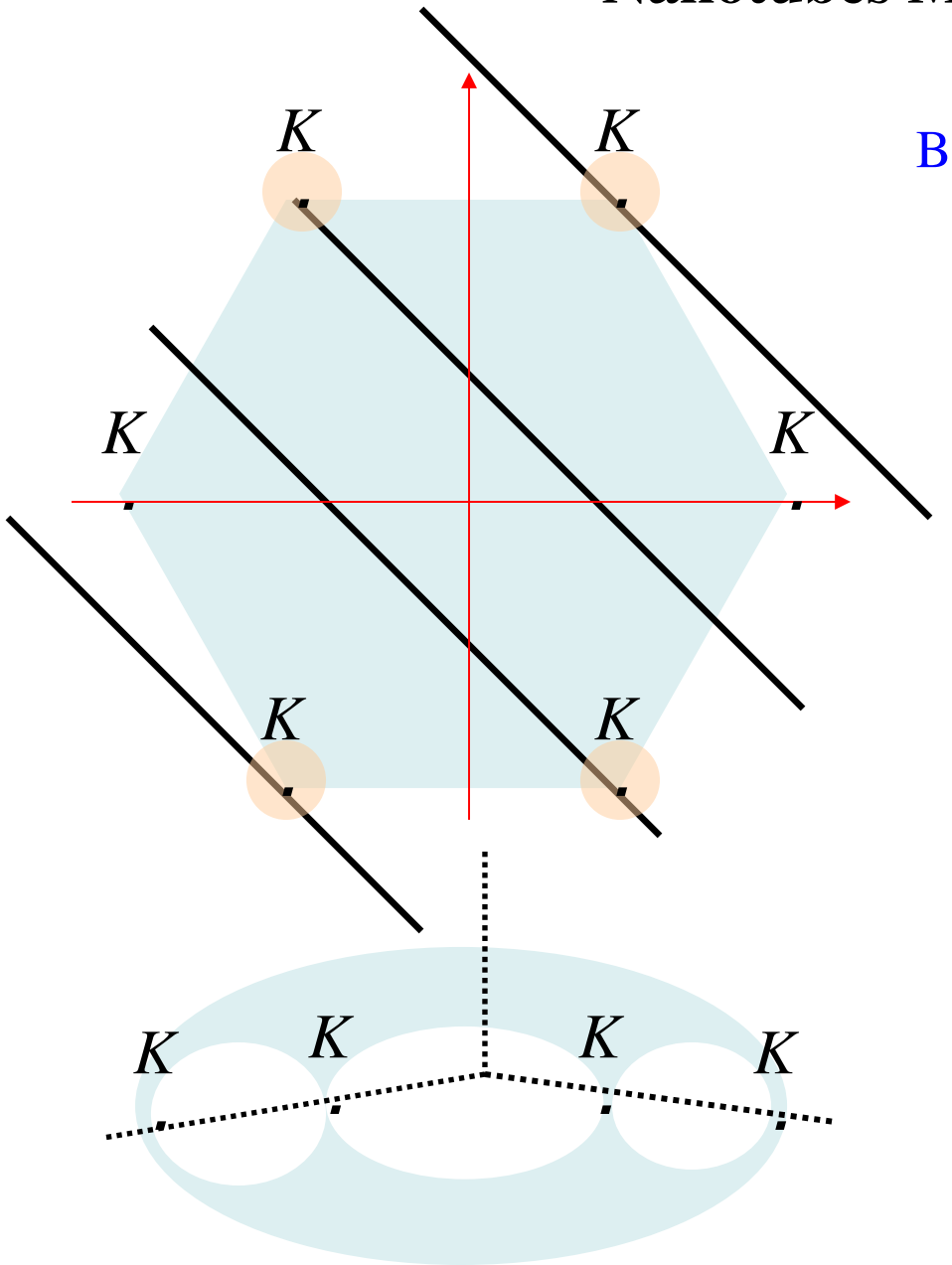
Bande d'énergie du graphène

Bandes d'énergie **semiconductrices** pour le nanotube

sections des conditions aux bords périodiques

← niveau de Fermi : $E = 0$

Nanotubes Metalliques



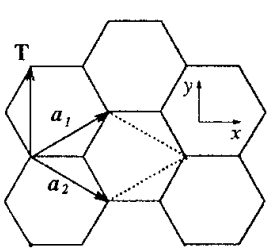
Bande d'énergie du graphène

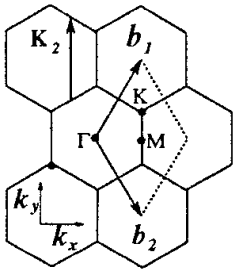
Bandes d'énergie **métalliques** pour le nanotube

sections des conditions aux bords périodiques

← niveau de Fermi : $E = 0$

Nanotubes « Armchair » (*n*,*n*)





$$\boldsymbol{C}_h = n\boldsymbol{a}_1 + n\boldsymbol{a}_2 \equiv (n,n)$$

$$\boldsymbol{T} = \boldsymbol{a}_1 - \boldsymbol{a}_2$$

$$N = 2n$$

$$\boldsymbol{K}_1 = \frac{1}{2n}(\boldsymbol{b}_1 + \boldsymbol{b}_2) = \left(\frac{2\pi}{\sqrt{3}\,a\,n}, 0\right)$$

$$\boldsymbol{K}_2 = \frac{1}{2}(\boldsymbol{b}_1 - \boldsymbol{b}_2) = \left(0, \frac{2\pi}{a}\right)$$

π bande d'énergie du graphène: $E_{gr} = \pm t\sqrt{1 + 4\cos\left(\frac{\sqrt{3}\,k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$

π bandes d'énergie du nanotube:

$$E_q(k) = E_{gr}\left(k_x = \frac{2\pi q}{\sqrt{3}\,a\,n}, k_y = k\right), \quad q = 0,1,\ldots,2n-1, \quad -\frac{\pi}{a} \le k \le +\frac{\pi}{a}$$

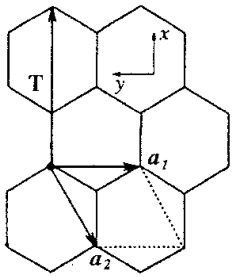
$$= \pm t\sqrt{1 + 4\cos\left(\frac{\pi q}{n}\right)\cos\left(\frac{k a}{2}\right) + 4\cos^2\left(\frac{k a}{2}\right)}$$

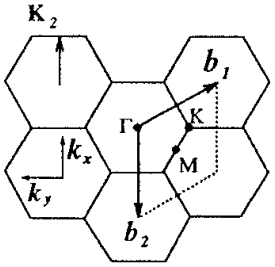
$$E_q\left(ka = \pm\frac{2\pi}{3}\right) = \pm t\sqrt{2 + 2\cos\left(\frac{\pi q}{n}\right)}$$

métallique car pas de « gap » (q=n)

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

Nanotubes « zigzag» (n,0)





$$\boldsymbol{C}_h = n\,\boldsymbol{a}_1 \equiv (n,0)$$

$$\boldsymbol{T} = \boldsymbol{a}_1 - 2\,\boldsymbol{a}_2$$

$$N = 2\mathrm{n}$$

$$\boldsymbol{K}_1 = \frac{1}{2n}(2\boldsymbol{b}_1 + \boldsymbol{b}_2) = \frac{1}{2\mathrm{n}}\left(\frac{6\pi}{\sqrt{3}a}, \frac{2\pi}{a}\right)$$

$$\boldsymbol{K}_2 = -\frac{1}{2}\boldsymbol{b}_2 = \frac{1}{2}\left(-\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}\right)$$

π bandes d'énergie du nanotube:

$$E_q(k) = E_{gr}\left(\frac{\sqrt{3}\pi q}{n a} - \frac{k}{2}, \frac{\pi q}{n a} + \frac{\sqrt{3}k}{2}\right), \quad -\frac{\pi}{a\sqrt{3}} \le k \le \frac{\pi}{a\sqrt{3}} \qquad 0 \le q < 2\mathrm{n}$$

$$\rightarrow \pm t\sqrt{1 + 4\cos\left(\frac{\sqrt{3}\,k\,a}{2}\right)\cos\left(\frac{q\pi}{n}\right) + 4\cos^2\left(\frac{q\pi}{n}\right)}$$

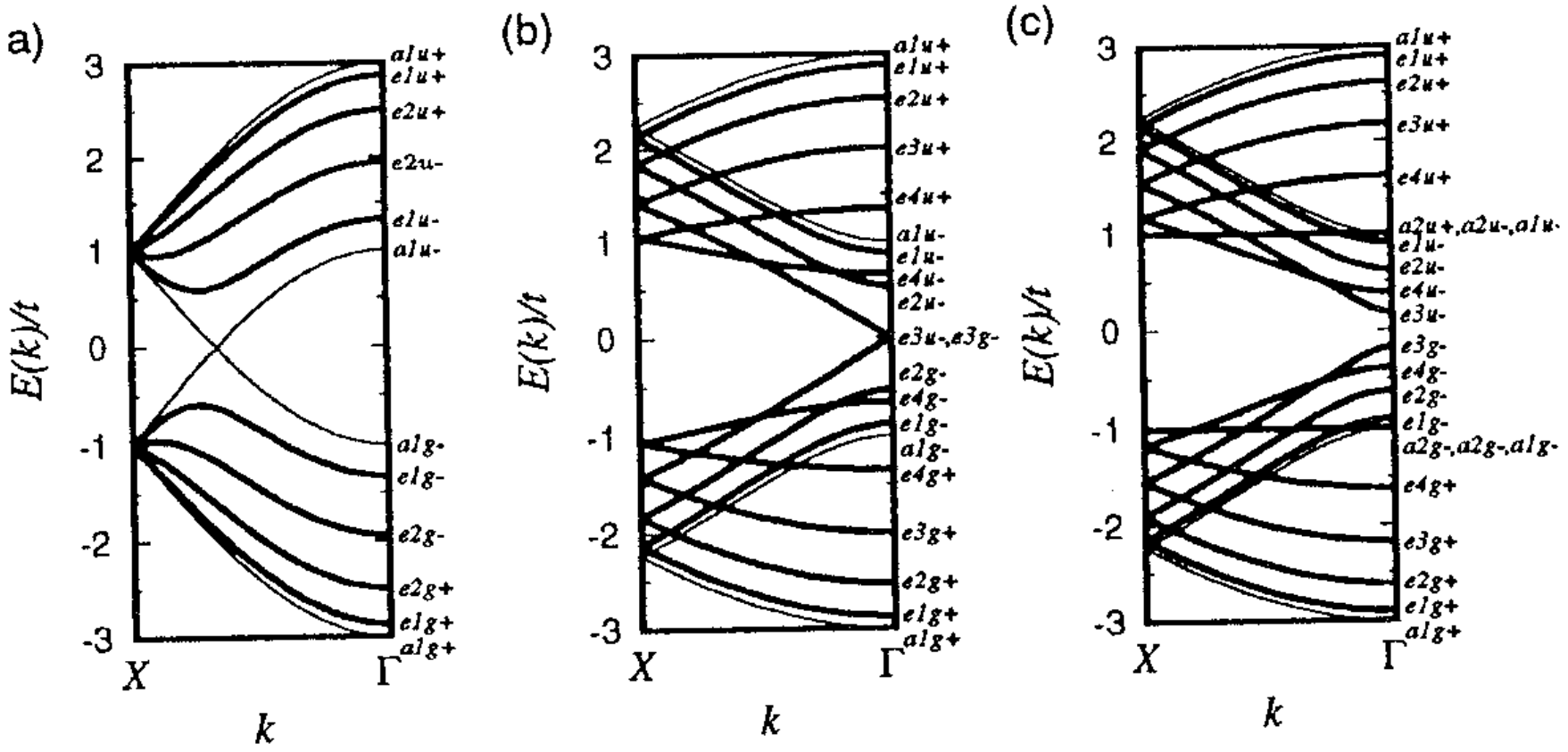
$$E_q(k=0) = \pm t\sqrt{1 + 4\cos\left(\frac{q\pi}{n}\right) + 4\cos^2\left(\frac{q\pi}{n}\right)} = 0 \Leftrightarrow \frac{q\pi}{n} = \frac{2\pi}{3} \Leftrightarrow q = \frac{2n}{3}$$

Possible seulement si n est un multiple de 3.

Si n est un nombre pair $E_{n/2}(k) = \pm t$ "dispersionless"

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

Nanotube : bandes d'énergie



« armchair » (5,5)
métallique

« zigzag » (9,0)
métallique

« zigzag » (10,0)
semiconducteur

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

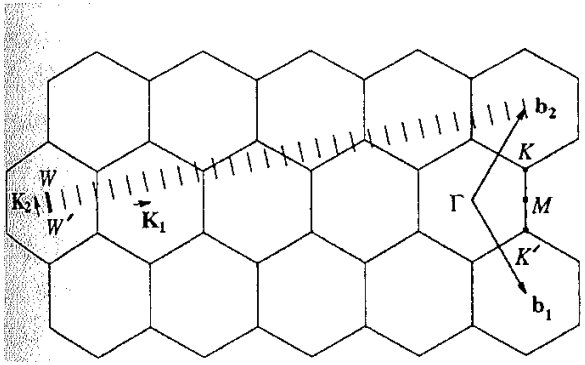
Rappel : Density of states et van Hove singularity

Donc, le nombre des etat avec energie E(k)

$$g(E)\,dE = \int \delta(e(\boldsymbol{k}) - E)\,d\,\boldsymbol{k} = \int_{e^{-1}(E)} \frac{1}{|\nabla e(\boldsymbol{k})|}\,d\,\boldsymbol{S}$$

$$|\nabla e(\boldsymbol{k})| = 0 \Leftrightarrow \textit{van Hove singularity}$$

Resume : bandes d'energie du nanotube



vecteurs de base du réseau réciproque:

$$\boldsymbol{K}_1 = \frac{1}{N}\left(-t_2\boldsymbol{b}_1 + t_1\boldsymbol{b}_2\right)$$

$$\boldsymbol{K}_2 = \frac{1}{N}\left(m\boldsymbol{b}_1 - n\boldsymbol{b}_2\right)$$

Bandes d'énergie du nanotube à partir de la bande d'énergie du graphène:

$$E_{\mathrm{gr}}(k) = \pm t\sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$

$$E = E_{gr}\left(n_C\,\boldsymbol{K}_1 + k\frac{\boldsymbol{K}_2}{|\boldsymbol{K}_2|}\right),\quad 0 \le n_C < N\,,\quad 0 \le k \le \frac{2\pi}{|\boldsymbol{T}|},\ \text{si}\ N_T \gg 1$$

propriété	$\gcd(n-m,3)$	d_R	multiplicité	
semiconducteur	1	d	0	$\left(\text{gap d'énergie} = \lvert t\rvert a_{C-C}/d_t\right)$
métal I	3	d	4	en $k = 0$
métal II	3	3d	2	en $k = \pm 2\pi/3T$

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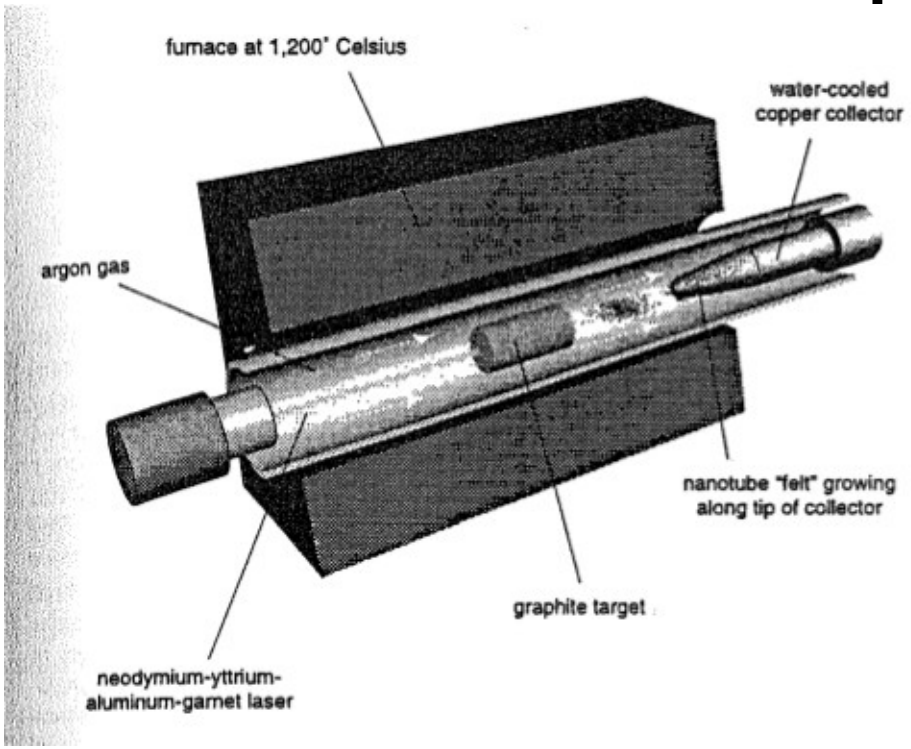
  - Hybridization
- Tight-binding calculations
  - Principe
  - Example: trans
  - Graphene π-liens
  - Graphene σ-liens
- Structure de carbone nanotubes
- Structure Electronique
- Synthesis
- Transport
- Multi-walled nanotubes

Histoire de synthesis

- La découverte de nanotubes de carbone
  - Nanotubes Multifeuillets (Iijima, Nature, 1991)
  - Nanotubes Monofeuillets (Iijima & Ichihashi Nature 1993, Bethune et al Nature 1993)
- La découverte de méthodes efficaces de production des nanotubes monofeuillets (quantité de 1 gramme).
  - Laser vaporisation (Thess et al, Science, 1996).
  - Carbon arc method (Journet et al, Nature 1997).

Je présente seulement deux méthodes - il ya beaucoup d'autres.

Laser vaporisation



Cible: graphite + catalyseur métallique à base de Ni, Co et Fe (pour produit des nanotubes monofeuillets).

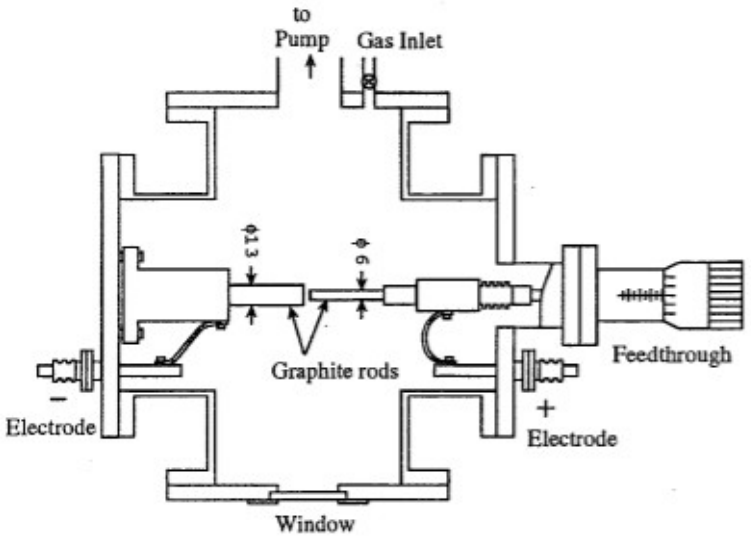
Température élevée empêche crystallziation

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

Le gaz inerte agit pour transporter les tubes au collecteur.

Propriétés très spécifiques: par exemple, presque seulement les nanotubes (10,10), (9,9) et (12,8)

Arc vaporisation



Le graphite se sublime à 3200C

Arc electrique: ~30V, 50-120A

avec deux electrode de graphite (plus catalyseur pour faire les nanotubes monofeuillet).

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

L'anode se consume pour former un plasma.

Le plasma se condense sur la cathode.

Le gaz inerte fonction seulement pour contrôle la température.

Un method qui n'est pas cher, qui est flexible, et qui produit le grand quantitie.

Vitesse dans l'etats Bloch

Alors, il suit que

$$E(\boldsymbol{k}+\boldsymbol{q})=E(\boldsymbol{k})+\int \bar{u}(\boldsymbol{r})\left(\boldsymbol{q}\cdot\frac{\hbar^2}{m}\left(\frac{1}{i}\nabla+\boldsymbol{k}\right)\right)u(\boldsymbol{r})\,d\boldsymbol{r}+O(q^2)$$

On prende la limite $\boldsymbol{q}\to\boldsymbol{0}$ de sorte que

$$\frac{\partial E}{\partial \boldsymbol{k}}=\lim_{\boldsymbol{q}\to 0}\frac{\partial E(\boldsymbol{k}+\boldsymbol{q})}{\partial \boldsymbol{q}}=\int \bar{u}(\boldsymbol{r})\left(\frac{\hbar^2}{m}\left(\frac{1}{i}\nabla+\boldsymbol{k}\right)\right)u(\boldsymbol{r})\,d\boldsymbol{r}$$

$$=\int \bar{\psi}(\boldsymbol{r};\boldsymbol{k})\left(\frac{\hbar^2}{m}\frac{1}{i}\nabla\right)\psi(\boldsymbol{r};\boldsymbol{k})\,d\boldsymbol{r}$$

$$=\langle\psi_{\boldsymbol{k}}|\frac{\hbar^2}{i\,m}\nabla|\psi_{\boldsymbol{k}}\rangle$$

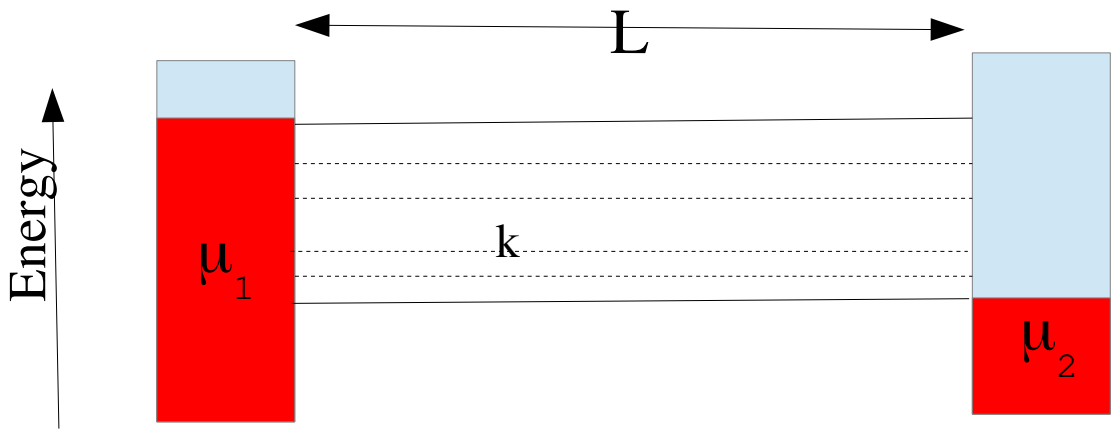
Mais, l'opérateur de vitesse est défini par

$$\boldsymbol{v}=\frac{d\boldsymbol{r}}{dt}=(1/i\hbar)[\boldsymbol{r},H]=\boldsymbol{p}/m=\hbar\nabla/mi$$

Donc, on voit que

$$\frac{\partial E}{\partial \boldsymbol{k}}=\hbar\langle\boldsymbol{v}\rangle_{\boldsymbol{k}}$$

Ballistic transport



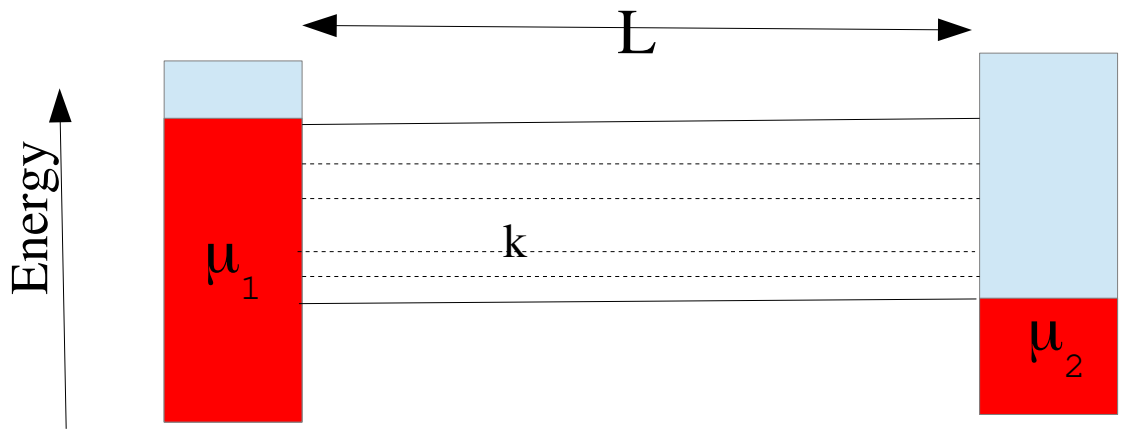
$L \ll L_m, L_\phi$

$\mu_2 - \mu_1 = eV$

Ballistic transport ⇔ pas le diffusion des électrons; le libre mouvement des électrons.

Le courant est transporté par des électrons ayant des énergies entre les deux resevoirs: $\mu_1 > E_q(k) > \mu_2$

Ballistic transport



$$L \ll L_m, L_\phi$$

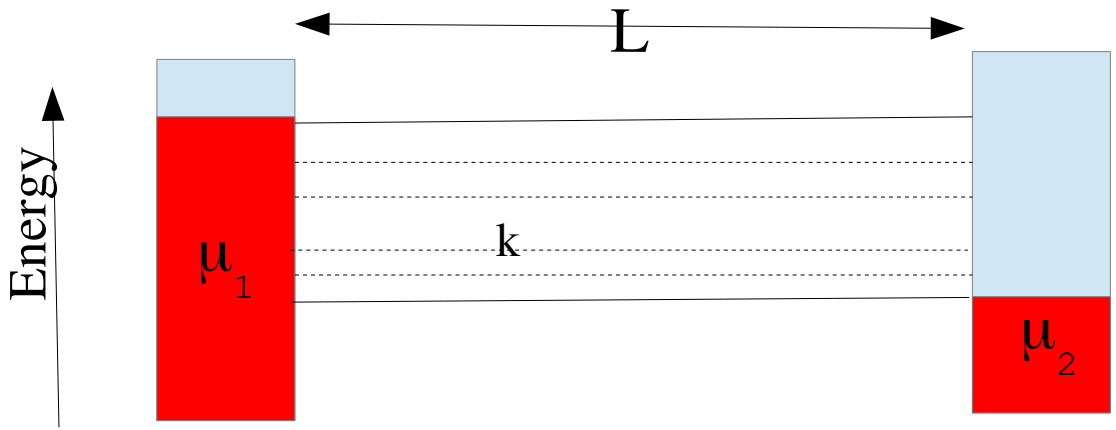
$$\mu_2 - \mu_1 = eV$$

$$I = \sum_{\mu_1 > E_q(k) > \mu_2} \frac{e}{\underbrace{t(q,k)}_{\textit{time of flight}}} \Bigg(\underbrace{f(E_q(k)-\mu_1)(1-f(E_q(k)-\mu_2))}_{\text{prob. qu'il y a un electron dans 1 et un trou dans 2 avec } E_q(k)} - \underbrace{f(E_q(k)-\mu_2)(1-f(E_q(k)-\mu_1))}_{\text{prob. pour la courant inverse}} \Bigg)$$

$$= \sum_{\mu_1 > E_q(k) > \mu_2} \frac{e}{L/v(q,k)} \Big(f(E_q(k)-\mu_1) - f(E_q(k)-\mu_2) \Big)$$

$$= \frac{e}{L} \sum_{\mu_1 > E_q(k) > \mu_2} v(q,k) \Big(f(E_q(k)-\mu_1) - f(E_q(k)-\mu_2) \Big)$$

Ballistic transport



$$L \ll L_m, L_\phi$$

$$\mu_2 - \mu_1 = eV$$

$$I = \frac{e}{L} \sum_{\mu_1 > E_q(k) > \mu_2} v(q,k) \left| f(E_q(k) - \mu_1) - f(E_q(k) - \mu_2) \right|$$

$$= \frac{e}{L} \sum_{\mu_1 > E_q(k) > \mu_2} \hbar^{-1} \frac{\partial E_q(k)}{\partial k} \left| f(E_q(k) - \mu_1) - f(E_q(k) - \mu_2) \right|$$

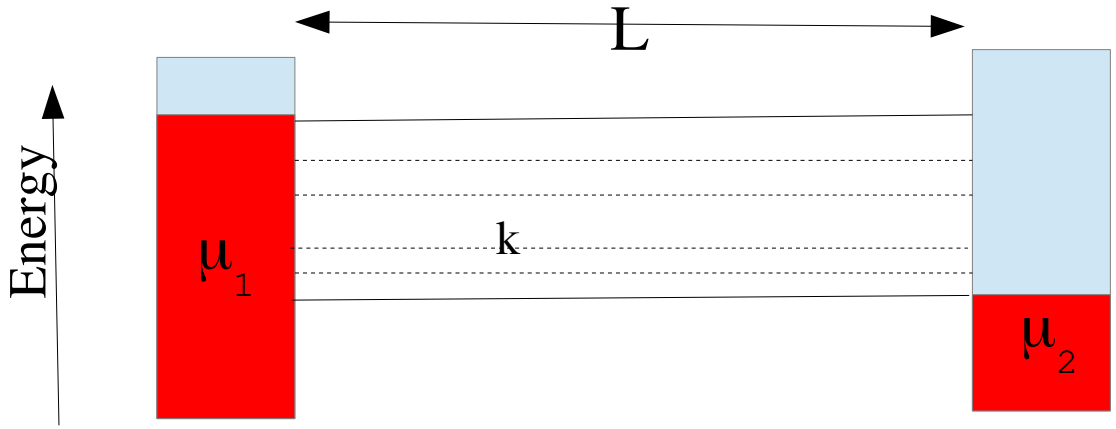
Repellez-vous que $\Delta k = \frac{2\pi}{L}$ donc

$$I = \frac{e}{L} \times \underbrace{2}_{\text{dégénérescence spin}} \times \frac{L}{2\pi} \times \sum_q \int_{k>0} \hbar^{-1} \frac{\partial E_q(k)}{\partial k} \left| f(E_q(k) - \mu_1) - f(E_q(k) - \mu_2) \right| dk$$

$$= \frac{2e}{h} \int \left| f(E - \mu_1) - f(E - \mu_2) \right| M(E)\, dE$$

Nombre des états (somme sur q, k) avec l'énergie E

Ballistic transport



$$L \ll L_m, L_\phi$$

$$\mu_2 - \mu_1 = eV$$

$$I = \frac{2e}{h}\int \left(f(E-\mu_1) - f(E-\mu_2) \right) M(E)\, dE$$

$$\sim \frac{2e}{h} M(\mu_1 - \mu_2)$$

$$\sim \frac{2e^2}{h} M V_C$$

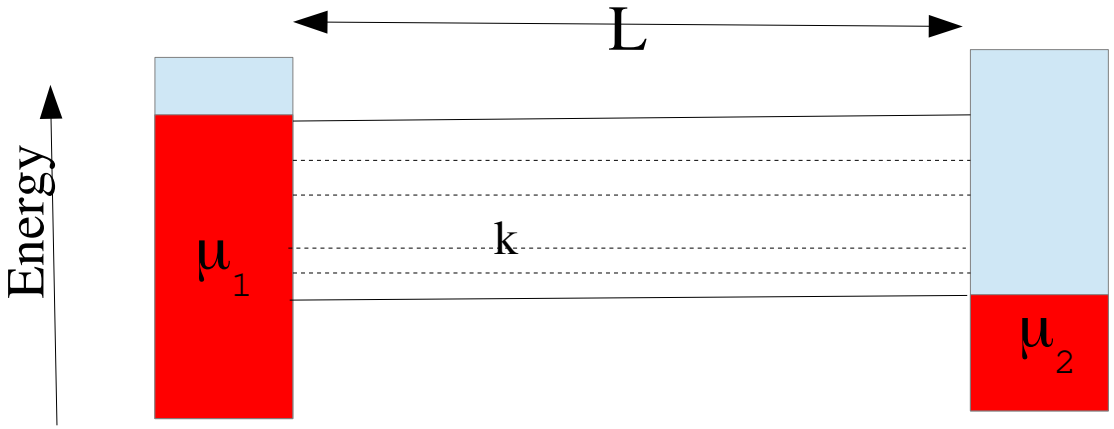
"Contact resistence":
resistence sans diffuseur

$$R_C = \frac{h}{2e^2}\frac{1}{M} \equiv R_0 \frac{1}{M} = \frac{12.9}{M}\,\mathrm{k}\Omega$$

$$G_C = G_0 M = M \times 77.5 \times 10^{-6}\,\Omega^{-1}$$

"Contact conductance"

Classique transport



$$L_\phi \ll L_m \ll L$$

Limite incohérentes: grande changement de phase dans le moyenne parcours libre

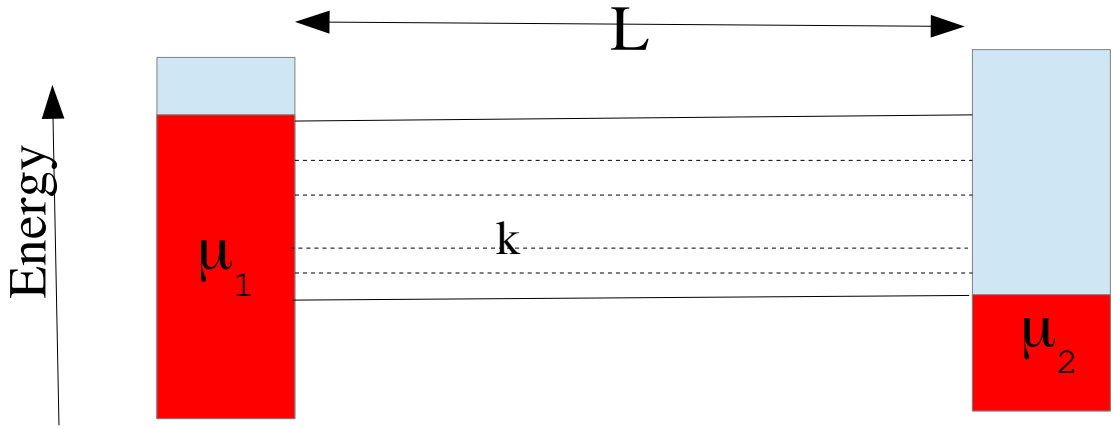
$$\mu_2 - \mu_1 = eV$$

Avec un seul diffuseur $(L \sim L_m)$

$$G = \frac{2e^2}{h} M\,\mathcal{T} \equiv \frac{2e^2}{h} \sum_{ij}^{M} |t_{ij}|^2$$ "Landauer formula" $\mathcal{T}$ = transmission probability

$$R = R_0 \frac{1}{M\,\mathcal{T}} \qquad R_{fil} = R - R_c = R_0 \frac{1-\mathcal{T}}{M\,\mathcal{T}} = R_0 \frac{\mathcal{R}}{M\,\mathcal{T}}$$ $\mathcal{R} = 1 - \mathcal{T}$ = reflection probability

Classique transport



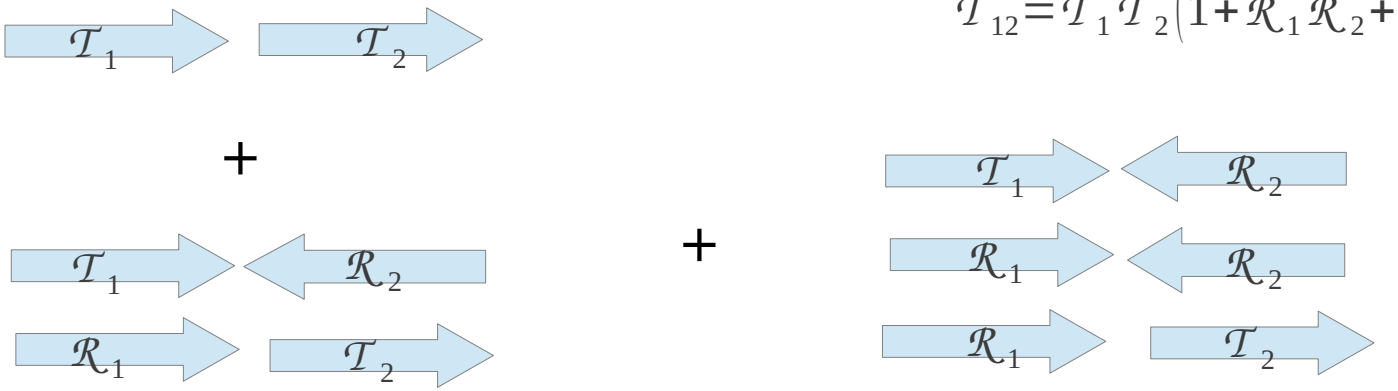
$$L_\phi \ll L_m \ll L$$

$$\mu_2 - \mu_1 = eV$$

$$R_{fil} = R_c \frac{1-\mathcal{T}}{\mathcal{T}}$$

Avec deux diffuseur $(L \gg L_m)$

$$\mathcal{T}_{12} = \mathcal{T}_1 \mathcal{T}_2 \left(1 + \mathcal{R}_1 \mathcal{R}_2 + (\mathcal{R}_1 \mathcal{R}_2)^2 + \ldots\right)$$

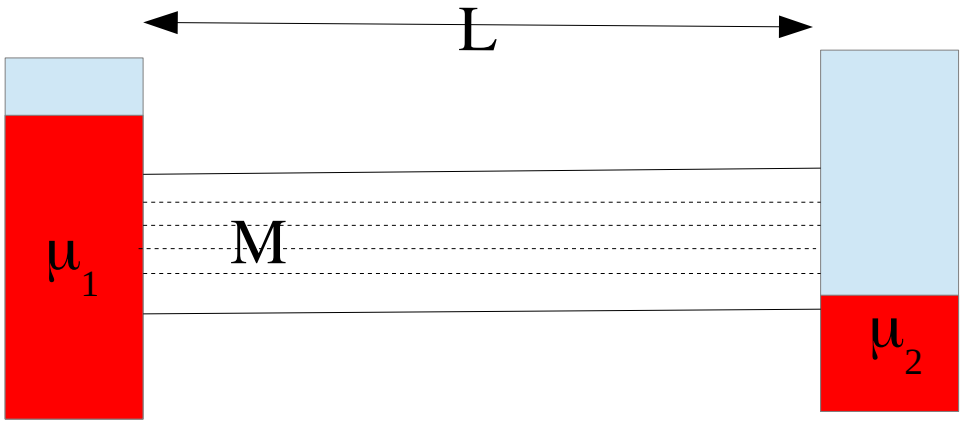


$$\mathcal{T}_{12} = \frac{\mathcal{T}_1 \mathcal{T}_2}{1 - \mathcal{R}_1 \mathcal{R}_2}$$

$$\frac{1-\mathcal{T}_{12}}{\mathcal{T}_{12}} = \frac{1-\mathcal{T}_1}{\mathcal{T}_1} + \frac{1-\mathcal{T}_2}{\mathcal{T}_2}$$

Limite incohérentes: pas d'interférence donc, les probabilités somme.

Classique transport



$$L_\phi \ll L_m \ll L$$

$$\mu_2 - \mu_1 = eV$$

Avec deux diffuseur $(L \gg L_m)$

$$\frac{1-\mathcal{T}_{12}}{\mathcal{T}_{12}} = \frac{1-\mathcal{T}_1}{\mathcal{T}_1} + \frac{1-\mathcal{T}_2}{\mathcal{T}_2}$$

$$R_{fil} = R_0 \frac{1-\mathcal{T}}{M\,\mathcal{T}}$$

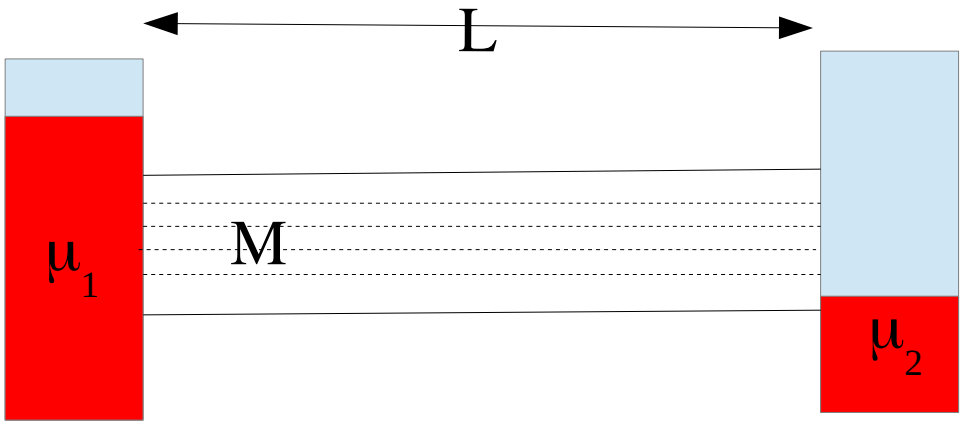
(M constante)

$$R_{2\,scatterers} = R_{scatterer_1} + R_{scatterer_2}$$

(N diffuseur)

$$R_N = R_0 \frac{1}{M} \times \sum_{j=1}^{N} \frac{1-\mathcal{T}_j}{\mathcal{T}_j} = R_0 \frac{1}{M} \frac{L}{L_m} \frac{1-\mathcal{T}}{\mathcal{T}}, \quad \mathcal{T} = \text{transmission probabilite per } L_m$$

Classique transport



$$L_\phi \ll L_m \ll L$$

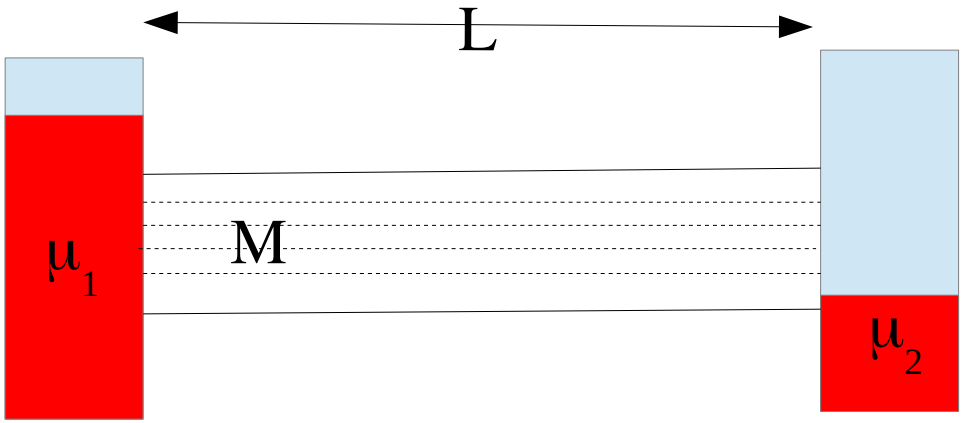
$$\mu_2 - \mu_1 = eV$$

$$R_{fil} = \frac{R_0}{M\, L_m} \frac{1-\mathcal{T}}{\mathcal{T}} L\,, \quad \mathcal{T} = \text{transmission probabilite per } L_m$$

Résultat classique: constante résistance pour unité de longueur

“Ohm’s law”

Localization



$$L_m \ll L_\phi \ll L$$

Limite cohérentes: l'interférence est importante donc, les amplitudes somme.

$$\mu_2 - \mu_1 = eV$$

$$t_{12} = \frac{t_1 t_2}{1 - r_1 r_2 e^{i\theta}}$$

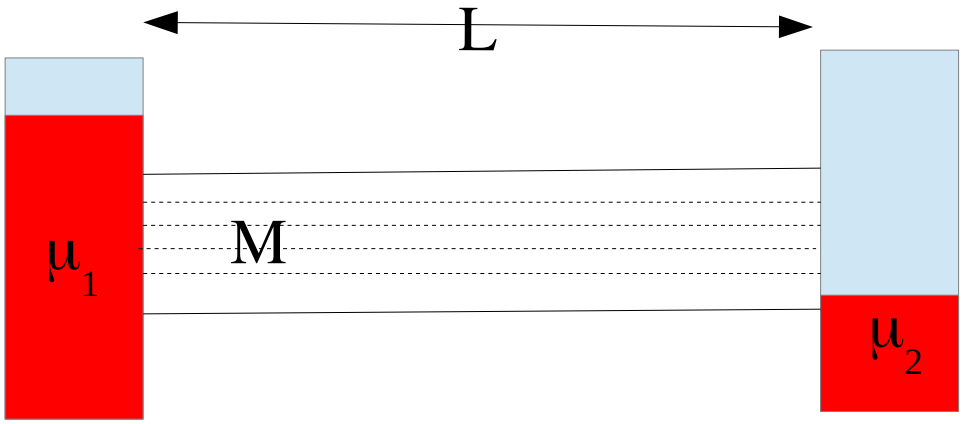
ou θ est le décalage de phase

$$\mathcal{T}_{12} = |t_{12}|^2 = \frac{\mathcal{T}_1 \mathcal{T}_2}{1 - 2\sqrt{\mathcal{R}_1 \mathcal{R}_2}\cos\theta + \mathcal{R}_1 \mathcal{R}_2}$$

$$R_{12} = \frac{R_0}{M}\left\langle \frac{1-\mathcal{T}_{12}}{\mathcal{T}_{12}} \right\rangle_\theta = \frac{R_0}{M}\frac{1 + \mathcal{R}_1 \mathcal{R}_2 - \mathcal{T}_1 \mathcal{T}_2}{\mathcal{T}_1 \mathcal{T}_2}$$

$$R_{12} = R_1 + R_2 + 2R_1 R_2 (M / R_0)$$

Localization



$$L_m \ll L_\phi \ll L$$

Limite cohérentes: l'interférence est importante donc, les amplitudes somme.

$$\mu_2 - \mu_1 = eV$$

$$R_{12} = R_1 + R_2 + 2R_1 R_2 (M/R_0)$$

Soit partie 1 a longueur L est partie 2 longueur $\Delta L \sim L_m \ll L_\phi$

$$R(L+\Delta L) = R(L) + R(\Delta L) + 2R(L)R(\Delta L)(M/R_0)$$

$$\rightarrow \Delta L \frac{dR(L)}{dL} = R(\Delta L) + 2R(L)R(\Delta L)(M/R_0)$$

$$\rightarrow \Delta L \frac{dR}{dL} = (R_0/M) + 2R$$

$$\rightarrow R(L) = (R_0/2M)\left(e^{2L/\Delta L} - 1\right)$$

$$\lim_{L\rightarrow\infty} \frac{R(L)}{L} \rightarrow \infty$$

"Localization"

Résumé: Types de Transport

$L \ll L_m, L_\phi$ Ballistique

$L_\phi \ll L_m \ll L$ Classique

$L_m \ll L_\phi \ll L$ Localization

L_m diminue par rapport de la concentration d'impurities.

L_ϕ diminue par rapport de la concentration de phonons (e g la température).