NANOPHYSIQUE
INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch 5. Carbon Structres

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Lecture 6, 2018-2019

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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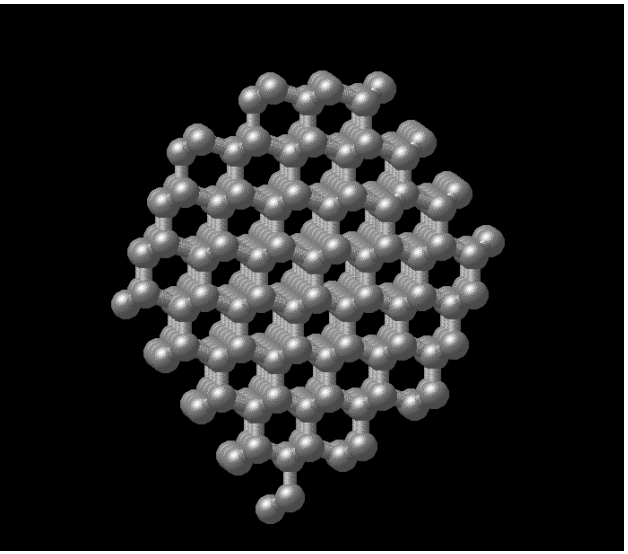
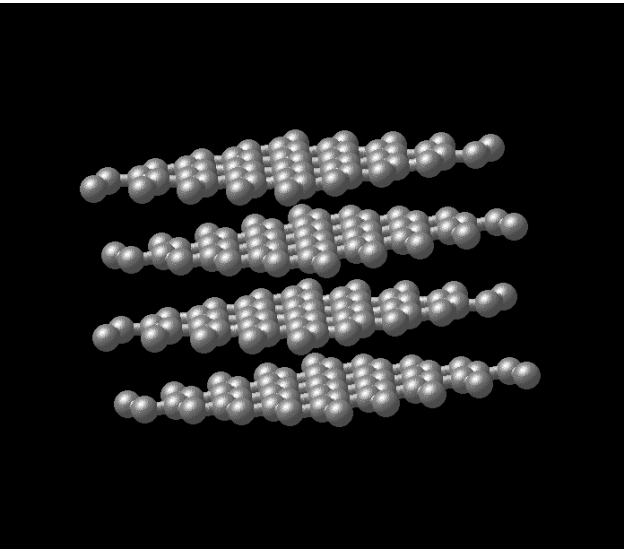
Une petite histoire

- 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).

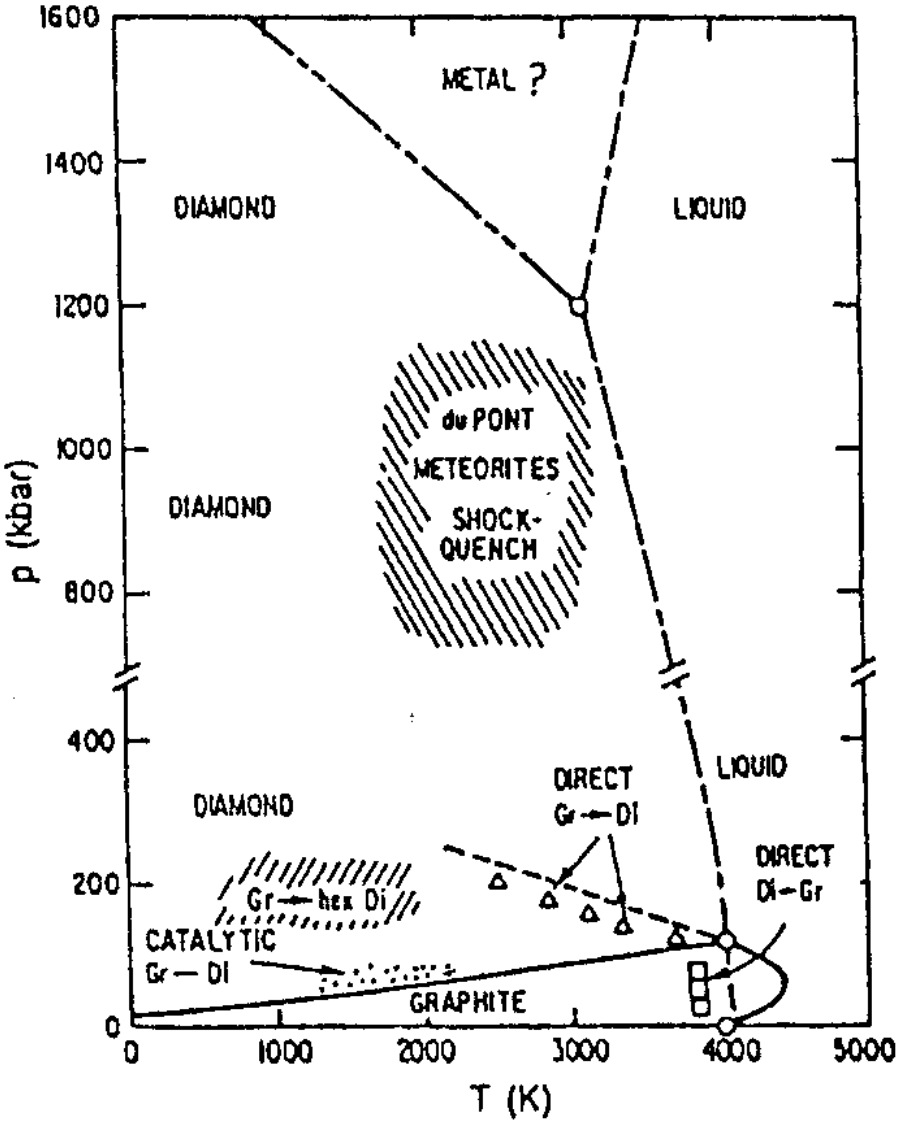
Propriétés du carbone



diamant

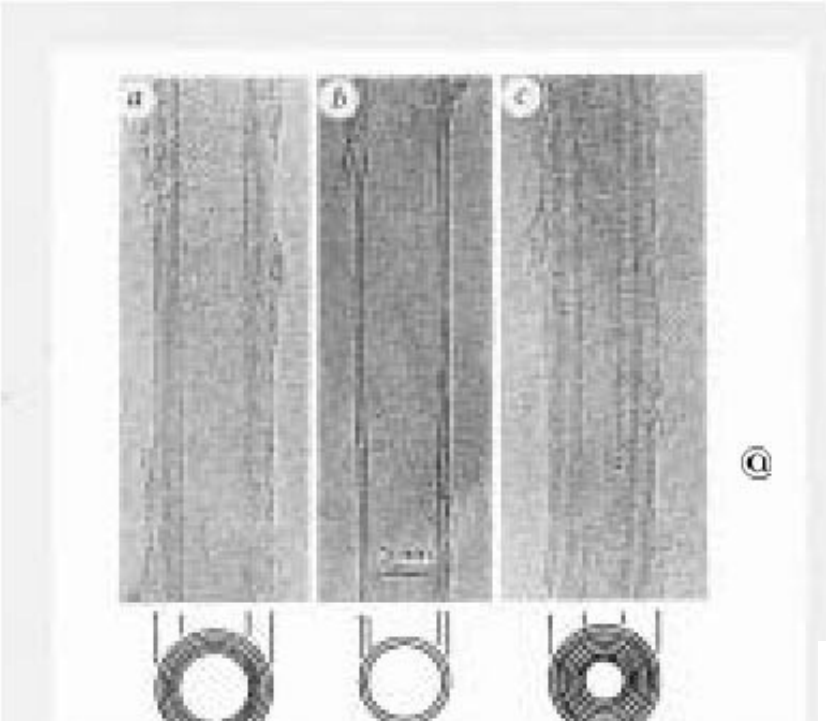


graphite

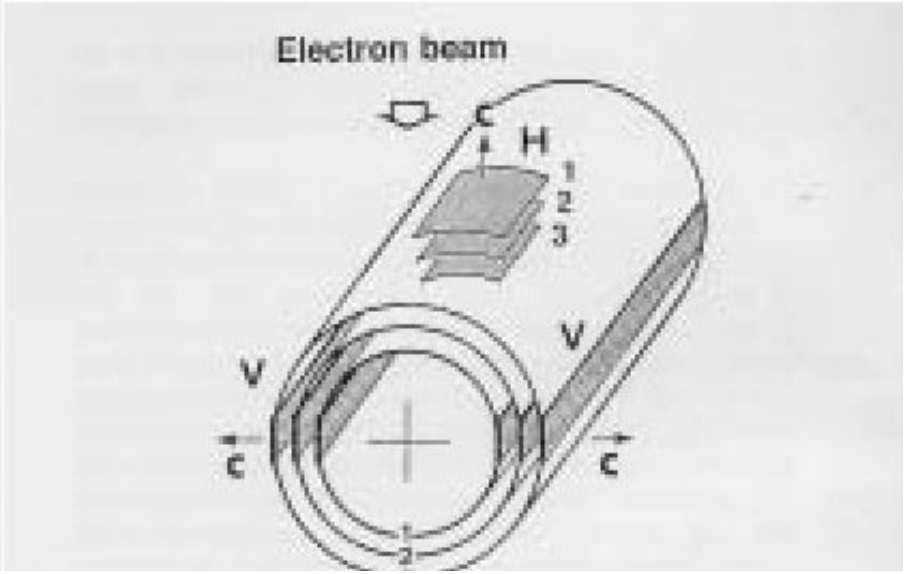


Nano materials

Carbon nanotubes(CNT) (Iijima Nature 354 56 (1992))

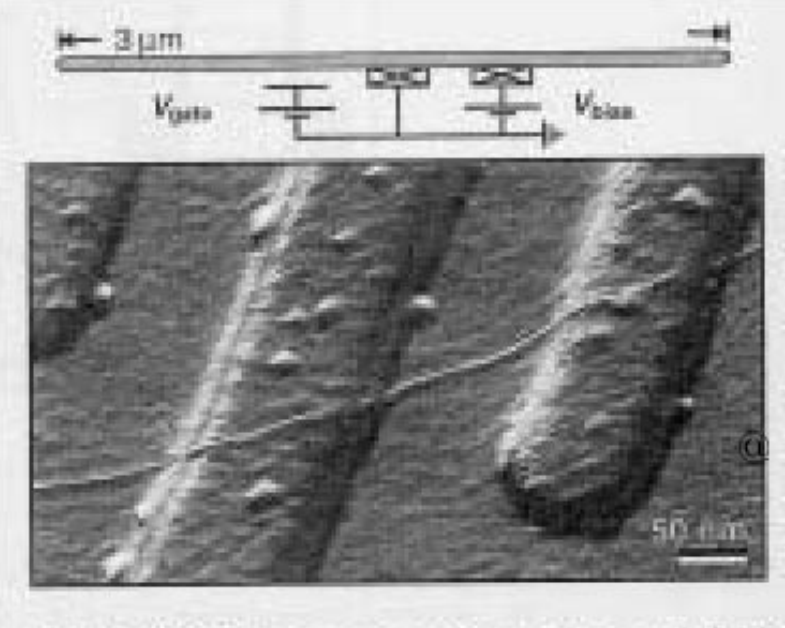


Electron microscope image



Interpretation of the images

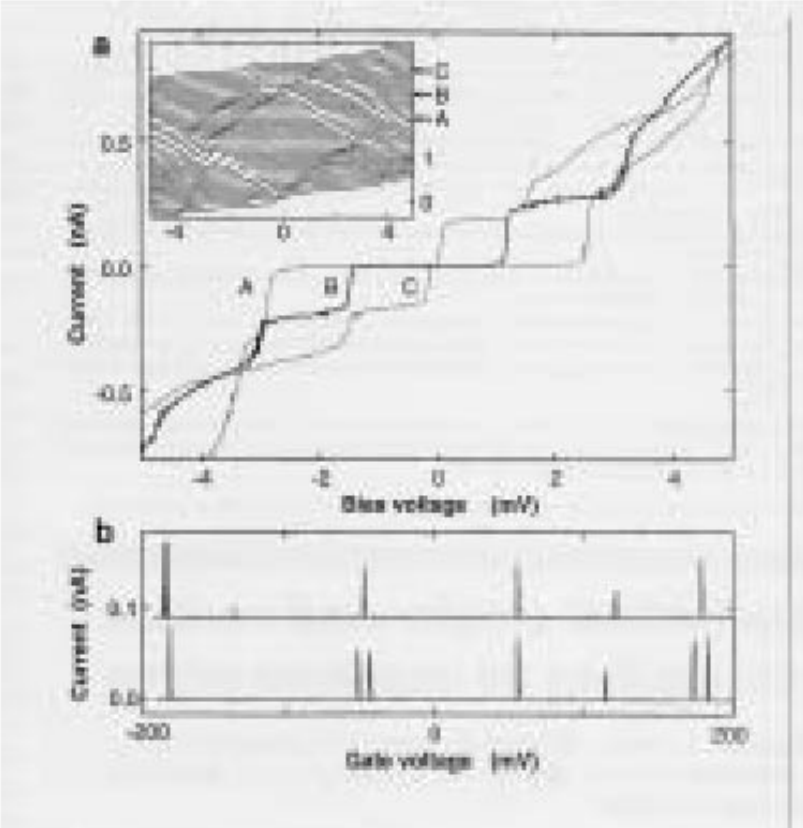
Current-voltage characteristics of CNT (S.J. Tans et al. Nature 386 474 (1997))



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

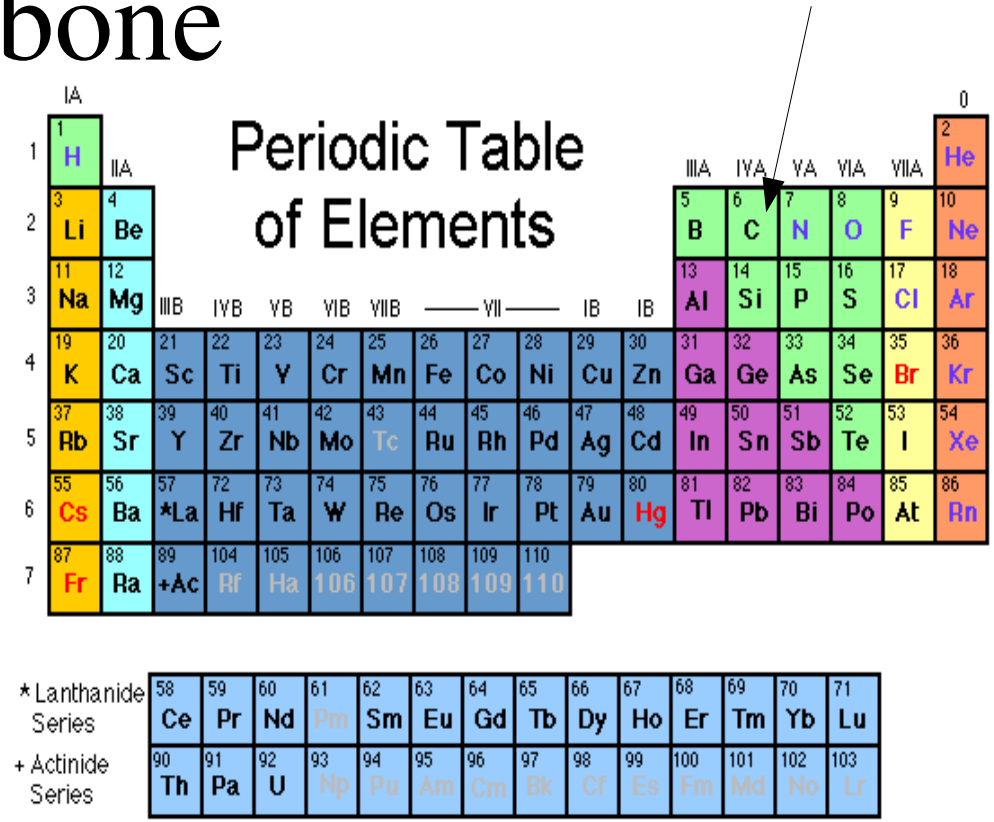
Carbone:

$Z = 6$

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

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

(carbon dating)



Configuration Electronique:

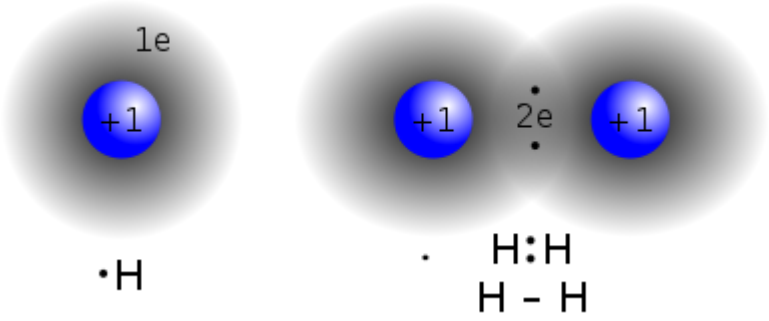
$1s^2 2s^2 2p^2$

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

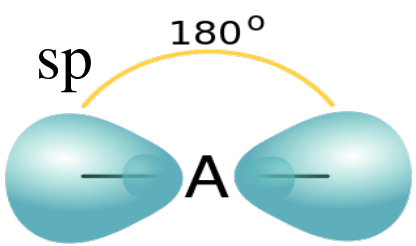
Hybridization

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

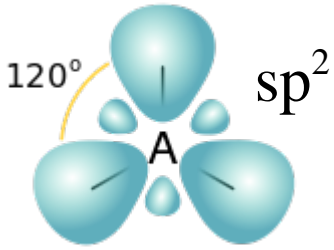
C^* $\frac{\uparrow\downarrow}{1s}$ $\frac{\uparrow}{2s}$ $\frac{\uparrow}{2p_x}$ $\frac{\uparrow}{2p_y}$ $\frac{\uparrow}{2p_z}$

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

sp



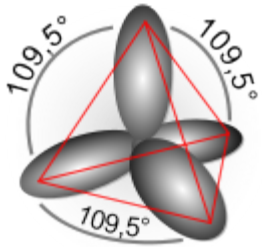
C^* $\frac{\uparrow\downarrow}{1s}$ $\frac{\uparrow}{sp^2}$ $\frac{\uparrow}{sp^2}$ $\frac{\uparrow}{sp^2}$ $\frac{\uparrow}{2p}$



sp^2

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

sp^3



SP Hybridization

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

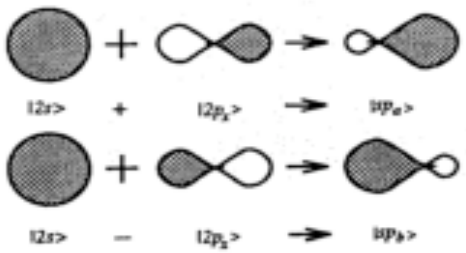
Orthonormality: $\langle sp_i | sp_j \rangle = \delta_{ij}$

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

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

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

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



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

ORBITALES & LEURS HYBRIDATIONS

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:

acétylène: HCCH liaison triple: 1 lien σ + 2 liens π

1 lien σ = orbitale moléculaire sp +sp

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

2 liens π = orbitales moléculaires $2p_y$, $2p_z$

sp = hybridation $2s + 2p_x$

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

Hybridation sp^2:

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

1 lien σ = orbitale moléculaire $sp^2 + sp^2$

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

1 lien π = orbitale moléculaire $2p_z$

sp^2 = hybridation $2s + 2p_x + 2p_y$

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

Hybridation sp^3:

méthane: CH_4 liaison simple: 1 lien σ

1 lien σ = orbitale moléculaire $sp^3 + sp^3$

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

sp^3 = hybridation $2s + 2p_x + 2p_y + 2p_z$

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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,

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

Et c'est evident que $T_{\boldsymbol{R}_1} T_{\boldsymbol{R}_2} = T_{\boldsymbol{R}_2} T_{\boldsymbol{R}_1} = T_{\boldsymbol{R}_1+\boldsymbol{R}_2}$ (*)

Alors, il ya vecteurs propres simultanés:

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

Puis, (*) implique que $c(\boldsymbol{R}_1)c(\boldsymbol{R}_2) = c(\boldsymbol{R}_1+\boldsymbol{R}_2)$

$$c(\boldsymbol{R}_n) = c(n_1\boldsymbol{a}_1+n_2\boldsymbol{a}_2+n_3\boldsymbol{a}_3) = c(\boldsymbol{a}_1)^{n_1}c(\boldsymbol{a}_2)^{n_2}c(\boldsymbol{a}_3)^{n_3} = e^{2\pi i(n_1x_1+n_2x_2+n_3x_3)}, \qquad x_j = \frac{\ln c(\boldsymbol{a}_j)}{2\pi i}$$

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

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.

La fonctionelle

$$E[\psi] \equiv \frac{\int d\boldsymbol{r} \frac{h^2}{2m} (\nabla \psi(\boldsymbol{r}))^2 + V(\boldsymbol{r}) |\psi(\boldsymbol{r})|^2}{\int d\boldsymbol{r} |\psi(\boldsymbol{r})|^2}$$

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

Preuve: Définir

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

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

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

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:

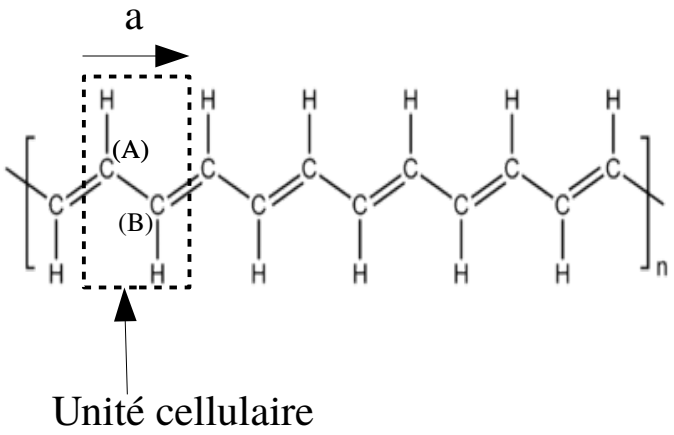
$$\frac{\partial E_{TB}(\boldsymbol{k})}{\partial \bar{C}_j} = 0 = \frac{\sum_{j'} H_{jj'}(\boldsymbol{k}) C_{j'}}{\sum_{j,j'} \bar{C}_j S_{jj'}(\boldsymbol{k}) C_{j'}} - \frac{\sum_{j,j'} \bar{C}_j H_{jj'}(\boldsymbol{k}) C_{j'}}{\sum_{j,j'} \bar{C}_j S_{jj'}(\boldsymbol{k}) C_{j'}} \frac{\sum_{j'}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

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

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

Tight-binding method

Example: *trans*-polyacétylène



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

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

sp^2 hybridization $\rightarrow$ σ-liens dans le plan, π-lien (p-p) dehors le plan
On cherche les niveau pour les π-electrons.

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

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

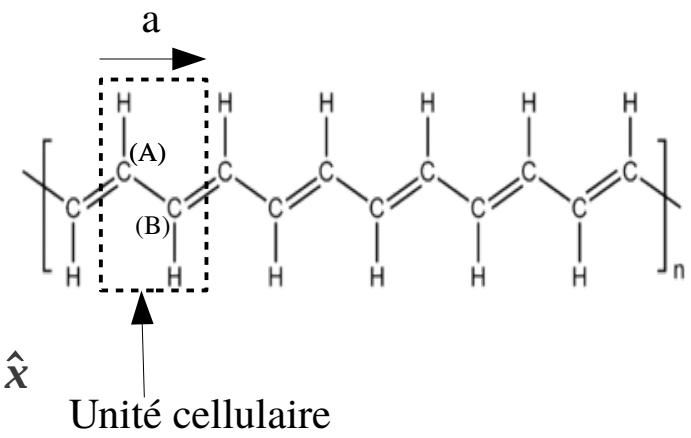
$$H_{AA}(\boldsymbol{k}) = \langle \Phi_{A\boldsymbol{k}} | H | \Phi_{A\boldsymbol{k}} \rangle = \frac{1}{N} \sum_{n,m=0}^{N} e^{ik(n-m)a} \langle \phi_{2p_z}(\boldsymbol{r} - ma\,\hat{\boldsymbol{x}}) | H | \phi_{2p_z}(\boldsymbol{r} - na\,\hat{\boldsymbol{x}}) \rangle$$

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

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

Tight-binding method

Example: *trans*-polyacétylène



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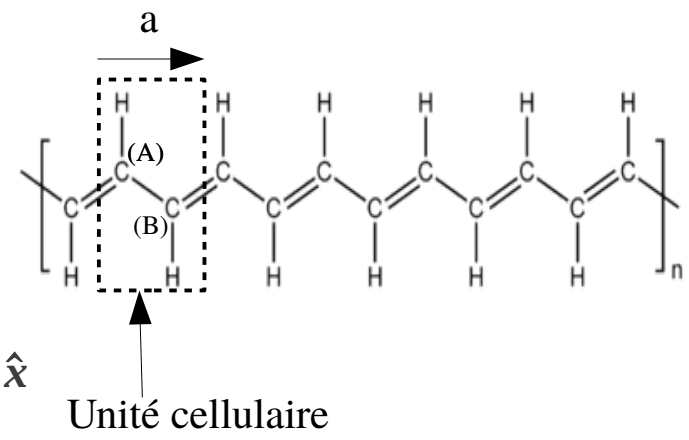
$$\Phi_B(\boldsymbol{r};\boldsymbol{k}) = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R_n} \in B}^{N} e^{i\boldsymbol{k}\cdot(\boldsymbol{R_n}+\boldsymbol{R_B})} \phi_{2p_z}(\boldsymbol{r} - \boldsymbol{R_n} + \boldsymbol{R}_B) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N} e^{ikna + ikR_x} \phi_{2p_z}(\boldsymbol{r}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

$$\boldsymbol{k} = 2\pi \frac{p_i}{N} \frac{1}{a}, \quad 0 \le p_i < N \quad \Longrightarrow \quad 0 \le k \le 2\pi/a$$

Tight-binding method

Example: *trans*-polyacétylène



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

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

$$= e^{ikR_x} \langle \phi_{2p_z}(\boldsymbol{r}) | H | \phi_{2p_z}(\boldsymbol{r} - \boldsymbol{R_B}) \rangle + e^{ik(R_x - a)} \langle \phi_{2p_z}(\boldsymbol{r}) | H | \phi_{2p_z}(\boldsymbol{r} - \boldsymbol{R_B} + \boldsymbol{a}) \rangle$$

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

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

if $R_x = a/2$

Tight-binding method

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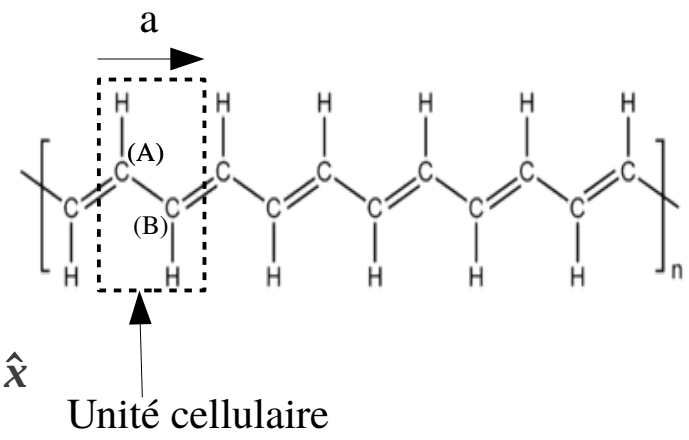


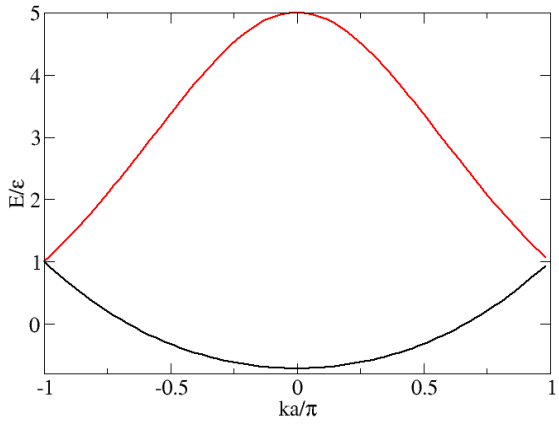
Vecteur de reseau: $\boldsymbol{a} = a\,\hat{\boldsymbol{x}}$

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

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

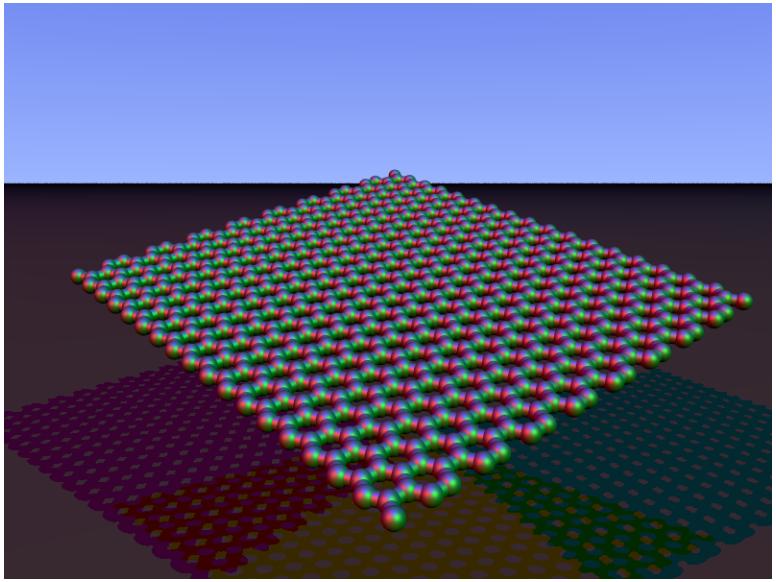
$$0 = det\begin{pmatrix} \epsilon_{2p} - E & 2(t - sE)\cos(ka/2) \\ 2(t - sE)\cos(ka/2) & \epsilon_{2p} - E \end{pmatrix}$$
$$= (\epsilon_{2p} - E)^2 - 4(t - sE)^2\cos^2(ka/2)$$

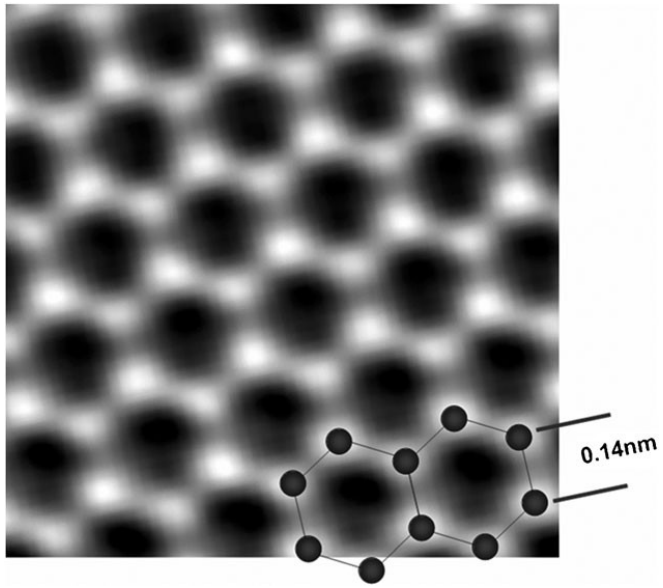
$$E_{\pm}(k) = \frac{\epsilon_{2p} \pm 2t\cos(ka/2)}{1 \pm 2s\cos(ka/2)}, -\frac{\pi}{a} < k < \frac{\pi}{a}$$



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

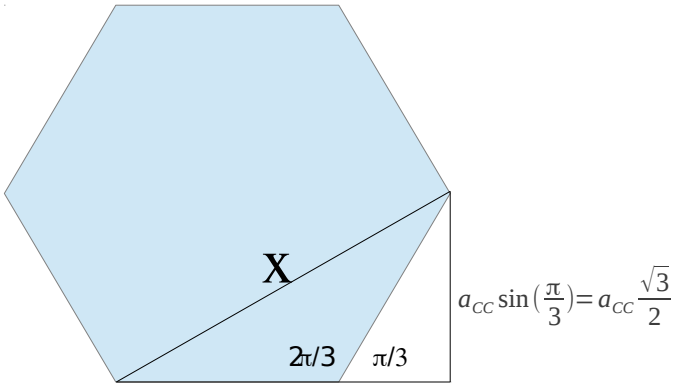
Graphene 2

réseau

zone de Brillouin

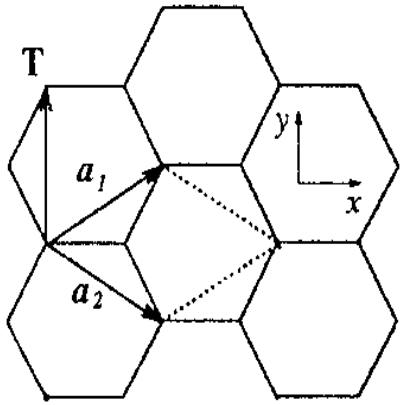
$x_i b_i, \quad 0 \le x_i < 1$

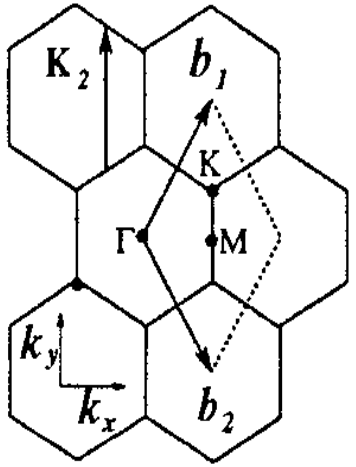
$a_{CC} = 0,142 \text{ nm}$



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

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





$$\boldsymbol{a}_1 = \left(\frac{\sqrt{3}}{2}a, +\frac{a}{2}\right) \qquad b_1 = \left(\frac{2\pi}{\sqrt{3}a}, +\frac{2\pi}{a}\right)$$

$$\boldsymbol{a}_2 = \left(\frac{\sqrt{3}}{2}a, -\frac{a}{2}\right) \qquad b_2 = \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a}\right)$$

$$a = \|a_1\| = \|a_2\| = a_{CC}\sqrt{3} = 0,246 \text{ nm}$$

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

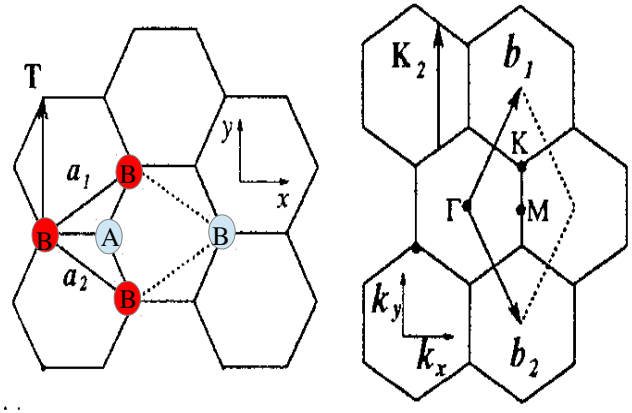
$$H_{AA} = H_{BB} = \epsilon_{2p}$$

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

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

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

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



$$a_1 = \left(\frac{\sqrt{3}}{2}a, +\frac{a}{2}\right) \qquad b_1 = \left(\frac{2\pi}{\sqrt{3}a}, +\frac{2\pi}{a}\right)$$

$$a_2 = \left(\frac{\sqrt{3}}{2}a, -\frac{a}{2}\right) \qquad b_2 = \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a}\right)$$

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

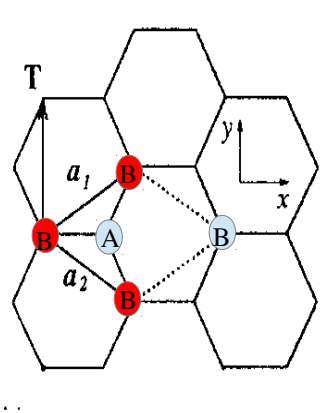
$s = 0 \Leftrightarrow$ "Slater-Koster approximation"

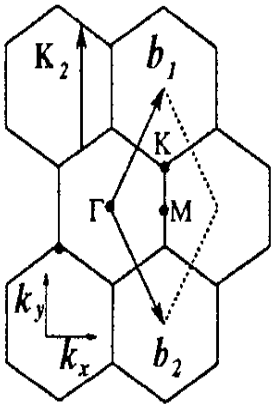
R. Saito, G. Dresselhaus & M. S. Dresselhaus,
Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998)

Graphene Tight-binding : σ-bands

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

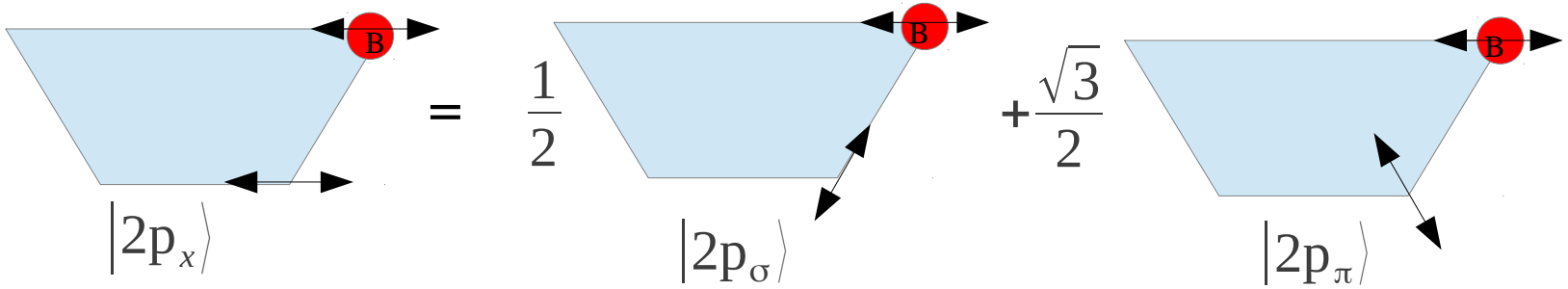
$$H_{AA}=\begin{pmatrix}\epsilon_{2s} & 0 & 0\\ 0 & \epsilon_{2p} & 0\\ 0 & 0 & \epsilon_{2p}\end{pmatrix}, \quad S_{AA}=\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}$$





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.

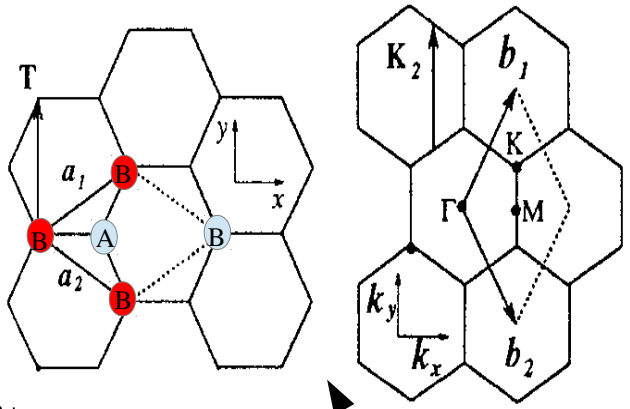


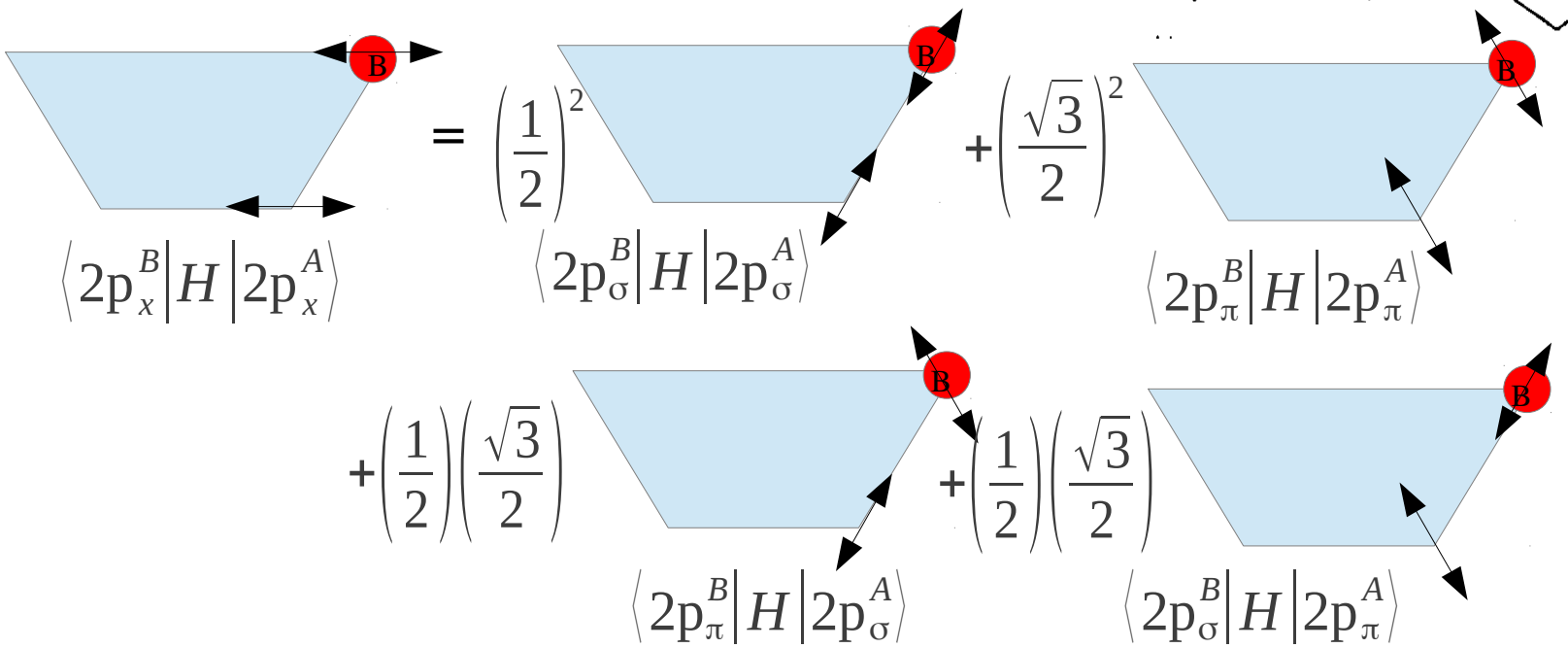
R. Saito, G. Dresselhaus & M. S. Dresselhaus,
Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998)

Graphene Tight-binding : σ-bands

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

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





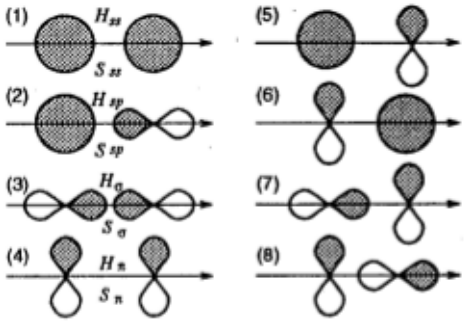
$$= \left(\frac{1}{2}\right)^2 \left\langle 2p_\sigma^B \middle| H \middle| 2p_\sigma^A \right\rangle + \left(\frac{\sqrt{3}}{2}\right)^2 \left\langle 2p_\pi^B \middle| H \middle| 2p_\pi^A \right\rangle$$

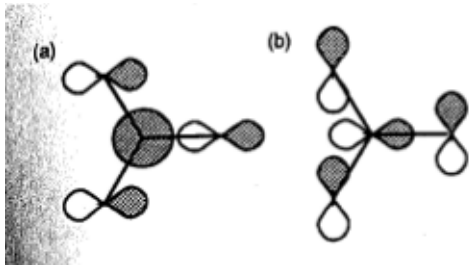
$$+ \left(\frac{1}{2}\right)\left(\frac{\sqrt{3}}{2}\right) \left\langle 2p_\pi^B \middle| H \middle| 2p_\sigma^A \right\rangle + \left(\frac{1}{2}\right)\left(\frac{\sqrt{3}}{2}\right) \left\langle 2p_\sigma^B \middle| H \middle| 2p_\pi^A \right\rangle$$

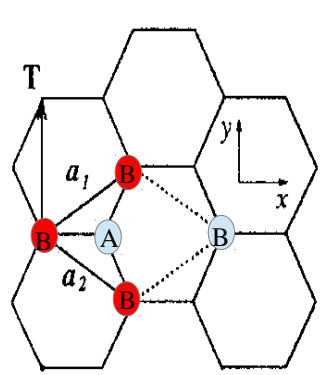
$$= \left(\frac{1}{4}H_{\sigma\sigma} + \frac{3}{4}H_{\pi\pi}\right) e^{i\left(k_x R_x + k_y R_y\right)} = \left(\frac{1}{4}H_{\sigma\sigma} + \frac{3}{4}H_{\pi\pi}\right) e^{i\left(\frac{k_x a}{2\sqrt{3}} + \frac{k_y a}{2}\right)}, \qquad H_{\sigma\pi} = 0$$

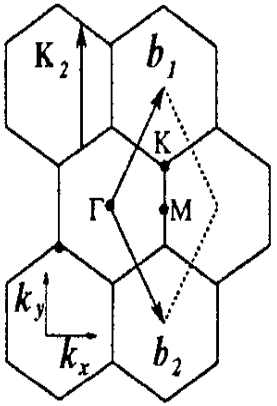
Graphene Tight-binding : σ-bands

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







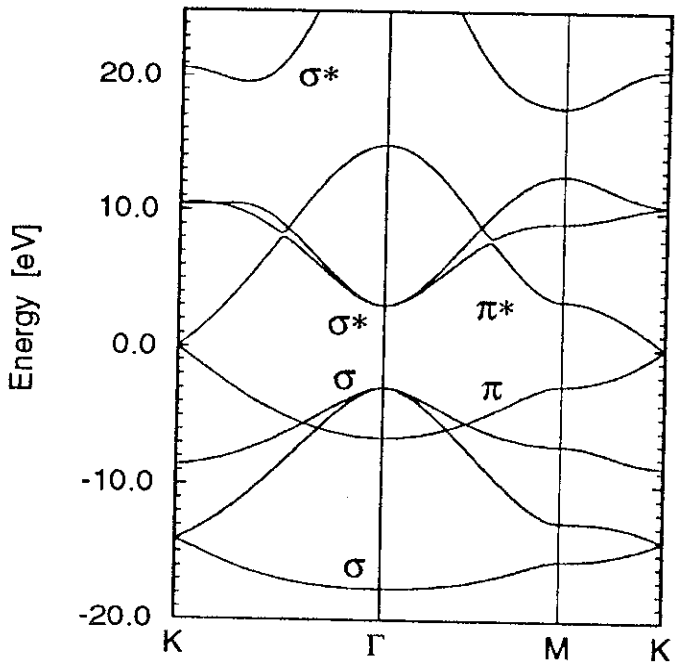


R. Saito, G. Dresselhaus & M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998)

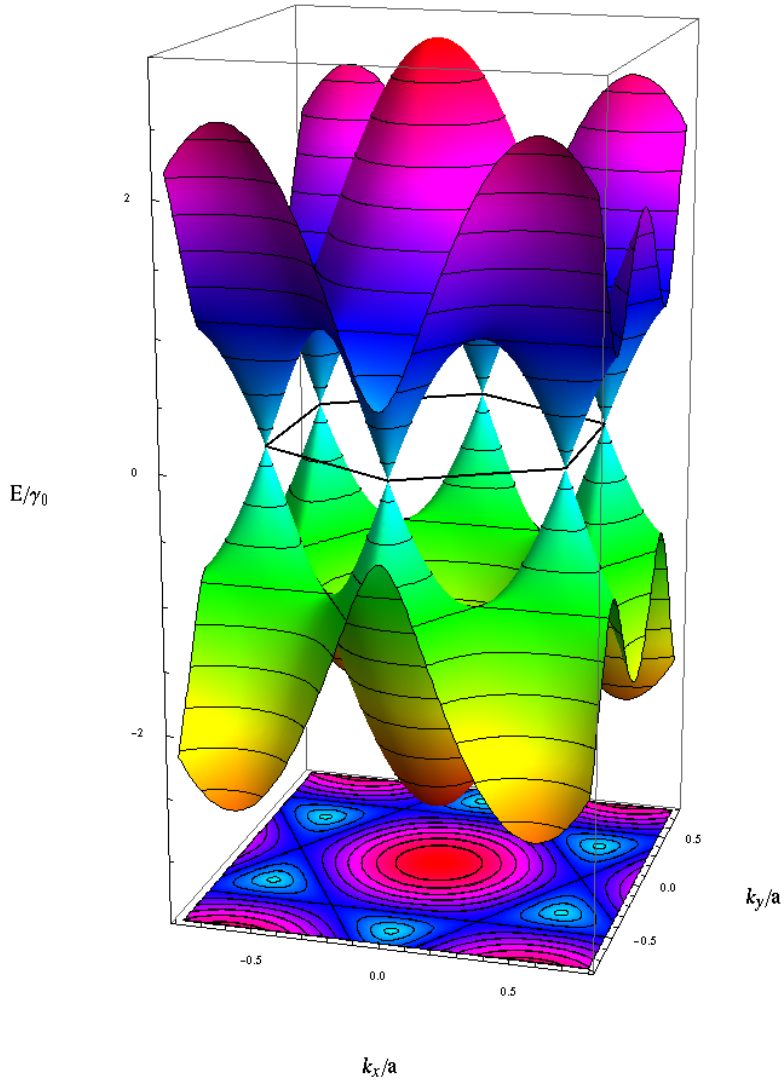
$$\left\langle 2s^B \middle| H \middle| 2p_x^A \right\rangle = H_{sp}\left(-e^{ik_x a/\sqrt{3}} + e^{ik_x a/(2\sqrt{3})}\right)$$

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

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)

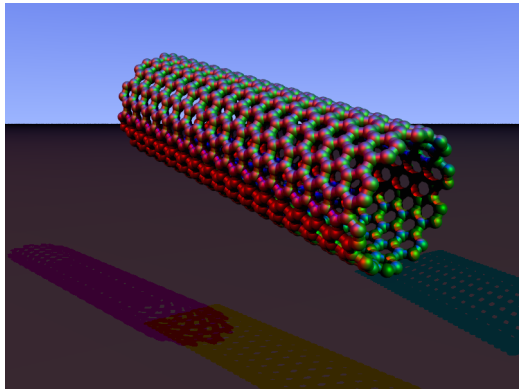
Carbon Structures

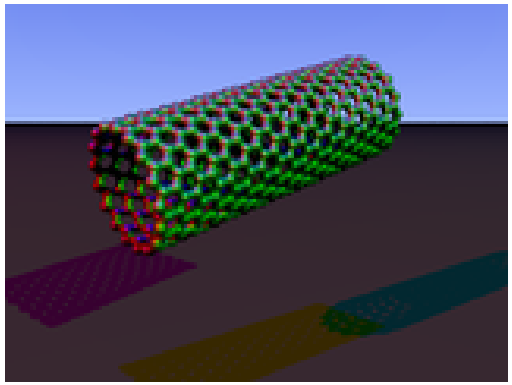
- Introduction
  - Histoire
  - Carbone
  - Hybridization
- Tight-binding calculations
  - Principe
  - Example: trans
  - Graphene π-liens
  - Graphene σ-liens
- Structure de carbone nanotubes
- Structure Electronique
- Synthesis
- Transport
- Multi-walled nanotubes

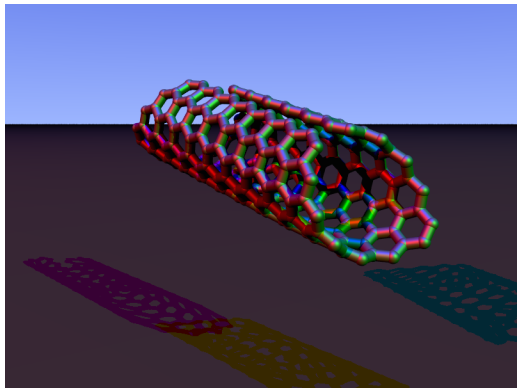
Nanotube structure

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

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

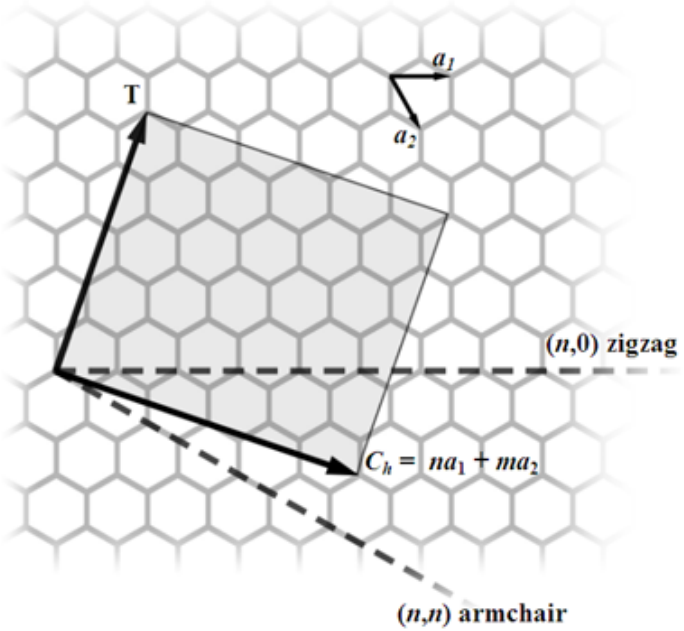






Antonio Ferreira Ávila*; Guilherme Silveira Rachid Lacerda,
“Molecular mechanics applied to single-walled carbon nanotubes”,
Mat. Res. vol.11 no.3 São Carlos July/Sept. 2008

Nanotube structure



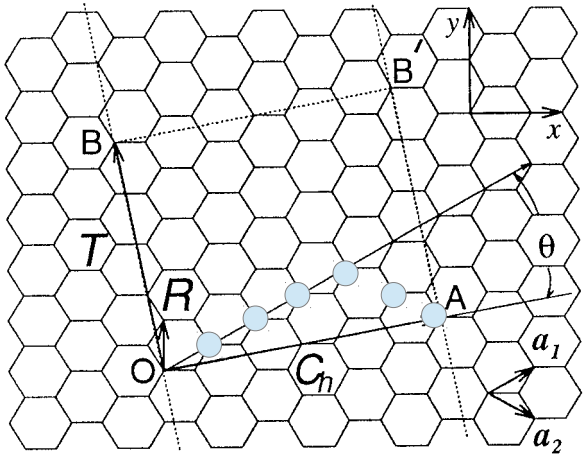
Antonio Ferreira Ávila*; Guilherme Silveira Rachid Lacerda, "Molecular mechanics applied to single-walled carbon nanotubes", Mat. Res. vol.11 no.3 São Carlos July/Sept. 2008

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



$C_h=(4,2)$

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

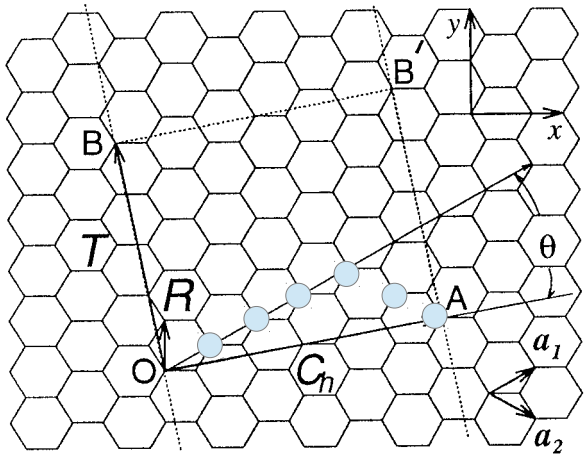
Angle chiral: $\cos\theta\equiv\frac{\boldsymbol{C}_h\cdot\boldsymbol{a}_1}{|\boldsymbol{C}_h||\boldsymbol{a}_1|}=\frac{2n+m}{2\sqrt{n^2+m^2+nm}}$

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)

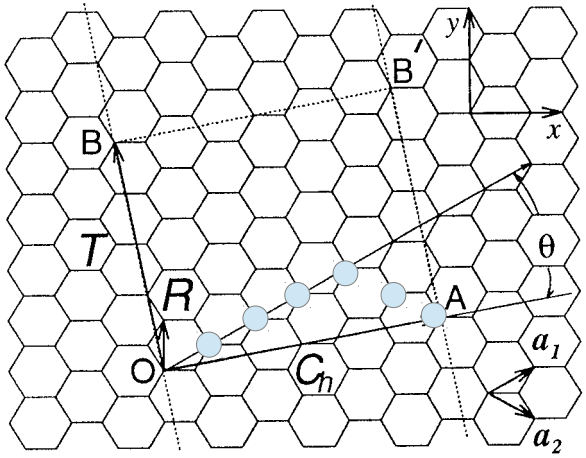
Le nombre d'atoms par unite cellulaire est: 2N

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

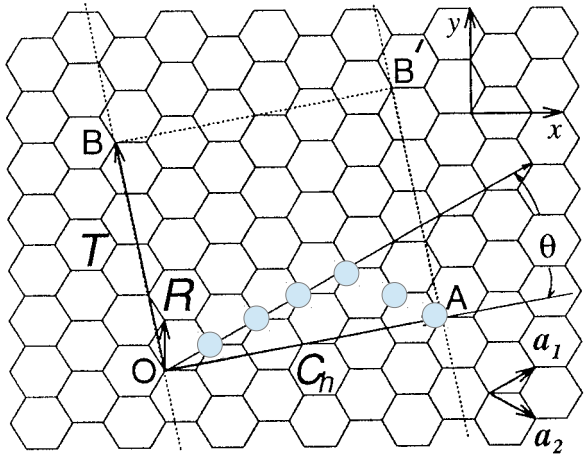
$$\Leftrightarrow 0 < mp - nq \le N$$

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)

$C_h=(4,2)$



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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

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

$$t_1 q - t_2 p = 1$$

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

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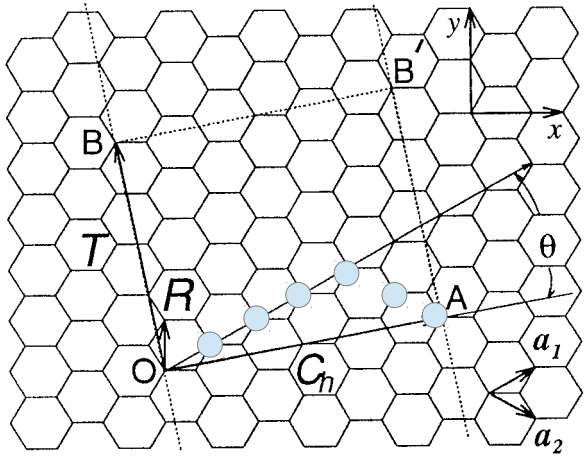
Physical Properties of Carbon Nanotubes
(Imperial College Press, London, 1998)

$C_h = (4,2)$



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

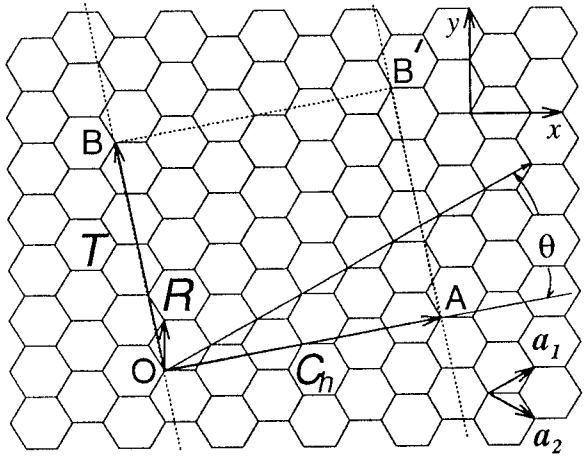
	zigzag	armchair	chiral
C	(n,0)	(n,n)	(n,m)
T	(1,-2)	(1,-1)	$(\frac{2\mathrm{m}+n}{d_R}, -\frac{2\mathrm{n}+m}{d_R})$
R	(1,-1)	(1,0)	
L/a	n	$\sqrt{3}n$	$\sqrt{m^2+n^2+nm}$
T	$\sqrt{3}$	1	$\sqrt{3}L/d_R$
N	2n	2n	$2\mathrm{L}^2/(a^2 d_R)$

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

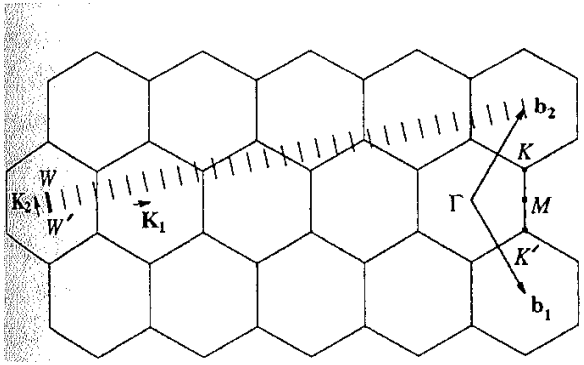
$$= \begin{pmatrix} d & \text{if } n-m \text{ is not a multiple of } 3d \\ 3d & \text{if } n-m \text{ is a multiple of } 3d \end{pmatrix}, \quad d = gcd(n, m)$$

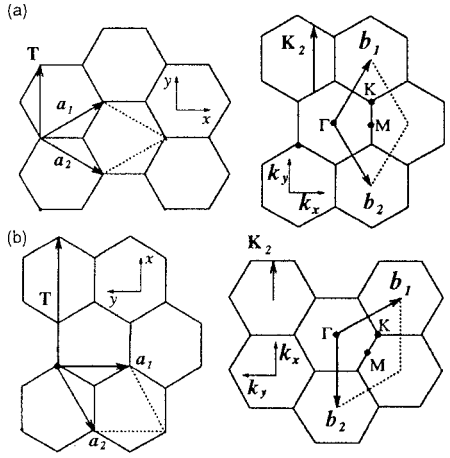
Nanotube structure

réseau



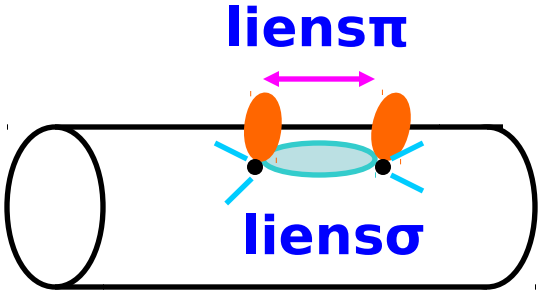
zone de Brillouin





« armchair » (n,n)

« zigzag » $(n,0)$



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