NANOPHYSIQUE
INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch 5. Carbon Structres

James Lutsko

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

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

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, ...)

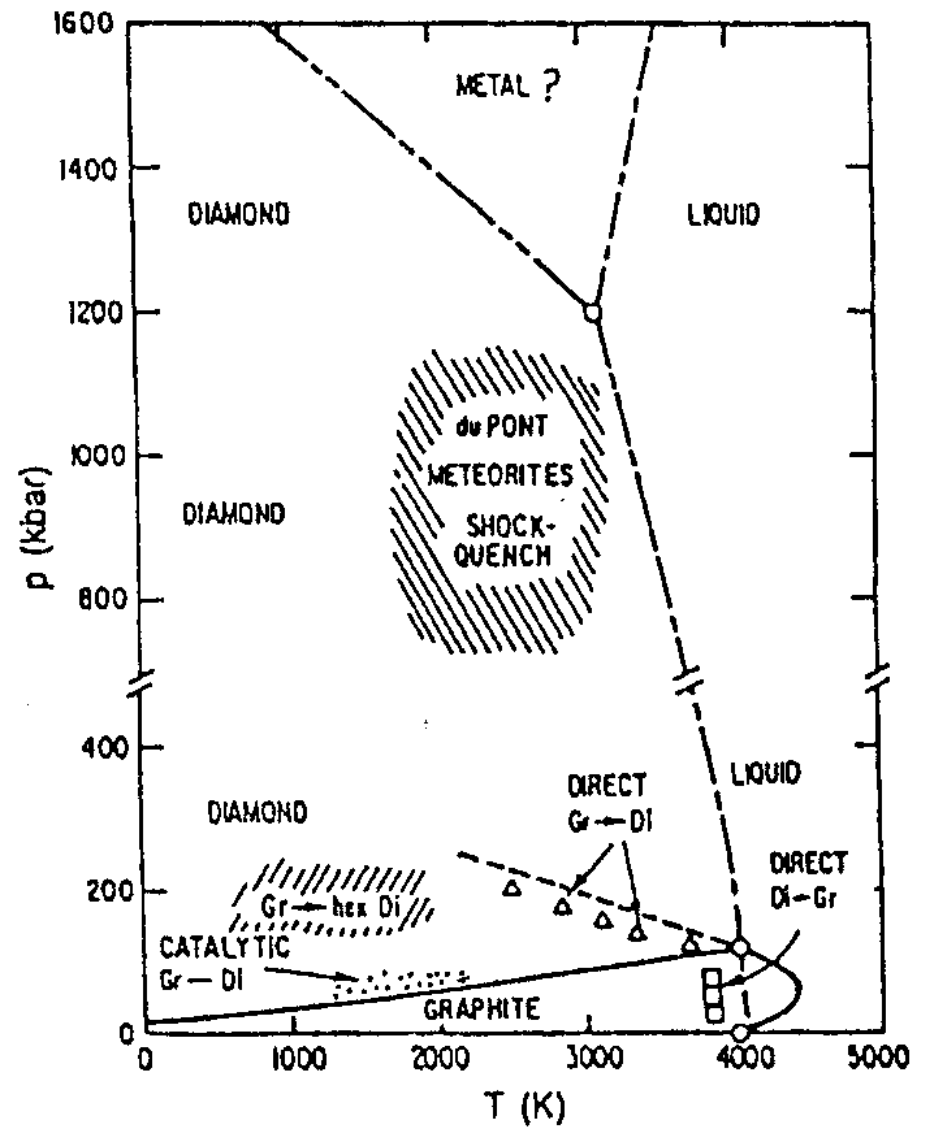- Observation de carbone nanotubes (Iijima, 1992 – utilisant TEM).
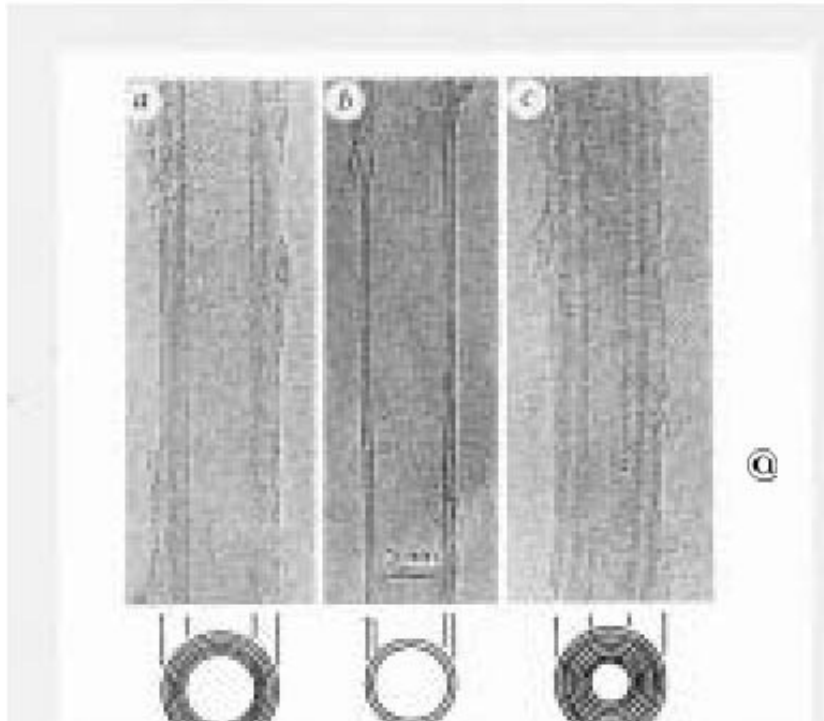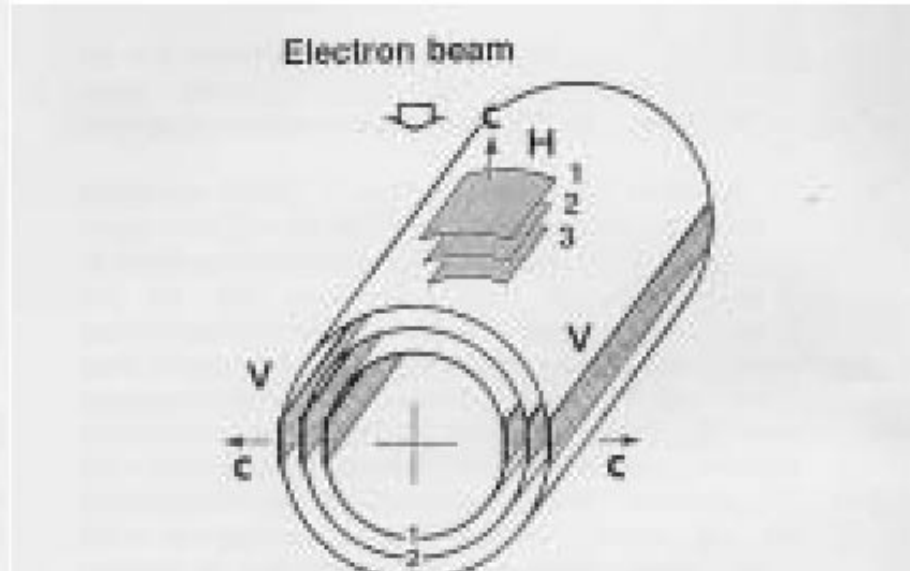
Propriétés du carbone
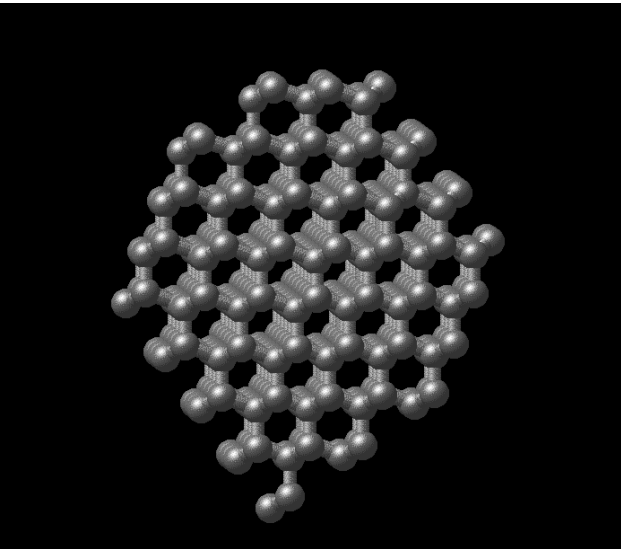
diamant
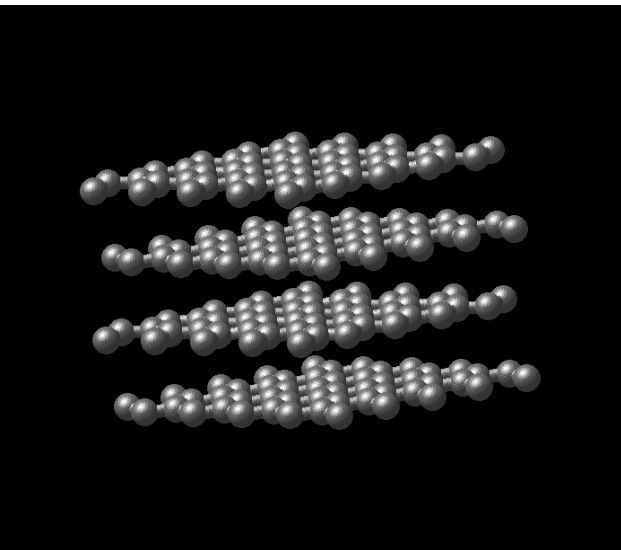
graphite

Discovery of Carbon Nanotubes
Iijima, Nature 354, 56 (1992)

Electron microscope image

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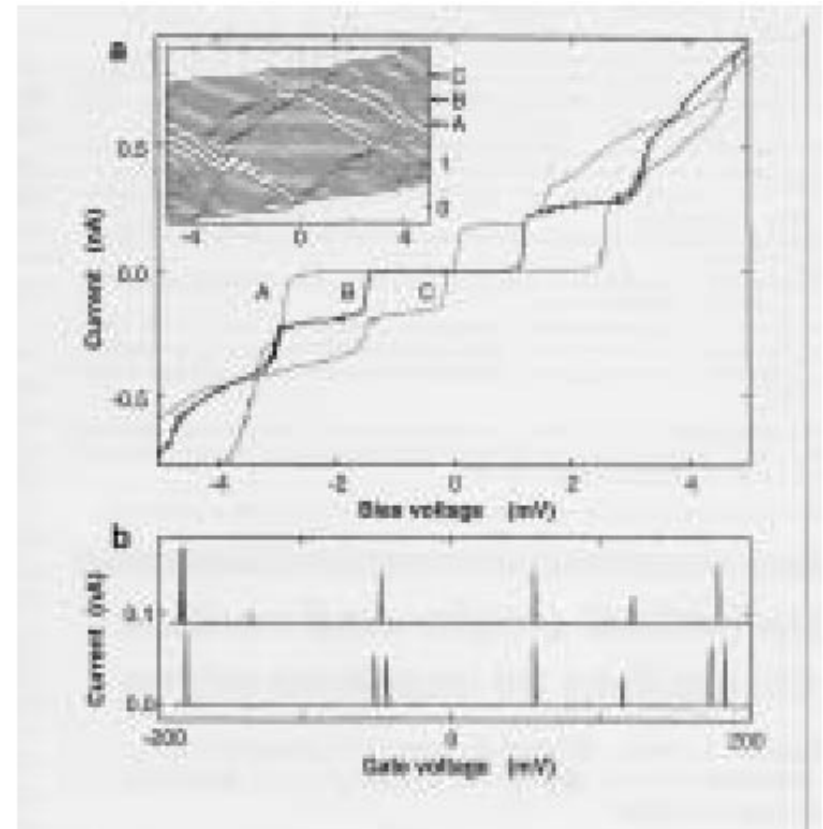

Interpretation of the images

Current-voltage characteristics of CNT

S.J. Tans et al. Nature 386 474 (1997)
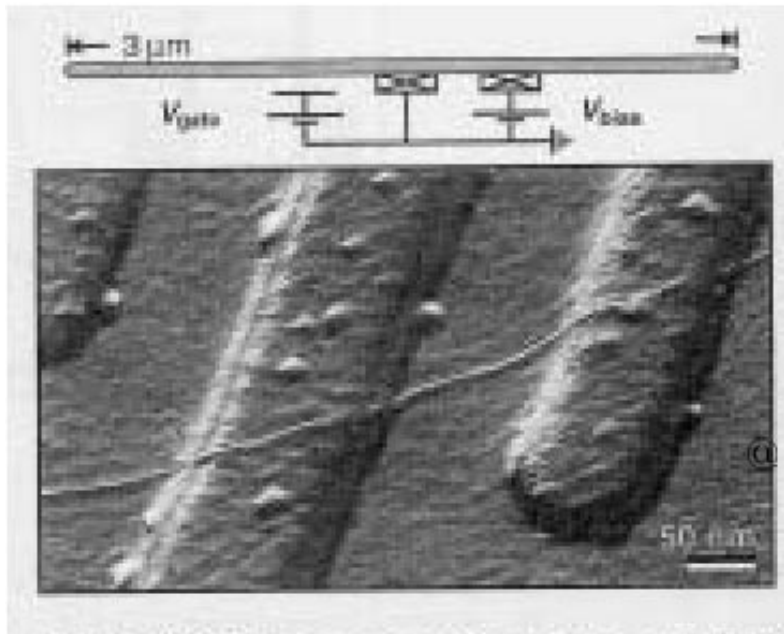
Electron microscope image of the system
- **thin filament: Single-wall CNT**
- **hills: electrodes**

a.Nonlinear conductance
   (Coulomb staircase)
b.Controlling the number
   of electrons

Carbone

Carbone:
$Z = 6$

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

$^{14}C \rightarrow$ half-life $= 5,730$ an

(carbon dating)

Periodic Table of Elements

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

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

Configuration Electronique:

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

occupancy
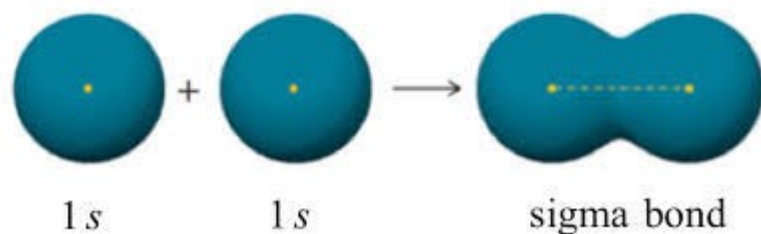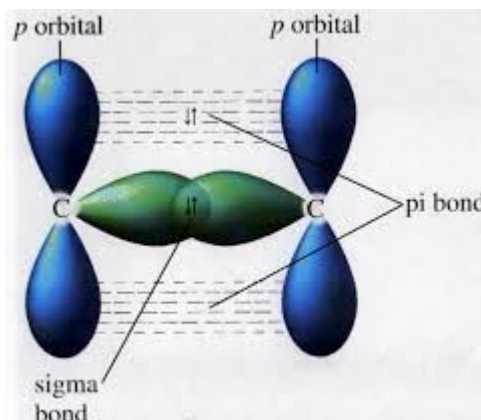
principle quantum number
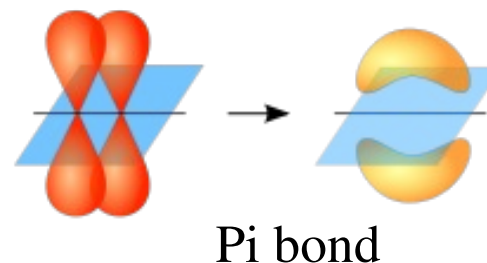
1s   2p
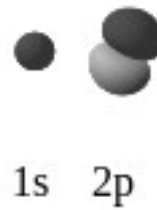
Covalent bonds: sharing electrons
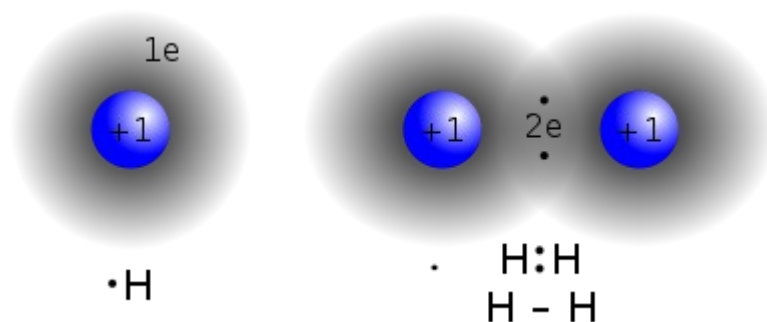
T (kinetic energy)   : lower energy by delocalizing electrons
V (potential energy): lower energy by localizing electrons near ions
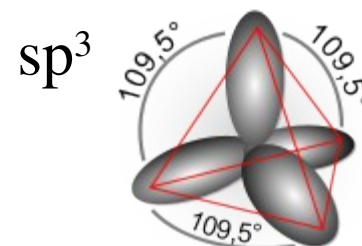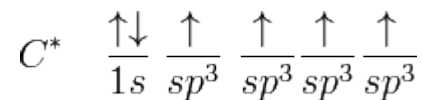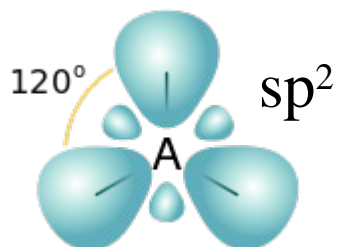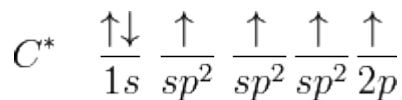
Types of molecular bonds

Sigma bond

Pi bond

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

Hybridization

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

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

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

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

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

sp   180°

120°   sp^2

sp^3 109,5°   109,5°   109,5°

A
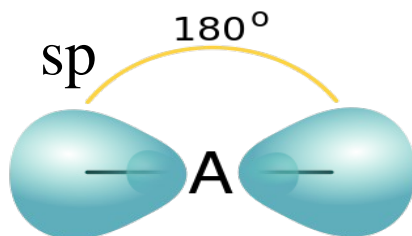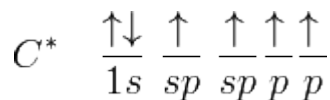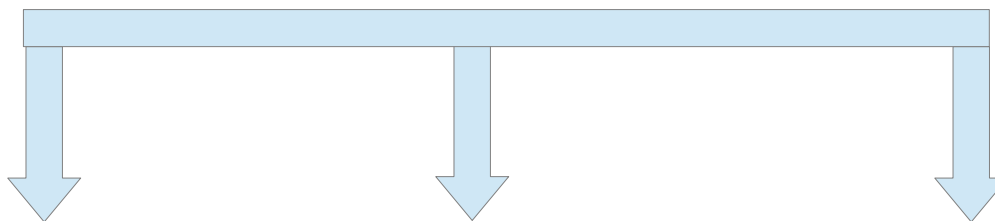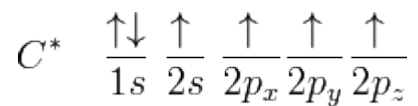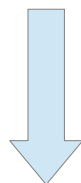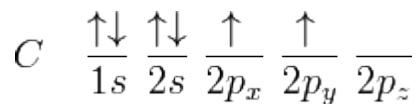
SP Hybridization

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

Orthonormality:

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

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

$$C_4 = \pm C_1$$
$$C_3 = \mp C_2 = \mp\sqrt{1 - C_1^2}$$
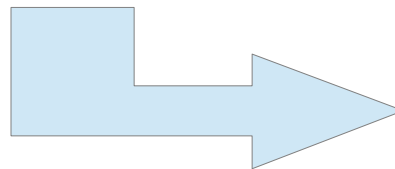
$$E_a = C_1^2 E_s + C_2^2 E_p$$
$$= C_1^2 \underbrace{(E_s - E_p)}_{<0} + E_p$$
$$E_b = C_3^2 E_s + C_4^2 E_p$$
$$= E_s + C_1^2 (E_p - E_s)$$
$$= E_a + (1 - 2C_1^2)(E_s - E_p)$$
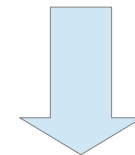
$$|sp_a\rangle = \frac{1}{\sqrt{2}}\left(|s\rangle + |p_x\rangle\right)$$
$$|sp_b\rangle = \frac{1}{\sqrt{2}}\left(|s\rangle - |p_x\rangle\right)$$
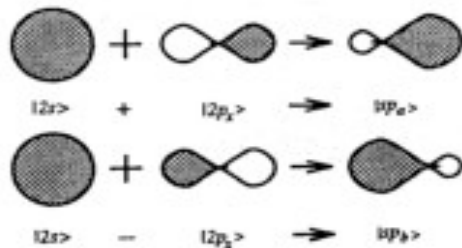
|2s> + |2p_x> → sp_a>

|2s> − |2p_x> → sp_b>

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

$$\left|sp_{a,b}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|2s\right\rangle\pm\left|2p_x\right\rangle\right)$$
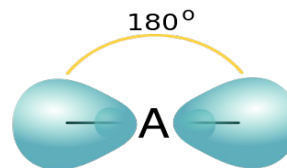
Hybridation sp^2: $2s + 2p_x + 2p_y$, $2p_z$

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

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

$$\left|sp_{b,c}^2\right\rangle=\pm\frac{1}{\sqrt{3}}\left|2s\right\rangle\pm\frac{1}{\sqrt{2}}\left|2p_x\right\rangle+\frac{1}{\sqrt{6}}\left|2p_z\right\rangle$$
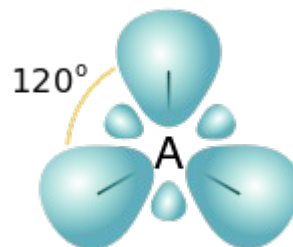
Hybridation sp^3: $2s + 2p_x + 2p_y+2p_z$

Example : méthane: CH_4 liaison simple: 4 liens σ

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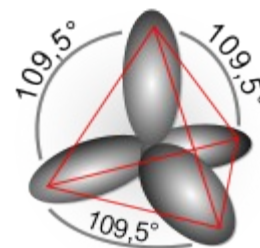
Carbon Structures

- 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

Tight-binding method

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

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

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

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

Alors, il ya vecteurs propres simultanés:

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

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

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

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

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

Conditions à la limite periodique $\qquad \psi(\mathbf{r} + N_i\mathbf{a}_i) = \psi(\mathbf{r}), \qquad i = 1,2,3$

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

Tight-binding method

2. **<u>Tight-binding fonctions de base</u>**

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

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. **<u>Tight-binding fonction d'onde</u>**

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

4. **<u>Tight-binding éléments de matrice</u>**

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

Principe de variation pour l'équation de Schrodinger.

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

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

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

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

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

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

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

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

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:

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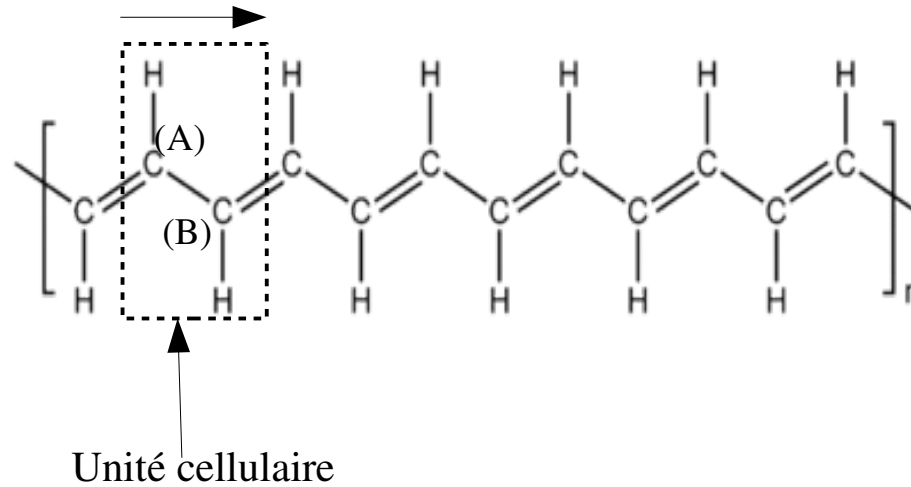
$$\rightarrow \sum_{j'} H_{jj'}(\boldsymbol{k}) C_{j'} = \lambda(\boldsymbol{k}) \sum_{j'} S_{jj'}(\boldsymbol{k}) C_{j'}$$

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

Tight-binding method

Example: *trans*-polyacétylène

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

(A)

(B)

Unité cellulaire

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

Tight-binding method

Example: *trans*-polyacétylène

Unité cellulaire

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

Vecteur de reseau reciproque: $\boldsymbol{b} = \dfrac{2\pi}{a}\,\hat{\boldsymbol{x}}$
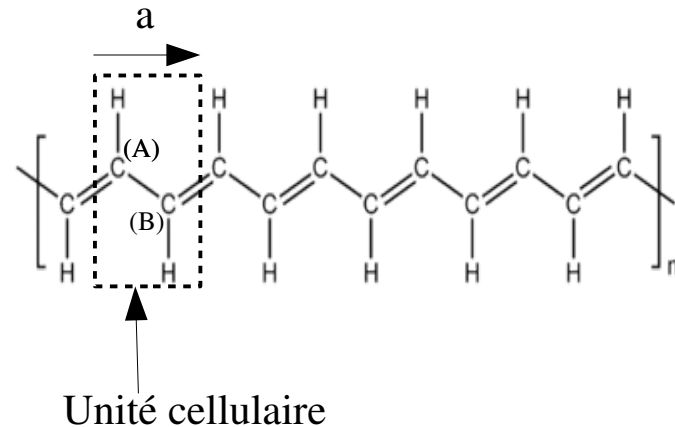
sp^2 hybridization $\rightarrow$ σ-liens dans le plan, π-lien (p-p) dehors le plan

On cherche les niveau pour les π-electrons:

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

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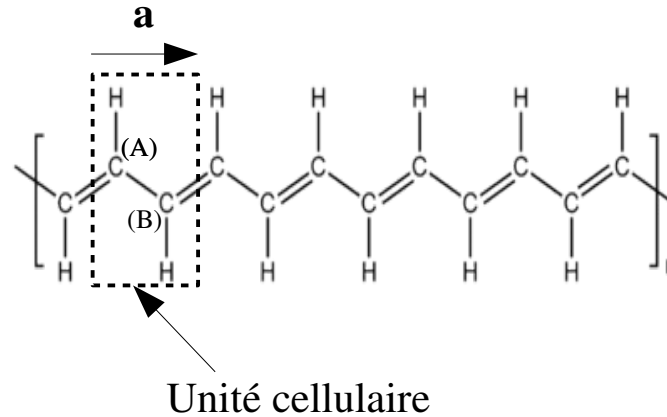
$$\boldsymbol{k} = \frac{2\pi}{a}\frac{p_i}{N}\,\hat{\boldsymbol{x}}, \quad 0 \le p_i < N \qquad \Longrightarrow \qquad 0 \le k \le 2\pi/a$$

Tight-binding method

Example: *trans*-polyacétylène

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

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

Unité cellulaire

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

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

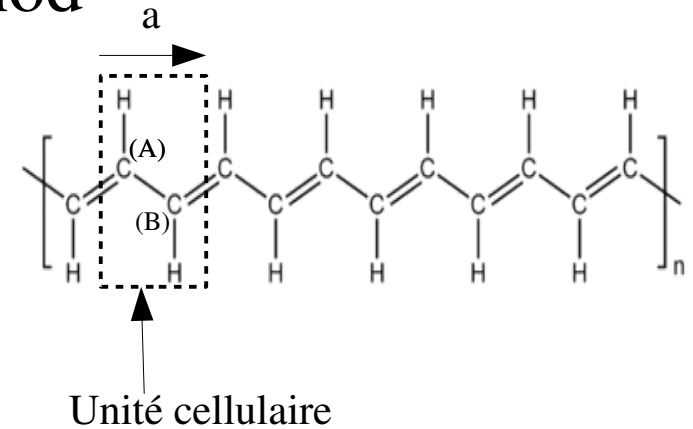$$H_{AA}(\mathbf{k}) = \langle \Phi_{A\mathbf{k}}|H|\Phi_{A\mathbf{k}}\rangle = \frac{1}{N}\sum_{n,m=0}^{N} e^{ik(n-m)a}\langle \phi_{2p_z}(\mathbf{r}-ma\,\hat{\mathbf{x}})|H|\phi_{2p_z}(\mathbf{r}-na\,\hat{\mathbf{x}})\rangle$$

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

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

Tight-binding method

Example: *trans*-polyacétylène

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

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

Unité cellulaire

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

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

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

if $\quad r_{ABx} = a/2$

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

Tight-binding method

Example: *trans*-polyacétylène

Unité cellulaire

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

Vecteur de reseau reciproque:
$$\boldsymbol{b} = \frac{2\pi}{a}\,\hat{\boldsymbol{x}}$$
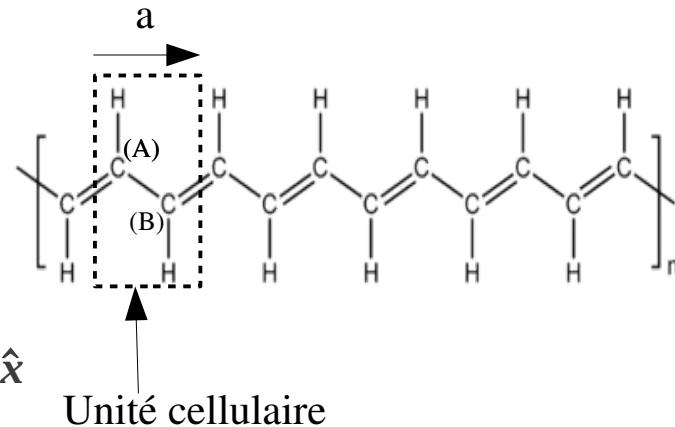
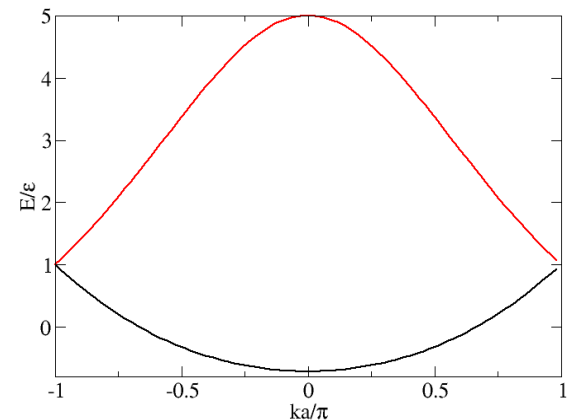$$H_{ij} = \begin{pmatrix} \epsilon_{2p} & 2t\cos(ka/2) \\ 2t\cos(ka/2) & \epsilon_{2p} \end{pmatrix} \qquad S_{ij} = \begin{pmatrix} 1 & 2s\cos(ka/2) \\ 2s\cos(ka/2) & 1 \end{pmatrix}$$

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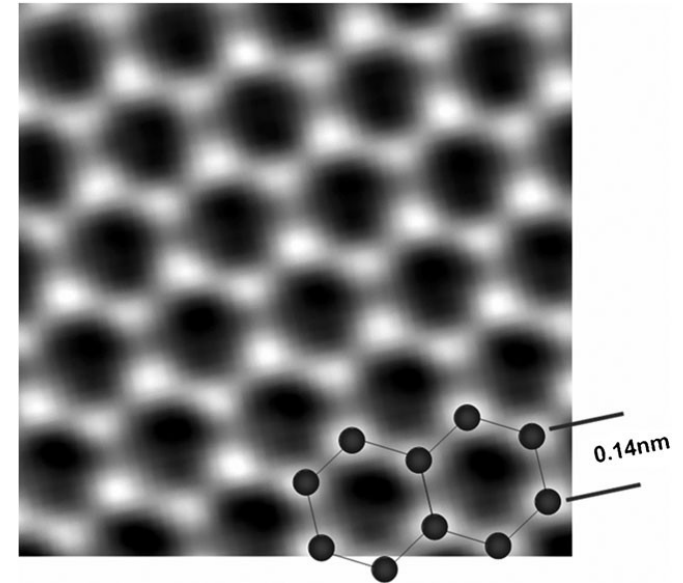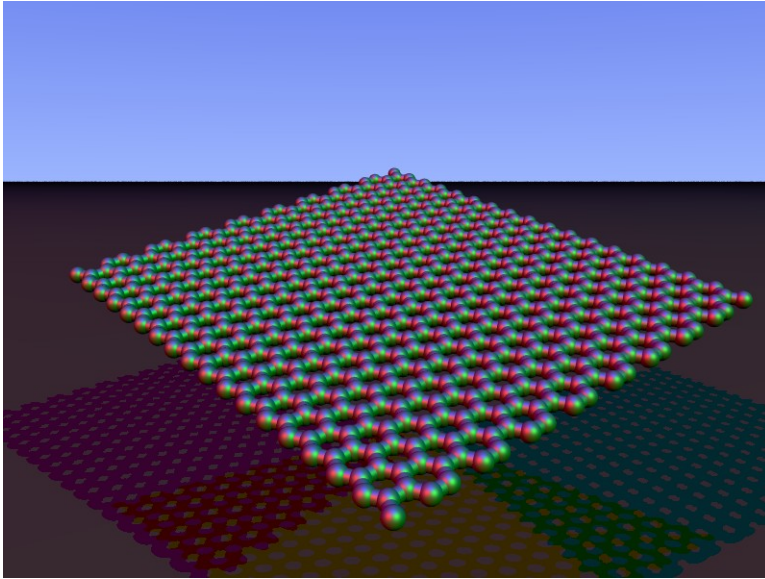
$$= (\epsilon_{2p} - E)^2 - 4(t - sE)^2 \cos^2(ka/2)$$

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

Graphene 1

graphène = un seul feuillet de graphite

0.14nm

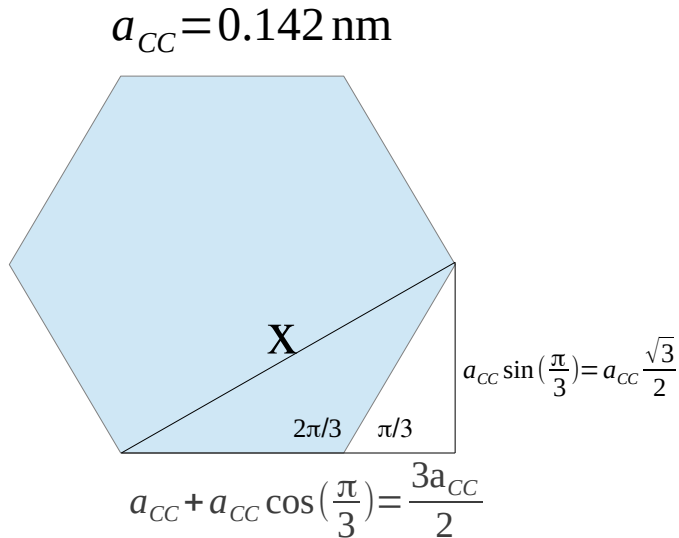Structure électronique d'un atome de carbone = $1s^2\ 2s^2\ 2p^2$

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

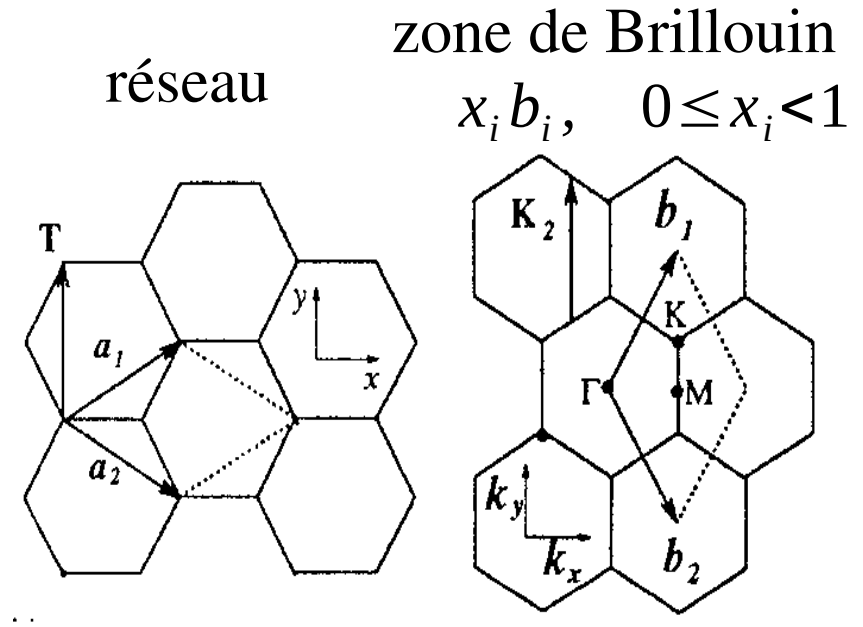Chaque atome de carbone offre 3 orbitales atomiques sp^2 et une orbitale $2p_z$

Les orbitales atomiques sp^2 forment les liens σ

Les orbitales atomiques $2p_z$ forment les liens π

Graphene 2

$a_{CC} = 0.142$ nm

réseau

zone de Brillouin

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

X

$a_{CC} \sin\left(\frac{\pi}{3}\right) = a_{CC} \frac{\sqrt{3}}{2}$

$2\pi/3 \quad \pi/3$

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

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

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

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

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

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

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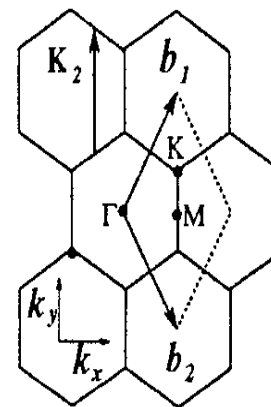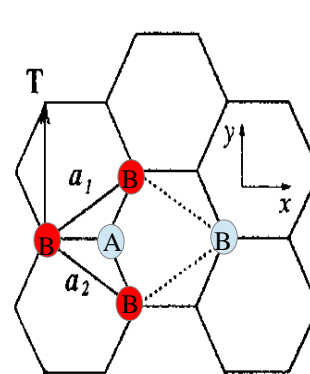$$\equiv tf(\boldsymbol{k})$$

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

$$S_{AB} = sf(\boldsymbol{k})$$

$$E_{\pi\pi} = \frac{\epsilon_{2p} \pm tw(\boldsymbol{k})}{1 \pm sw(\boldsymbol{k})}$$

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

$$w(\boldsymbol{k}) = \sqrt{\left[f(\boldsymbol{k})\right]^2} = \sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$
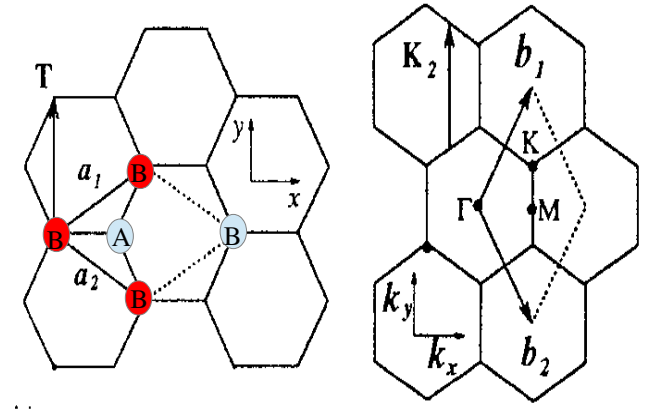
$s = 0 \Leftrightarrow$ "Slater-Koster approximation"

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

Graphene Tight-binding : σ-bands

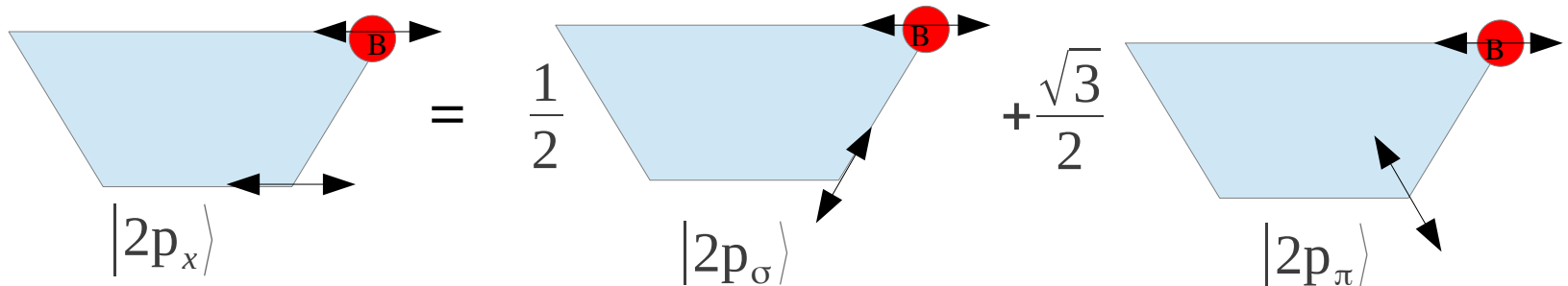Basis: $\left(2s^A, 2p_x^A, 2p_y^A, 2s^B, 2p_x^B, 2p_y^B\right)$

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

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

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

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

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

Graphene Tight-binding : σ-bands

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

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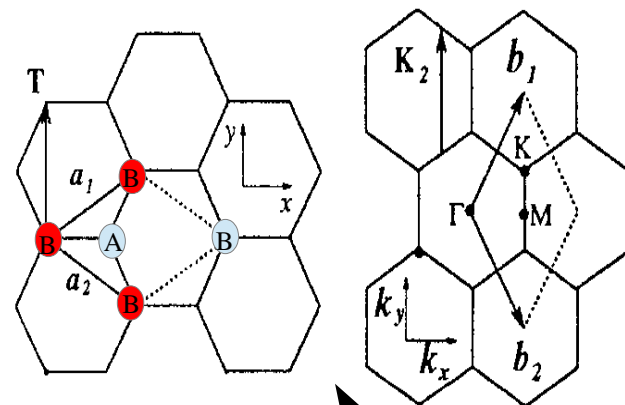
$$\left\langle 2p_x^B\right|H\left|2p_x^A\right\rangle = \left(\frac{1}{2}\right)^2 \left\langle 2p_\sigma^B\right|H\left|2p_\sigma^A\right\rangle + \left(\frac{\sqrt{3}}{2}\right)^2 \left\langle 2p_\pi^B\right|H\left|2p_\pi^A\right\rangle$$

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

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

Graphene Tight-binding : σ-bands
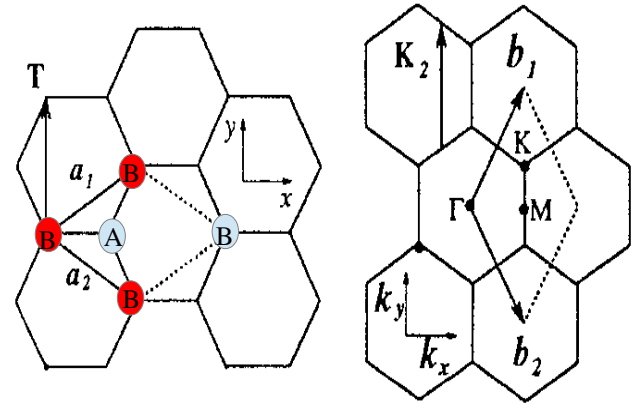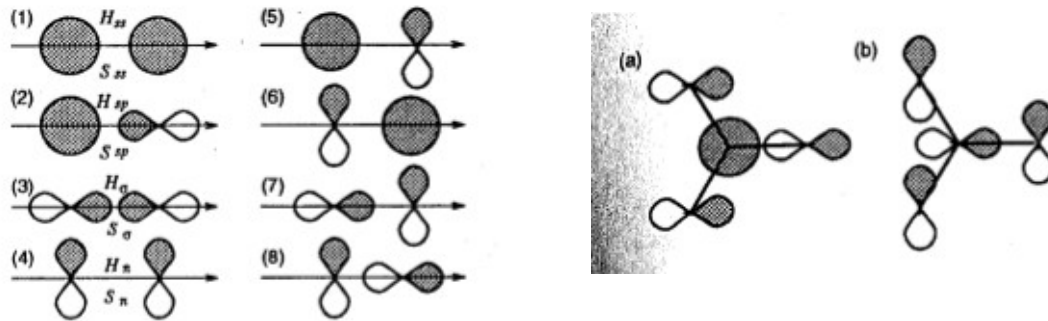
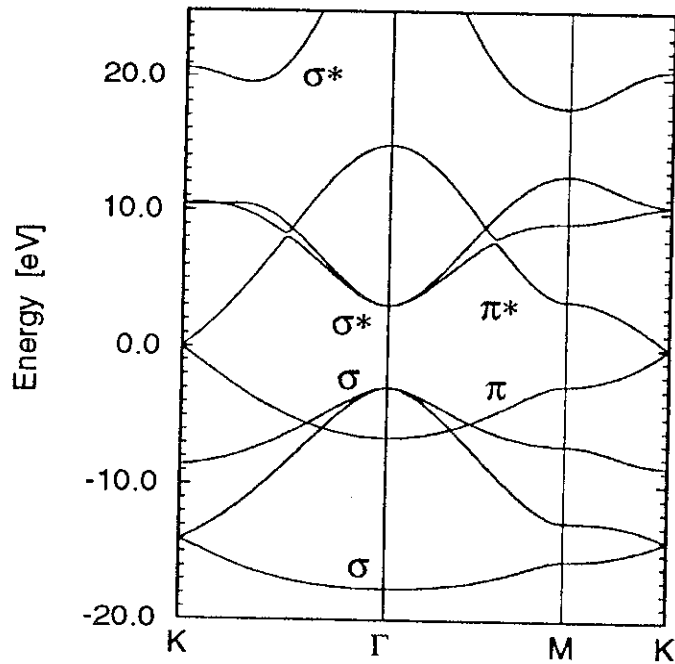Basis: $\left(2s^A, 2p_x^A, 2p_y^A, 2s^B, 2p_x^B, 2p_y^B\right)$

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

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

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

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

Graphene

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

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