Master Nanosciences Nanotechnologies: ”Solid state, electrons and phonons”
Exercises, Thursday 22nd, October 2020 (Xavier Blase)

Exercise 17 Peierls distorsion in the 1D chain of atoms with one atomic orbital per atom

The **2000 Chemistry Nobel Prize** was awarded to Heeger, MacDiarmid and Shirakawa ”for the development of conductive polymers.” Why is it such a big deal to have conductive polymers ?

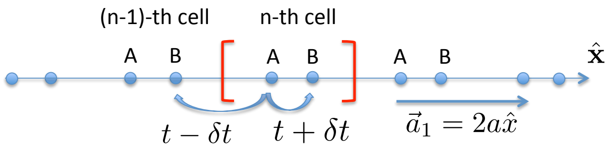
We study the electronic properties of a 1D chain of atoms with 2 atoms A and B per unit cell. The interatomic nearest-neighbours distance is (a). There is one atomic orbital $\phi_A^{at}(x-\tau_A-n2a)$ on atoms A located in $(\tau_A - n2a)$ and one atomic orbital $\phi_B^{at}(x-\tau_B-n2a)$ on atoms B located in $(\tau_B - n2a)$. All Bloch states ψ_k can be build as a linear combination: $\psi_k = \alpha\psi_k^A + \beta\psi_k^B$ with for example:

$$\psi_k^A(x) = \frac{1}{\sqrt{Nc}} \sum_{n=1}^{Nc} e^{ik(\tau_A+n2a)} \phi_A^{at}(x-\tau_A-n2a) \quad \text{with Nc = number of cells,}$$

and the equivalent for ψ_k^B with $A \Rightarrow B$. We assume that atoms A and B are chemically equivalent with the same onsite atomic energy: $\epsilon_A^0 = \epsilon_B^0 = \epsilon_0$, where: $\epsilon_A^0 = \langle \phi_A^{at}(x-\tau_A-n2a)|\hat{H}|\phi_A^{at}(x-\tau_A-n2a)\rangle$ and equivalent expression for ϵ_B^0 with $A \Rightarrow B$. We call (t) the hopping energy between first nearest neighbours atomic orbitals: $t = \langle \phi_A^{at}(x-\tau_A-n2a)|\hat{H}|\phi_B^{at}(x-\tau_B-n2a)\rangle$.

a) What is the system of equations satisfied by (α) and (β) used to find the eigenstates ψ_k and the energy $\epsilon(k)$. Provide $\epsilon(k)$ and plot the corresponding band structure in the Brillouin zone.

b) We assume now that the atoms A and B in the same unit cell get closer from each other (see Picture below), namely their spacing reduces from (a) to (a-δa). As a result, the hopping term between two A and B atoms in the same cell increases from (t) to (t+δt). On the contrary, the distance between two atoms A and B in neighbouring cells increases from (a) to (a+δa) and the hopping term decreases to (t-δt). The onsite energies $\epsilon_A^0 = \epsilon_B^0 = \epsilon_0$ do not change.



Show that $H_{AB} =< \psi_k^A|\hat{H}|\psi_k^B >$ becomes proportional to: $\left[t\cos(ka) + i(\delta t)\sin(ka)\right]$ where (i) indicates a complex number. Hint : remember that $2cos(x) = e^{ix} + e^{-ix}$ and $2(i)sin(x) = e^{ix} - e^{-ix}$.

c) What are the Bloch states energies $\epsilon(k)$ as a function of $(\epsilon_0, t, \delta t, k, a)$? Plot the corresponding band structure in the Brillouin zone. Comment on what happens at the zone boundary. What should you recover in the limit (δt=0) ? Hint: remember that H_{BA} is the complex conjugate of H_{AB}.

d) This phenomenon of alternation of short and long bonds happens spontaneously at “half-filling” (one electron per atom in the system). Can you explain why ?

Exercise 23. The tight-binding band structure of graphene

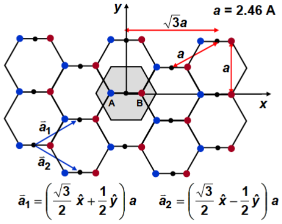
The **Nobel Prize in Physics 2010** was awarded jointly to Andre Geim and Konstantin Novoselov ”for groundbreaking experiments regarding the two-dimensional material graphene.”

Graphene is a 2D materials with 2 carbon atoms (A and B) per unit-cell and an hexagonal structure. We plot below in grey a primitive unit cell and the lattice primitive vectors $\vec{a}_1$ and $\vec{a}_2$. Atoms A are represented in blue and atoms B in red. We assume that there is only one atomic orbital ϕ^{at} per atom so that all Bloch states can be expressed as a linear combination of the two basis Bloch states:

$$\psi^A_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N_c}} \sum_{ml} e^{i\vec{k}\cdot(\vec{\tau}_A+\vec{R}_{ml})} \phi^{at}(\vec{r}-\vec{\tau}_A-\vec{R}_{ml}) \;\; \text{and} \;\; \psi^B_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N_c}} \sum_{ml} e^{i\vec{k}\cdot(\vec{\tau}_B+\vec{R}_{ml})} \phi^{at}(\vec{r}-\vec{\tau}_B-\vec{R}_{ml})$$

with $\vec{R}_{ml} = m\vec{a}_1 + l\vec{a}_2$ the lattice vectors (m and l integers), N_c the number of cells, $(\vec{\tau}_A + \vec{R}_{ml})$ and $(\vec{\tau}_B + \vec{R}_{ml})$ the position of atoms A and B in the cell indexed by (m,l).

We call $\varepsilon_0 = \langle\phi^{at}(\vec{r}-\vec{\tau}_A-\vec{R}_{ml})|\hat{H}|\phi^{at}(\vec{r}-\vec{\tau}_A-\vec{R}_{ml})\rangle$ the onsite energy (the same for atoms A and B) and $t = \langle\phi^{at}(\vec{r}-\vec{\tau}_A-\vec{R}_{ml})|\hat{H}|\phi^{at}(\vec{r}-\vec{\tau}_B-\vec{R}_{m'l'})\rangle$ the hopping term when $(\vec{\tau}_A+\vec{R}_{ml})$ and $(\vec{\tau}_B+\vec{R}_{m'l'})$ are first-nearest neighbours.



a) Show that $H_{AB} =< \psi^A_{\vec{k}}|\hat{H}|\psi^B_{\vec{k}} >$ can be written

$$H_{AB} = tf(\vec{k})e^{i\vec{k}\cdot(\vec{\tau}_B-\vec{\tau}_A)} \quad \text{with} \quad f(\vec{k}) = 1+e^{-i\vec{k}\cdot\vec{a}_1}+e^{-i\vec{k}\cdot\vec{a}_2}$$

where $\hat{H}$ is the crystal Hamiltonian.

b) Deduce from the previous question that the band structure of graphene reads:

$$\varepsilon(\vec{k}) = \varepsilon_0 \pm |t|\sqrt{3 + 2cos(\vec{k}\cdot\vec{a}_1) + 2cos(\vec{k}\cdot\vec{a}_2) + 2cos[\vec{k}\cdot(\vec{a}_2-\vec{a}_1)]}$$

c) Provide the band energies $\varepsilon(\vec{k})$ in $\vec{k} = 0$ and $\vec{k} = \vec{K} = 2(\vec{b}_1+\vec{b}_2)/3$ where $(\vec{b}_1, \vec{b}_2)$ are the reciprocal space primitive lattice vectors defined by $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$. Plot qualitatively the band structure between $\vec{k} = 0$ and $\vec{k} = \vec{K}$. What is the Fermi energy at half filling (one 2pz electron per atom) ?

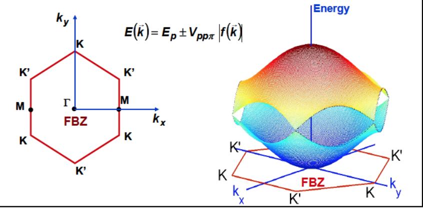


Figure: zone de Brillouin (gauche) et structure de bande (droite) du graphene dans le modèle "une orbitale p_z par atome". Le terme $V_{pp\pi}$ correspond au terme de saut |t| dans l'énoncé, c'est-à-dire l'énergie d'interaction entre deux orbitals p_z sur des atomes voisins.

d) We now look for the band structure for $\vec{k} = \vec{K} + \vec{q}$ and $|\vec{q}| << 1$. By using the Taylor expansion $e^{-i\vec{q}\cdot\vec{a}_i} \simeq 1 - i\vec{q}\cdot\vec{a}_i$ show that:

$$f(\vec{K}+\vec{q}) \simeq \frac{a\sqrt{3}}{2}[iq_x + q_y]$$

and that as a consequence in the vicinity of $\vec{K}$:

$$\varepsilon(\vec{K}+\vec{q}) - \varepsilon_0 \simeq \pm\hbar v_F|q| \quad \text{where} \quad v_F = \frac{\sqrt{3}a|t|}{2\hbar}$$

Why do we talk about the graphene "Dirac cone" close to E_F ?

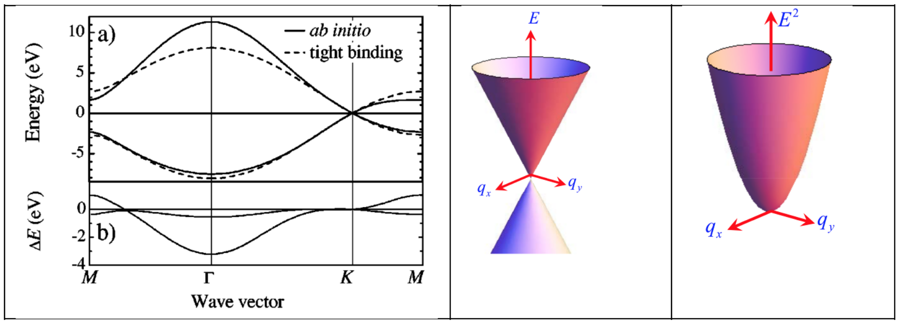


Figure: (Left) Tight-binding versus ab initio (”accurate”) p_z-band structure of graphene; (Center) Band structure close to $\vec{K}$ in graphene; (Right) Usual parabolic dispersion for a 2D electron gaz.

In relativistic theory, one has the fundamental energy-momentum relation: $E^2 = (pc)^2 + (mc^2)^2$. For a massless particle: $E = \pm pc$, namely a linear relation between energy and impulsion. With: $p = (\hbar)q$ in the vicinity of $\vec{K}$ and replacing the light velocity c by the Fermi velocity: $v_F \simeq c/300$ in graphene, one obtains a behaviour for graphene electrons at the Fermi energy similar to ”massless relativistic fermions”.

Exercise 24. Band structure of the 2D square lattice (the minimal cuprate !)

The **Nobel Prize in Physics 1987** was awarded to J. Georg Bednorz and K. Alexander Müller ”for their important break-through in the discovery of superconductivity in ceramic materials [cuprates].”

Typical high-T$_C$ superconductors are built from CuO_2 planes. Around the Fermi level, the minimal model can be obtained by considering one $d_{(x^2-y^2)}$ orbital per Cu atom. We therefore consider a 2-dimensional (2D) square lattice with one (Cu) atom per unit cell and primitive lattice vectors $(\vec{a}_1, \vec{a}_2)$.

a) What are the reciprocal lattice vectors $(\vec{b}_1, \vec{b}_2)$ and the Brillouin zone (BZ) ?

b) We assume that there is one atomic orbital per site: $\phi^{at}(\mathbf{r} - \mathbf{R}_{ml})$ where $\mathbf{R}_{ml}$ are the lattice vectors, namely: $\mathbf{R}_{ml} = m\vec{a}_1 + l\vec{a}_2$ (l and m integers). What is/are the possible Bloch state(s) for this crystal ?

c) We label: $\varepsilon_0 = \langle \phi^{at}(\mathbf{r} - \mathbf{R}_{ml}) | \hat{H} | \phi^{at}(\mathbf{r} - \mathbf{R}_{ml}) \rangle$ the onsite energies and for the hopping terms: $t = \langle \phi^{at}(\mathbf{r} - \mathbf{R}_{ml}) | \hat{H} | \phi^{at}(\mathbf{r} - \mathbf{R}_{m'l'}) \rangle$ with $\mathbf{R}_{ml}$ and $\mathbf{R}_{m'l'}$ first nearest neighbours. Show that the band structure reads:

$$\varepsilon(k_x, k_y) = \varepsilon_0 + 2t[cos(k_x a) + cos(k_y a)]$$

d) Plot the Fermi surface in the Brillouin zone at half filling (namely in the case of one electron per atom). Show that it is a square.

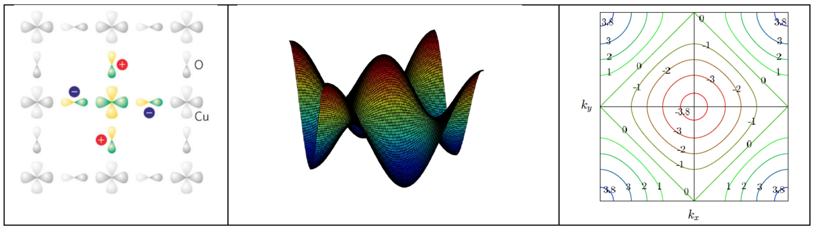


Figure: (Gauche) Symbolic representation of CuO plane and orbitals close to the Fermi level. (Center) 2D square lattice band structure (with t>0). (Right) Isocontour: $\varepsilon(k_x, k_Y)$ = constant, in units of |t| and with $\varepsilon_0 = 0$.